162.7, 142.5, 144.7, 139.0, 132.0, 127.2, 122.6, 116.0, 112.3, 87.6, 61.6, 56.1, 55.4, 45.5, 35.6, 35.2, 14.0. Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.2; H, 6.4; N, 4.2. Found: C, 65.1; H, 6.6; N, 4.2.

(C) From Diacid 32. A solution of **30** (from 183 mg, 0.41 mmol of **29**) in methanol (5 mL) was treated with potassium hydroxide (86 mg, 1.3 mmol) in water (5 mL) and heated to reflux for 3 h. Acetic acid (0.10 mL) was added, the solvent was evaporated, and the residue was dried at 90 °C (0.05 mm) for 18 h. The crude diacid was heated at reflux in acetic anhydride (10 mL) for 24 h and evaporated to a white solid. This residue was dissolved in ethanol, treated with boron trifluoride etherate (1.0 mL, 8.1 mmol), heated at reflux for 24 h, and poured into saturated $NaHCO_3$ solution. Extraction with chloroform, drying, solvent evaporation, and chromatography (MPLC, 75/25 ether/isooctane) afforded 12.5 mg (9%) of the α isomer followed by 81.0 mg (60%) of the β isomer.

Spiro[7-methoxybenzofuran-2-carboxylic acid-3(2*H*),4′-1′-methyl-3′-methylene-2′-piperidinone] (2). Ethyl ester **31** (84.0 mg, 0.254 mmol) in methanol (5 mL) at 0 °C was treated with 1 M aqueous KOH (5 mL). The mixture was stirred for 1.25 h, acidified with 1 M HCl (10 mL), and extracted with $CHCl_3$ which was dried and evaporated to afford 77.0 mg (100%) of a white solid: mp 185–187 °C (lit.[3] mp 184–186 °C); ^1H NMR δ 6.85 (dd, 1 H, J = 7.8 Hz), 6.72 (d, 1 H, J = 7 Hz), 6.57 (d, 1 H, J = 8 Hz), 6.55 (s, 1 H), 5.40 (s, 1 H), 5.08 (s, 1 H), 3.71 (s, 3 H), 2.98 (s, 3 H), 3.0–3.4 (m, 2 H), 1.8–2.2 (m, 2 H).

Acknowledgment. This researched was supported in part by the National Institute on Drug Abuse.

Registry No. α-**2**, 87903-06-8; β-**2**, 87903-24-0; **3**, 68981-86-2; **4**, 68981-78-2; **5**, 87903-19-3; **7**, 87902-89-4; **8**, 87903-21-7; **9**, 87903-20-6; **10**, 87902-86-1; **11**, 87902-87-2; **12**, 87902-88-3; **15**, 87308-11-0; **16**, 87902-90-7; **17**, 87902-91-8; **18**, 87902-95-2; **19**, 73220-26-5; **20**, 87902-92-9; **22**, 87902-93-0; **23**, 87902-94-1; **24a**, 87903-07-9; **24b**, 87903-08-0; **24c**, 87921-95-7; **24d**, 87903-09-1; **24e**, 87903-10-4; **24f**, 87902-96-3; **25f**, 87902-97-4; **26a**, 87921-96-8; **26b**, 87903-11-5; **26c**, 87903-12-6; **26d**, 87903-13-7; **26e**, 87903-14-8; α-**26f**, 87902-98-5; β-**26f**, 87903-22-8; **27a**, 87903-15-9; **27b**, 87903-16-0; **27c**, 87903-17-1; **27d**, 87903-18-2; α-**28**, 87902-99-6; β-**28**, 87903-00-2; **29**, 87903-01-3; **30**, 87903-02-4; **30** acetate, 87903-03-5; **30** diacid, 87903-05-7; α-**31**, 87903-23-9; β-**31**, 87903-04-6; veratrole, 91-16-7; guaiacol, 90-05-1; chloromethyl methyl ether, 107-30-2; ethyl bromoacetate, 105-36-2; codeine, 76-57-3.

The Diverse Carbenic and Cationic Chemistry of 3-Diazo-2,5-diphenylpyrrole

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Received September 3, 1982

3-Diazo-2,5-diphenylpyrrole (**1**) thermolyzes and photolyzes to 2,5-diphenyl-3*H*-pyrrolylidene (**3**), which inserts into methylene hydrogen of cyclohexane and methyne hydrogen of cumene. Hydrogen abstraction to give 2,5-diphenylpyrrole (**7**) occurs competitively in these systems. Carbene **3** reacts with cyclohexene, allylbenzene, and 2,3-dimethyl-2-butene to give 3-(allylically substituted)-2,5-diphenylpyrroles (**15**, **20**, **21**, and **29**) as the only products of olefin incorporation along with **7**. The initial position of the double bond in the olefin may be altered in the overall insertion process, and cyclopropanes are not isolable. The apparent behavior of **3** with saturated and olefinic hydrocarbons is as singlet **8s** and triplet **9t**. Reactions of **3** with anisole (**31a**) and with toluene (**31b**), benzenes substituted by electron-donor groups, result in selective ortho and/or para substitution to give 2,5-diphenyl-3-(substituted-phenyl)pyrroles (**38a**, **35**, and **38b**) and in hydrogen abstraction to **7**. Insertion into the methyl groups and hydrogen abstraction also occur in reactions of **3** with **31b**, yielding 3-benzyl-2,5-diphenylpyrrole (**39**) and 1,2-diphenylethane (**40**). Benzene (**42a**), however, reacts thermally or photolytically with **1** to form 1,3-diphenyl-2*H*-cycloocta[*c*]pyrrole (**46a**), a member of a new heterocyclic system. Ring expansions to 4-, 5-, and 6-cyano-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles (**46b**, **46b′**, and **46b″**) and 4-, 5-, and 6-nitro-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles (**46c**, **46c′**, and **46c″**) are the principal reactions of **3** with benzonitrile (**42b**) and nitrobenzene (**42c**). 3-(*m*-Nitrophenyl)-2,5-diphenylpyrrole (**47b**) is also formed from **1** and **42c** at 170 °C. Thermolysis and photolysis of **1** to effect substitution and ring expansion of benzenes may involve electrophilic attack of **8s** to form spiropyrrolonorcaradienes (**32**). Directed heterolytic ring opening of **32** and (1,5 sigmatropic) rearrangements of hydrogen will rationalize the selective ortho and/or para substitution processes. Cycloocta[*c*]pyrroles may arise from (electrocyclic) isomerization of **32** to spirocycloheptatrienes **44**, (1,5 sigmatropic) rearrangement involving ring expansion to **45**, and then hydrogen migration. Triplet photosensitization of **1** in **42a** and **42b** leads to 2,3,5-triphenylpyrrole (**47a**) and 3-(*o*-cyanophenyl)-2,5-diphenylpyrrole (**47c**), products of aromatic substitution rather than ring expansion. Such photolytic processes may involve generation and then addition of **9t** to **42a** and **42b**, spin inversion of the triplet to singlet diradical intermediates, and successive hydrogen migrations. Aniline (**59a**), *N*-methylaniline (**59b**), and *N*,*N*-dimethylaniline are nucleophiles in that they are pyrrylated on nitrogen by **1** at 180 °C. Primary and secondary alcohols and **1** undergo oxidation/reduction to carbonyls and **7**; conversion to 3-alkoxy-2,5-diphenylpyrroles is minor except in the presence of external acid. 2,5-Diphenyl-3-pyrrolediazonium salts (**2**) effect 2,5-diphenylpyrrylation of aromatics upon thermolysis and photolysis. The orientation, utility, and mechanisms of reactions of **2** with benzenes are significantly different than for thermolysis, photolysis, and photosensitization of **1**.

Although diazopyrroles were first synthesized over 70 years ago,[1] very little is known about their chemistry. Photolysis of 3-diazo-2,4,5-triphenylpyrrole in benzene and in methanol produces 2,3,4,5-tetraphenylpyrrole and 2,3,5-triphenylpyrrole, respectively.[2] [3 + 2] Cycloaddition of 3-diazo-2,4,5-triphenylpyrrole with cyclooctyne and then 1,5-rearrangement gives 2,3-cyclooctano-4,5,7-triphenylpyrazolo[1,5-*c*]pyrimidine.[3] 3-Diazo-2,5-diphenylpyrrole

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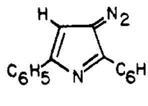
(1) Angelico, F. *Atti Accad. Naz. Lincei, Cl. Sci. His. Mat. Nat., Rend.* **1905**, *14*, II, 167.

(2) Bartholomew, R. F.; Tedder, J. M. *J. Chem. Soc. C* **1968**, 1601.

(3) Dürr, H.; Ranade, A. C.; Halberstadt, I. *Synthesis* **1974**, 878.

0022-3263/84/1949-0062$01.50/0

(**1**) is reported to be photosensitive.[4] Further behavior of diazopyrroles is coupling with 2-naphthol with retention of nitrogen through intermediate diazonium ions.[5] We now summarize various reactions of **1** and of 2,5-diphenyl-3-pyrrolediazonium salts (**2**). A major facet of this investigation is elaboration of the chemistry of 2,5-diphenyl-3*H*-pyrrolylidene (**3**).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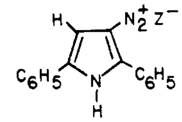
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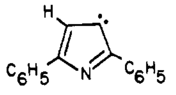
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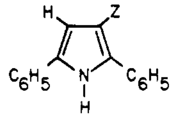
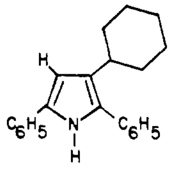
Results and Discussion

Diazopyrrole **1**, a safe, crystalline diazo compound, is prepared by hydrogenation of 3-nitroso-2,5-diphenylpyrrole (**4**)[6] over Raney nickel, diazotization of the resulting 3-amino-2,5-diphenylpyrrole (**5**) with nitrous acid in acetic acid,[6] and neutralization of diazonium acetate **2** (Z = $^{-}O_2CCH_3$) with sodium carbonate.


4, Z = NO

5, Z = NH_2

Photolysis and thermolysis (80 °C) in **1** in cyclohexane results in 3-cyclohexyl-2,5-diphenylpyrrole (**6**; 32% and 22%) and 2,5-diphenylpyrrole (**7**; 25% and 16%).[7] The structure of **6** is established from its elemental analysis and spectral properties; **7**, a reduction product, is identified by comparison with an authentic sample.[8] The mechanistic route to **6** is not clear. Loss of nitrogen from **1** upon thermolysis or direct photolysis will give **3** in its singlet state (**8s**); if **3** has a triplet state close in energy to **8s**, then intersystem crossing to **9t** is highly probable. Formation of **6** may then result from insertion (**8s**) or/and intimate abstraction–recombination (**9t**)[9] into cyclohexane and subsequent [1,5] rearrangement of 2,5-diphenyl-3-cyclohexyl-3*H*-pyrrole (**10**). Apparently **7** is derived by hydrogen abstraction by **9t** and then the 2,5-diphenyl-1-pyrrolyl radical (**11**).[10]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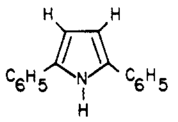
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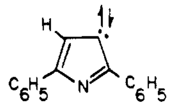
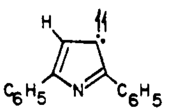
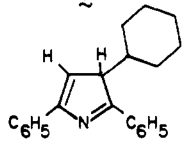

8s


9t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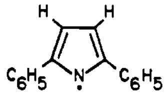
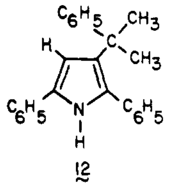

11

The mechanistic behavior upon photolysis of **1** in cumene is somewhat clearer in that 3-(1-methyl-1-phenylethyl)-2,5-diphenylpyrrole (**12**, 43%), 2,3-dimethyl-2,3-diphenylbutane (**13**, 25%), and **7** (46%) are formed.[11] Similarly, decomposition of **1** in cumene at 152 °C yields **12** (44%), **13** (23%), and **7** (47%).[11] Products **13**[12] and **7**[8] are known; **12** is identified by analytical and spectral methods (the IR spectrum shows a characteristic doublet for the *gem*-dimethyl group at 1380 and 1360 cm^{-1}). Formation of **13** implies hydrogen abstraction from cumene by **9t** yielding **11** and α-cumyl radicals (**14**). Further hydrogen stripping by **11** will give **7**, and dimerization of **14** results in **13**.[13] Insertion by **8s** and/or intimate abstraction–recombination by **9t** on the methine hydrogen of cumene and hydrogen migration will yield **12**.[9]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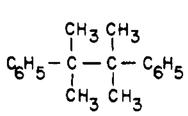
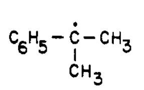
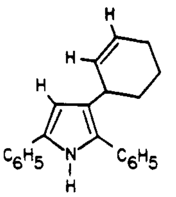

$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5$$
13


$$C_6H_5-\underset{CH_3}{\dot{C}}-CH_3$$
14

Unlike many carbenes **3** does not add to olefins to give isolable cyclopropanes. Thus, photolysis and thermolysis of **1** in cyclohexene result in 3-(3-cyclohexenyl)-2,5-diphenylpyrrole (**15**; 33% and 27%) and **7** (21% and 24%). Neither 2,5-diphenylspiro[2′,3′-tetraethylenecyclopropane-1′,3-pyrrole] (**16**), 3-(1-cyclohexenyl)-2,5-diphenylpyrrole (**17**), nor 2,5-diphenyl-3-(cyclohexylidene)-3*H*-pyrrole (**18**) is detectable. That **15** is the product as assigned is established by analysis, by the downfield shift of the NMR signal (δ 3.25–3.80) of the allylic hydrogen of the cyclohexenyl group on the pyrrole ring, and by catalytic hydrogenation to **6**. Formation of **7** is indicative of triplet **9t** in the reaction system. It cannot yet be concluded whether **15** is formed by allylic ab-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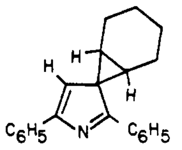
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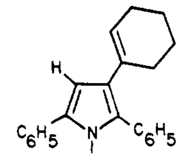
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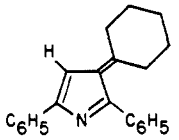
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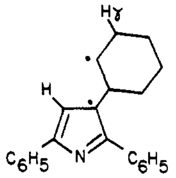
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[4] Angelico, F. *Gazz. Chim. Ital.* **1923**, *53*, 795.

[5] (a) Tedder, J. M.; Webster, B. *J. Chem. Soc.* **1960**, 3270; (b) *Ibid.* **1962**, 1638.

[6] Kreutzberger, A.; Kalter, P. *J. Org. Chem.* **1961**, *26*, 3790.

[7] (a) The yields reported in this manuscript are for purified products and thus are minimal. In thermal and photolytic decompositions of **1** in various experiments, there are always competing reactions of **3** with **1** and with pyrrole products leading to intractables. (b) In experiments in which conversions to **7** are extensive, the yields are also lowered by reaction of **11** with **1** and the capture substrates and products present.

[8] Overberger, G. G.; Valentine, M.; Anselme, J.-P. *J. Am. Chem. Soc.* **1969**, *91*, 687.

[9] For summary for some relevant literature with respect to insertion and abstraction–recombination reactions of carbenes with carbon–hydrogen bonds see (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; Vol. I, Chapter 7 and (b) Closs, G. L.; Gaspar, P. P.; Hammond, G. S. In "Carbenes"; Moss, R. A.; Jones, M. Jr., Eds.; J. Wiley and Sons: New York, 1975; Vol. II, Chapters 4 and 6.

[10] Formation of **7** might occur by transfer of hydrogen directly to nitrogen of **11** and/or by conversion of **11** to 2,5-diphenyl-3*H*-pyrrole and then hydrogen migration.

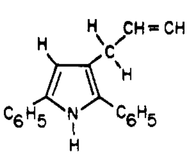
[11] The yields reported are based on 100% theoretical for each of the products isolated.

[12] Klages, A. *Chem. Ber.* **1902**, *35*, 2638.

[13] Dannley, R. L.; Zarensky, B. *J. Am. Chem. Soc.* **1955**, *77*, 1588.

straction–recombination on cyclohexene by **9t**, by direct allylic insertion on cyclohexene by **8s**, or/and by collapse of **16** to **19** and then transfer of γ-H of the cyclohexenyl moiety to the pyrrole nucleus.[9,14,15]

Photolysis of **1** in allylbenzene is of interest in that 2,5-diphenyl-3-(3-phenyl-2-propenyl)pyrrole (**20**) is formed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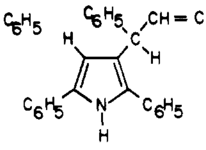
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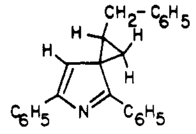
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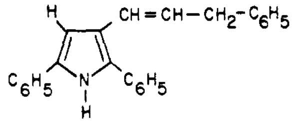
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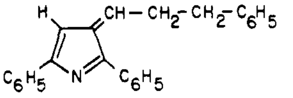
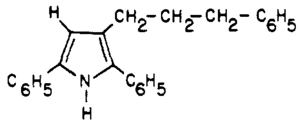

24

along with 2,5-diphenyl-3-(1-phenyl-2-propenyl)pyrrole (**21**, the conversion to **20** and **21** is 32%) and **7** (25%). Similarly, thermolysis of **1** in allylbenzene yields **20** and **21** (33%) and **7** (31%). There was no isomerization of allylbenzene to *cis*- and/or *trans*-1-propenylbenzenes during irradiation or thermal decomposition of **1**. Migration of the double bond in allylbenzene thus occurs upon reaction with **3**; **20** cannot be obtained by direct insertion of **8s** into the olefin. 2,5-Diphenylspiro[2′-benzylcyclopropane-1′,3-pyrrole] (**22**), 2,5-diphenyl-3-(3-phenyl-1-propenyl)pyrrole (**23**), and 2,5-diphenyl-3-(3-phenyl-1-propylidene)-3*H*-pyrrole (**24**) are not found in the photochemical or the thermal experiments. The structures of **20** and **21** could not be determined in admixture by IR and NMR methods. Catalytic hydrogenation (palladium on carbon) of **20** and **21** results, however, in 2,5-diphenyl-3-(3-phenyl-1-propyl)pyrrole (**25**) and 2,5-diphenyl-3-(1-phenyl-1-propyl)pyrrole (**26**). The methylenes flanked by the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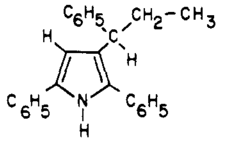
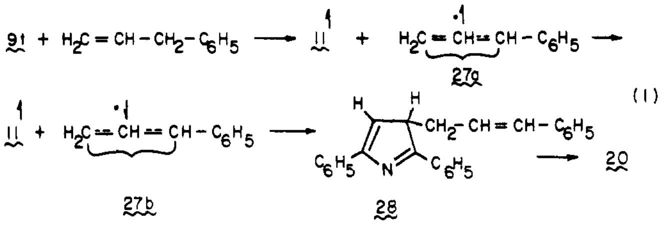

26

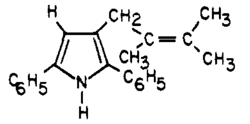
phenyl and the pyrrole rings in **25** and the methyl group in **26** are easily recognized in the NMR spectrum of the reduction product, thus indicating the precursors of **25** and **26** to be either **20** or **23** and **21**. The structure of **20** is unequivocally established by oxidation of the mixture of **20** and **21** with osmium tetraoxide and potassium periodate to benzaldehyde; phenylacetaldehyde is not obtained. The stereochemistry of **20** is unknown.

Formation of **20** is indicative of abstraction of methylene hydrogen from allylbenzene by **9t**, spin pairing of the 2,5-diphenyl-1-pyrrolyl (**11**) and phenylallyl (**27a**) radical system, recombination of **11** and **27b**, and isomerization of 3-allyl-2,5-diphenyl-3*H*-pyrrole (**28**). Production of **7** implies generation of **9t** in some part. Isomer **21** is thus



derivable by recombination of **11** and **27b**.[16] Direct insertion of **8s** into methylene C–H of allylbenzene, however, may also be a source of **21**.

The mechanistic complications in reactions of **3** with olefins are revealed further by photolysis of **1** in 2,3-dimethyl-2-butene to give 3-(2,3-dimethyl-2-butenyl)-2,5-diphenylpyrrole (**29**, 39%) as the only product of olefin incorporation. The structural assignment of **29** rests on (1) its analysis and mass spectrum, (2) two broad NMR singlets at δ 1.63 and 1.73 for the methyl hydrogens and another at δ 3.43 for allylic methylene hydrogens, and (3) the absence of IR bands for olefinic C–H bonds. Products derived by attack of **3** on the carbon–carbon double bond of the olefin or by hydrogen abstraction from the olefin by **9t** and recombination of **30** at C-3 with **11** are not found. Formation of **29** could thus occur by direct insertion of **8s**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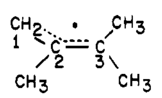
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into C–H of 2,3-dimethyl-2-butene and/or by selective recombination of **11** with **30** at C-1. It would appear, however, that the overall behavior of **3** with the olefins of the present study is as singlet **8s** and as triplet **9t**.[17]

To clarify the behavior of **3** further, a study of its reactions with aromatic substrates was envisaged. Since abstraction of aromatic hydrogen from benzene derivatives is difficult, it was conjectured that the singlet behavior (**8s**) of **3** might predominate in such systems. Also, by investigating the effects of various substituted benzenes on the reactivities and the orientations of substitution, the electrophilic or nucleophilic reactivities of **3** might be better understood. The present summary describes a study of reactions of benzenes and its electronegatively or electropositively substituted derivatives with **3**, parts of which have been reported briefly earlier.[18]

Reactions of **3** with anisole (**31a**) and with toluene (**31b**), benzenes substituted by electron-donor groups, result in selective ortho and/or para substitution (Scheme I) and in hydrogen abstraction. Thus, thermolysis (160 °C) or photolysis of **1** in **31a** yields 3-(*p*-methoxyphenyl)-2,5-diphenylpyrrole (**38a**, 50% and 43%) and **7** (16% and 9%), separable by column chromatography. The structure of **38a** is indicated by its analysis, mass spectrum, IR absorption at 830 cm^{-1} for a 1,4-disubstituted benzene, and partial AA′BB′ NMR pattern centered at δ 6.78 for a *para*-substituted benzene. Synthesis of **38a** as summarized later confirms its structure. Toluene (**31b**), upon decomposition (110 °C) or irradiation of **1**, is converted (Scheme I) to 2,5-diphenyl-3-*o*-tolylpyrrole (**35**), 2,5-diphenyl-*p*-tolylpyrrole (**38b**), and 3-benzyl-2,5-diphenylpyrrole (**39**) in ~1:1:1 ratio (41% and 34% yield) along with **7** (14%

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[14] Baldwin and Andrist (Baldwin, J. E.; Andrist, A. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1512) have found (1) by deuterium labeling methods that fluorenylidene reacts with cyclohexene via abstraction–recombination to form 3-(9′-fluorenyl)cyclohexene and (2) cyclohexene is a hydrogen donor in carbenic decomposition of 9-diazofluorene to give fluorene.

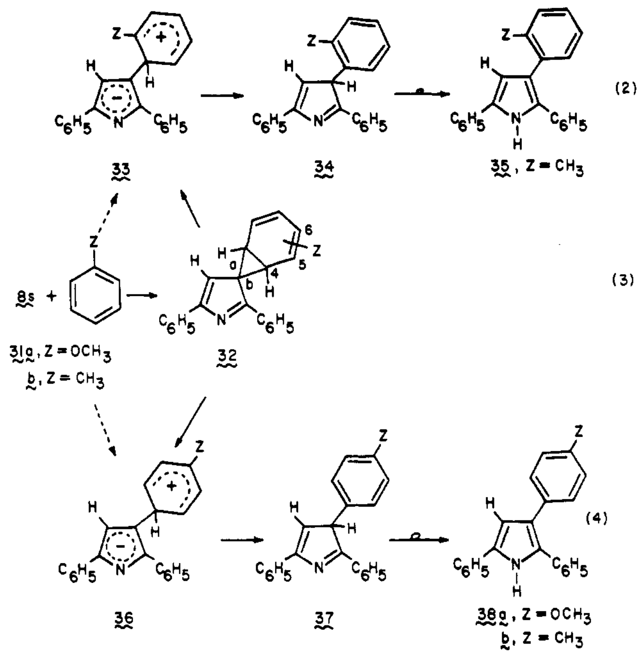
[15] For examples of spirocyclopropanes that isomerize by processes analogous to that for **16** to **19** and then **15** see: Jones, G. W.; Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 2000.

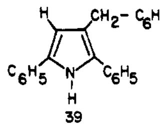
[16] An obvious factor involved in recombination as **11** and **27b** is the conjugation in the transition state leading to **28**.

[17] For a summary of classic examples of carbenes which exhibit simultaneous singlet and triplet behavior see ref 9a, Chapter 8.

[18] Nagarajan, M.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 2198.

Scheme I





39

$C_6H_5-CH_2-CH_2-C_6H_5$

40

$C_6H_5-CH_2\cdot$

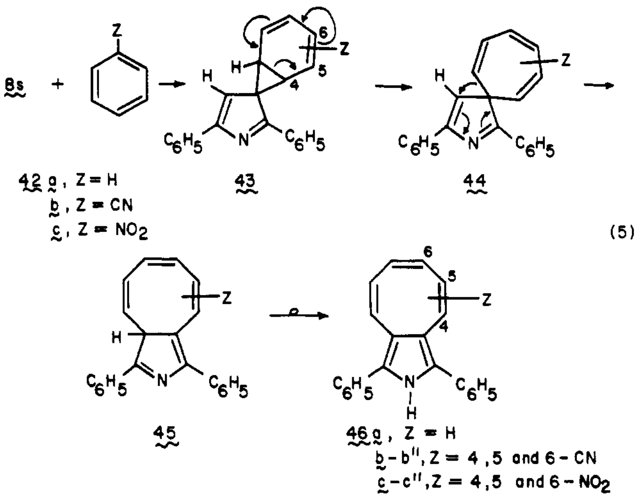
41

and 6%) and 1,2-diphenylethane (**40**; 3% and 4%). Identification of **38a** and **38b** is established upon preparation of authentic samples; **35** is indicated by spectral methods and by inference upon application of mechanistic principles.

The substitution reactions of 1 with anisole (**31a**) and toluene (**31b**) are essentially independent of the method of generation of **3**. The ortho and para orientations obtained with **3** are qualitatively similar to those of 3,5-dichlorobenzene 1,4-diazooxide[19] and of 5-*tert*-butyl-3-diazopyrazole,[20] except that **3** is more selective. The absence of meta substitution products apparently rules out reactions of **1** and **3** (as **9t**) by formal triplet (free radical) mechanisms since related homolytic arylations of substituted benzenes give mixtures of 2-, 3-, and 4-substituted biphenyls.[21] The gross behavior of **1** with electron-rich benzenes thus appears to involve substitution by electrophilic singlet processes.

A simple mechanism for reactions of **8s** with activated benzenes which has precedent[19,22-24] involves electrophilic attack of **8s** on the π system of the substituted benzene to yield spiropyrrolonorcaradienes **32**. As outlined in Scheme I, heterolytic cleavage of **32** at cyclopropane bonds a and b in which the transition states are close to products will give dipolar ions **33** and **36** selectively when Z (Z = OCH_3 and CH_3) is electron donating (ortho and para directing); [1,5] sigmatropic rearrangements of hydrogen possibly via **34** and **37** will yield **35** and **38**. A related alternate mechanism (Scheme I) that cannot yet be excluded, however, is direct reaction of **8s** and **31** to form dipolar σ complexes **33** and **36** selectively, which then convert to products. Since ortho substitution of **31a** is not found, **3** is apparently quite sensitive to steric and to repulsive field effects.

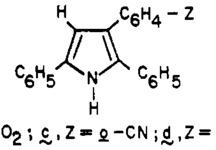
Scheme II



As presumed for the related previous results with olefins, production of **7** from reactions of **3** with **31a** and with **31b** implies that triplet hydrogen abstraction processes by **9t** occur. Such reactions are thus competitive with the presumed singlet aromatic substitution processes (Scheme I). Further, formation of **40** from toluene (**31b**) and **3** apparently results from hydrogen abstraction from the methyl group in toluene (**31b**) by **9t** and dimerization of the resulting benzyl radicals (**41**). The origins of **39** are speculative; **39** may arise (1) from hydrogen abstraction from toluene (**31b**) by **9t**, spin inversion and recombination to give **37** (Z = CH_3), and then hydrogen migration or/and (2) by concerted insertion of **8s** into the methyl group of toluene (**31b**) and then isomerization of **37** (Z = CH_3).

Study of the reactions of **1** was then extended to benzene (**42a**). At 175 °C in an autoclave, **1** effects ring expansion (Scheme II) of benzene (**42a**, 560 equiv) to yield 1,3-diphenyl-2*H*-cycloocta[*c*]pyrrole (**46a**, 68%), a member of a new heterocyclic system. In refluxing benzene (**42a**), conditions under which decomposition of **1** is incomplete, **46a** is the only isolable product. Further, photolysis of **1** in benzene (**42a**) at 25–30 °C gives **46a** (30–32%) along with intractables.[7a]

Surprisingly, 2,3,5-triphenylpyrrole (**47a**), although



47 a, Z = H ; b, Z = m-NO2 ; c, Z = o-CN ; d, Z = o-OCH3 ; e, Z = p-CN

stable under the various reaction conditions, was not found in any experiment.

The structure of **46a** is based primarily on physical evidence. Adduct **46a** analyzes for $C_{22}H_{17}N$ and displays a strong mass spectral peak *m/e* 295, indicating it to be a 1:1 adduct of **8s** and benzene (**42a**). Its proton NMR spectrum shows absorption in the olefinic (δ 5.79–6.36) and aromatic (δ 7.12–7.52) regions in the ratio 3:5 and a broad downfield signal for hydrogen on pyrrole nitrogen. The ^{13}C NMR spectrum of **46a** has nine lines, consistent with the symmetrical structure assigned. Decoupling reveals the presence of four kinds of aromatic carbons (one of them

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[19] Dewar, M. J. S.; Narayanaswami, K. *J. Am. Chem. Soc.* **1964**, *86*, 2422.

[20] Magee, W.; Shechter, H. *Tetrahedron Lett.* **1979**, 4697.

[21] Hey, D. H. In "Advances in Free-Radical Chemistry", Williams, G. H., Ed.; Academic Press: New York, 1967; Vol. II, pp 47–48.

[22] Schonleber, D. *Chem. Ber.* **1969**, *102*, 1789.

[23] (a) Dürr, H.; Schader, L. *Chem. Ber.* **1969**, *102*, 2026. (b) Dürr, H.; Scheppers, G. *Ibid.* **1970**, *103*, 380.

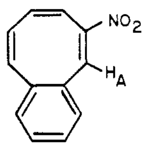
[24] Magee, W.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 633.

quaternary) and two types of pyrrole carbons, which together account for 16 of the 22 carbons of **46a**. The remaining six carbons are therefore of three different types and are olefinic (from the ^{1}H NMR data). The structure of **46a** is confirmed further in that the ^{1}H NMR spectra of its olefinic regions show strong similarities to that of cycloocta[*c*]furan.[25]

Ring expansion of benzene (**42a**) by **3** to **46a** is similar to those of diazocyclopentadienes[22,23] and of 5-*tert*-butyl-3-diazopyrazole[20] with various benzenes. A mechanism (Scheme II) which accounts for **46a** is reaction of **3** as its singlet (**8s**) with benzene (**42a**) to give **43** (Z = H), (electrocyclic) isomerization of spironorcaradiene **43** (Z = H) to spirocycloheptatriene **44** (Z = H), (1,5-sigmatropic) rearrangement to **45** (Z = H), and then hydrogen rearrangement. The important feature of the process is ring expansion (Scheme II) rather than ring opening (Scheme I) of **43** (Z = H). In an extension of the initial step(s) of Scheme I, **43** (Z = H) may form upon direct attack or/and stepwise addition of **8s** to benzene (**42a**).

The reactions of **3** were extended to benzonitrile (**42b**) and nitrobenzene (**42c**), benzenes substituted by electron-withdrawing groups. Thermolysis (180 °C) and photolysis of **1** in benzonitrile (**42b**) result in mixtures of 4-, 5-, and 6-cyano-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles (**46b**, **46b′**, and **46b″**) in 47% and 36% yields, respectively, and intractables. Though diligently sought, products of ring substitution of benzonitrile (**42b**) by **3** were not observed. The molecular formulas of **46b**–**46b″** are established as $C_{23}H_{16}N_2$ by analytical and mass spectral methods, and IR absorption at 2200 cm^{-1} confirms the presence of a cyano group. Resonance for olefinic protons (NMR, δ 5.50–6.88) and aromatic protons (δ 7.23–7.60) in a ratio of 1:2 is evidence for the cycloocta[*c*]pyrrole framework. Finally, signals in the ^{13}C NMR spectrum at 118.12, 117.25, and 116.61 ppm (Me_4Si = 0 ppm) indicate that three kinds of cyano groups are present and thus the isomers **46b**–**46b″**. The composition of the mixture of **46b**–**46b″** could not be determined.

Upon heating (170 °C) of **1** in nitrobenzene (**42c**), four products are found: (a) an inseparable mixture of 4- and 6-nitro-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles (**46c** and **46c″**, respectively; 14%), (b) 5-nitro-1,3-diphenyl-2*H*-cycloocta[*c*]pyrrole (**46c′**, 18%), and (c) 3-(*m*-nitrophenyl)-2,5-diphenylpyrrole (**47b**, 10%), all of proper analysis and mass spectrum. Assignment of **46c′** is based on its NMR olefinic proton signals, no magnetic resonance for hydrogen on carbon of a pyrrole ring, and a sharp singlet at δ 7.85 which is not that of an aromatic proton (such hydrogens appear at δ 7.03–7.67). The singlet comes from one of the olefinic hydrogens of the cyclooctatriene moiety, most likely at C-4 as indicated in **46c′**. The structural conclusion is supported by the NMR spectrum of 4-nitrobenzocyclooctatetraene (**48**) in which the singlet signal at δ 8.03 is assigned to proton H_A.[26] Further, the protons at C-3 and C-5 in benzocyclooctatetraene (**49**) are not coupled.[26] The structures of **46c** and **46c″** are indicated by olefinic hydrogen absorptions similar to **46c′**, no absorption for pyrrole hydrogen on carbon, and ^{13}C NMR signals at 150.21 and 147.98 ppm (carbon containing nitro groups). Substitution product **47b** is assigned by its IR absorption, a NMR doublet for hydrogen on carbon of a pyrrole ring (C-4), the absence of olefinic protons, and oxidative degradation by potassium permanganate and subsequent conversion by diazomethane to methyl *m*-nitrobenzoate.



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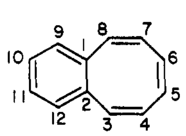

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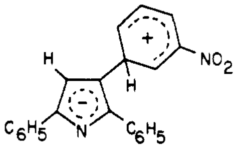
Production of the respective three isomeric cycloocta[*c*]pyrroles, **46b**–**46b″** and **46c**–**46c″**, from reactions of **3** with benzonitrile (**42b**) and with nitrobenzene (**42c**) is consistent with the mechanism of Scheme II in that the possible spiropyrrolonorcaradienes (**43** Z = CN or NO_2 at C-4, C-5, and C-6, respectively) are formed[27] and undergo ring isomerization and then rearrangement of hydrogen. A major mechanistic point is that cyano and nitro groups are expected to retard dipolar ring opening as for **32** to **33** and **36** in Scheme I. An additional factor is that cyano and nitro groups, both highly conjugating and electron-attracting substituents, might also accelerate the various electrocyclic isomerizations of **44** to **45** and thus accentuate formation of ring-expansion products (**46**). Although study of such effects is presently limited to nitrobenzene (**42c**), formation of **46c′** as the major ring-expansion product is interpretable by reaction of nitrobenzene (**42c**) at a meta position with preferential ring closure to give **43** (Z = NO_2 at C-5), which is maximally conjugated.

It is thus of interest that nitrobenzene (**42c**) undergoes some meta substitution, yielding **47b** (21–26% of the product), whereas analogous derivatives of benzene (**42a**) and benzonitrile (**42b**) are not found. It is reassuring that **47b** is the substitution product predicted on the basis of direct electrophilic attack of nitrobenzene (**42c**) as in Scheme I, to give dipolar ion **50**. Further, meta substitution of nitrobenzene (**42c**) might occur because collapse of pyrrolospironorcaradiene **32** (Z = NO_2 at C-5 and C-6) to **50** becomes competitive with ring opening because of a number of factors involved in the rate constants in the many (and possibly reversible) steps in the ring-expansion (Scheme II) and substitution (Scheme I) systems. It has also been found difficult to prevent acid(s) from being generated from nitrobenzene (**42c**) and **1** at 170 °C. Therefore, **47b** might have been formed by deprotonation of the 3-(2,5-diphenyl-3-pyrrolyl)-1-nitrobenzenium ion (**51**) as derived by attack of acid(s) on the pyrrole nitrogen(s) of **32** (Z = NO_2 at C-5 and C-6).[28]



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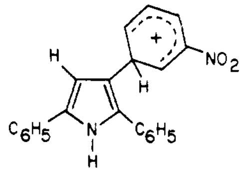

51

To obtain additional information with respect to the synthetic utility and to the variations in the mechanisms of reactions of **3** with benzenoid derivatives, investigation was made of the photolytic behavior of **1** with benzene (**42a**) and with benzonitrile (**42b**) in the presence of triplet photosensitizers. Irradiation of thioxanthen-9-one in **1** and benzene (**42a**) is found to give 2,3,5-triphenylpyrrole (**47a**, 45%) as the only isolable product. The identity of **47a** is established by comparison with an authentic sample.[29]

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[25] Le Goff, E.; La Count, R. B. *Tetrahedron Lett.* **1965**, 2787.

[26] Elix, J. A.; Sargent, M. V. *J. Am. Chem. Soc.* **1969**, *91*, 4734.

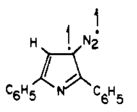
[27] Spiropyrrolonorcaradienes **43** may also exist in syn and anti forms.

[28] (a) Reference 22 has reported an analogous process in that spiro[2,4-cyclopentadien-1,7′-norcaradiene], as derived from photolysis of diazocyclopentadiene in benzene, is isomerized by acids to phenylcyclopentadiene.

When 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) is used as a photosensitizer, a mixture (~1:1) of **47a** and reduction product **7** is produced. Ring expansion of benzene (**42a**) to **46a** or formation of products therefrom is not observed in these systems.

Photosensitized decomposition of **1** in benzonitrile (**42b**) using thioxanthen-9-one as sensitizer also differs from photolysis and thermolysis. Formation of amorphous products is extensive, and the only isolable product is 3-(*o*-cyanophenyl)-2,5-diphenylpyrrole (**47c**, 19%). That **47c** is a 1:1 adduct of **3** and benzonitrile (**42b**) is evident from its mass spectrum and its IR absorption at 2230 cm^{-1} for a cyano group. The NMR spectrum has no olefinic signals but displays a doublet at δ 6.70 for hydrogen on carbon of a pyrrole ring, suggesting insertion of **3** into a C–H bond of **42b**. The exact position of the cyano group in **47c** cannot be determined spectrally and is presumed upon comparison with independently synthesized samples of 3-(*p*-cyanophenyl)-2,5-diphenylpyrrole and 3-(*m*-cyanophenyl)-2,5-diphenylpyrrole, as will be subsequently described. Since **47c** is different from the above *m*- and *p*-cyano derivatives, it is assigned as the ortho isomer.

Photosensitization of **1** in benzene (**42a**) and benzonitrile (**42b**) is significant with respect to synthesis and reaction mechanism and raises the general question as to the differences in behavior of singlet and triplet carbenes in substitution and/or ring expansion of aromatic substrates. Many mechanistic pathways may be envisaged for photosensitization of **1** in benzene (**42a**); two are discussed here. The first involves generation of triplet 3-diazo-2,5-diphenylpyrrole (**52**) and its decomposition to **9t**, addition of **9t** to benzene (**42a**) to form triplet diradical **53** which undergoes spin inversion to singlet diradical **54**, and successive hydrogen migrations to **47a**. Formation of **7** from photosensitization with Michler's ketone (which had to be used in high concentration) is interpretable as involving **9t**, which transfers hydrogen from the methyl groups of the photosensitizer to form 1-pyrrolyl radical **11**, which then abstracts hydrogen further. Since triplet diazo compounds are suspected to be capable of hydrogen abstraction and adding to double bonds,[15,30] an alternative to the previous mechanism is attack of **52** on benzene (**42a**) with spin inversion and ring closure to give pyrazoline **55**, which converts to **54** upon loss of nitrogen. The principal focus of these mechanisms is formation of **54** and hydrogen rearrangement rather than ring closure to **43** (Z = H). Avoidance of spiropyrrolonorcaradiene **43** (Z = H) is presumed since its fate apparently is thermal conversion to ring-expansion product **46a** (Scheme II). That singlet diradicals such as **54** undergo hydrogen migration instead of ring closure has precedent in that many 1-pyrazolines thermolyze and photolyze, presumably via singlet 1,3-diradicals, with rearrangement of hydrogen from C-2 to give olefins.[31] It is certainly expected that isomerization of **54** to **47a** (Z = H) will be a low activation energy process.



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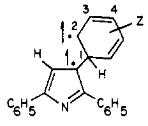
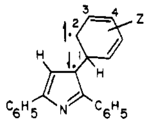
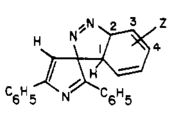


53, Z = H
56, Z = 2-CN



54, Z = H
57, Z = 2-CN

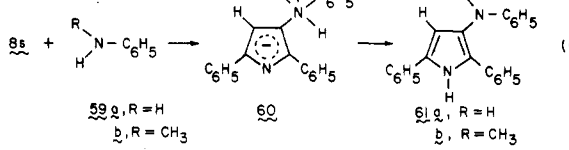


55, Z = H
58, Z = 2-CN

The difference in the behavior of **1** and benzonitrile (**42b**) upon photosensitization as compared to photolysis and thermolysis is also interpretable on the basis of reaction of **9t** and/or **52**, generation of **57** and then **47c**, and avoidance of spiropyrrolonorcaradiene intermediates (**43**, Z = CN) as in Scheme II. Conversion of **47c** is explainable on the basis of selective formation of **56** and/or **57**, the diradical(s) of greatest extended conjugation. The specificity of the photosensitized reaction resulting in the exclusion of 3-(*p*-cyanophenyl)-2,5-diphenylpyrrole and 3-(*m*-cyanophenyl)-2,5-diphenylpyrrole is indeed impressive.

During investigation of possible aromatic substitution of *N*,*N*-dimethylaniline with **1**,[32] it became apparent that **3** has significant electrophilic reactivity along with abilities to effect insertion or/and abstraction–recombination and dehydrogenation. Study was thus initiated of the thermal and/or photolytic behavior of **1** with aniline (**59a**) and *N*-methylaniline (**59b**).

Decomposition of **1** in aniline (**59a**) at 180 °C (eq 6)



(6)

results in N-pyrrylation of **59a** to form 2,5-diphenyl-3-(*N*-phenylamino)pyrrole (**61a**, 29%) along with **7** (>20%), the product of hydrogen transfer to **3**. Similarly, **1** and *N*-methylaniline (**59b**) at 185 °C (eq 2) give 3-(*N*-methyl-*N*-phenylamino)-2,5-diphenylpyrrole (**61b**, 27%) and **7** (>35%). Percentage compositions, specific IR and NMR absorptions, and mass spectral analyses confirm **61a** and **61b**. The major conclusions from these experiments follow: (1) aromatic substitution (and/or ring expansion) of aniline (**59a**) and *N*-methylaniline (**59b**) (electron-rich benzene derivatives) is not observed; (2) attack on nitrogen of aniline (**59a**) and *N*-methylaniline (**59b**) resulting in **61a** and **61b** is strong evidence for involvement of **3** in its singlet state (**8s**); and (3) there must be major spin inversion of **8s** to **9t** even in the nucleophilic environments of aniline (**59a**) and *N*-methylaniline (**59b**) to allow formation of **7** to be extensive. The experiments clearly support the earlier conclusion that the overall behavior of **3** with olefins having abstractable hydrogen is as singlet **8s** and triplet **9t**.

The possible electrophilic behavior of **1** with alcohols upon photolysis and thermolysis then became of interest. Solutions of **1** in primary and secondary alcohols are stable at 25–30 °C for long periods (~1 week). At much higher

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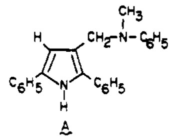
(29) Angelico, F.; Calvello, E. *Gazz. Chim. Ital.* **1901**, *31* (II), 4.

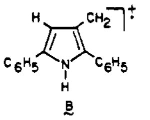
(30) Jones, M.; Ando, W. *J. Am. Chem. Soc.* **1968**, *90*, 2200.

(31) For a summary of experimental results and theory of decomposition of various 1-pyrazolines see (a) Koga, G.; Koga, N.; Anselme, J.-P. and (b) Drewer, R. J. In "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", Part 2; Patei, S., Eds.; J. Wiley and Sons: New York, 1978; Chapters 19 and 20.

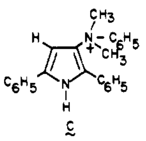
(32) Heating **1** in *N*,*N*-dimethylaniline at 185 °C results in 3-(*N*-methyl-*N*-phenylaminomethyl)-2,5-diphenylpyrrole (**A**, 19%), **61b** (10%), and **7** (9%). Insertion product **A** analyzes for $C_{24}H_{22}N_2$, exhibits NMR



A



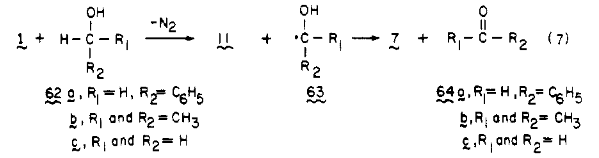
B



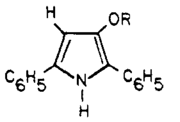
C

signals at δ 2.85 and 4.55 for *N*-methyl and *N*-methylene protons and has a base mass spectral peak at *m*/*e* 232 for the 3-(2,5-diphenylpyrryl)methyl cation radical (**B**) along with that of the parent at *m*/*e* 338. Of interest is that **61b** is formed identical with that from **1** and **59b**. It is presumed that **61b** arises from electrophilic attack of **3** on the nitrogen of *N*,*N*-dimethylaniline to form **C** which undergoes demethylation (possibly by N,N-dimethylaniline) and then protonation upon workup. Efforts to isolate any products derived from demethylation have been unsuccessful.

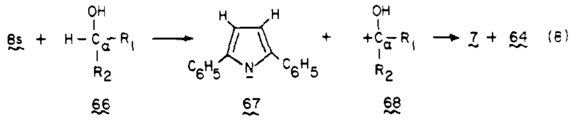
temperatures or upon irradiation, however, oxidation to aldehydes or ketones and reduction to 7 become major processes (eq 7). Thus, benzyl alcohol (**62a**) and **1** at 150



°C yield benzaldehyde (**64a**, 65%) and **7** (>70%), and photolysis or thermolysis of 2-propanol (**62b**) and **1** gives acetone (**64b**, 64%) and **7** (67% and 59%). In none of these experiments were the products (**65**) of capture of the alcohols, 3-(benzyloxy)-2,5-diphenylpyrrole (**65a**) and 2,5-diphenyl-3-(2-propoxy)pyrrole (**65b**), obtained. Irradiation of **1** in methanol (**62c**) at room temperature does result in methanolysis; however, formation of 3-methoxy-2,5-diphenylpyrrole (**65c**) is minor (12%) compared to oxidation–reduction to formaldehyde (**64c**) and **7** (eq 7). The structure of **65c** is self-evident from its analytical and spectral properties. That **1** does not photolyze or thermolyze efficiently in alcohols to give 3-alkoxy-2,5-diphenylpyrroles (**65**) implies that alcohols are insufficiently nucleophilic at oxygen, possibly because of steric and electrical factors, or else the strengths of their OH bonds are such that reactions with **8s** (singlet **3**) do not occur readily and thus spin inversion to **9t** and then hydrogen-abstraction processes take place as in eq 6. Alternate processes for **8s** may be envisaged (eq 8) involving hydride transfer from an α position of an alcohol (**66**) to give the 2,5-diphenyl-1-pyrrole anion (**67**) and α-hydroxycarbonium ion (**68**) intermediates, which then convert to **7** and aldehydes or ketones (**64**). Such processes would seem less likely, however, than electrophilic capture of an alcohol by **8s**.

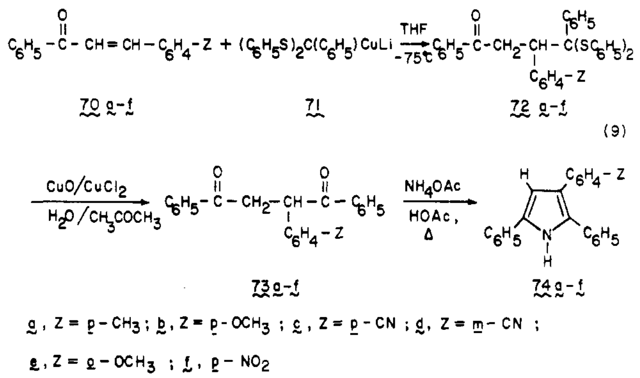


65 a, R = $CH_2C_6H_5$; b, R = $CH(CH_3)_2$; c, R = CH_3 ; d, R = $COCH_3$

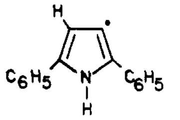


On the possibility that methoxy ether **65c** had been formed from 2,5-diphenyl-3-pyrrolediazonium intermediates (**2**, Z = $^-OCH_3$) upon irradiation of **1** in methanol (**63c**), acid-catalyzed photolyses of **1** in various hydroxylic environments were investigated. Indeed, irradiation of **1** in methanol (**62c**) containing trifluoroacetic acid (1.5 equiv) yields **65c** (44%), and the conversion to **7** is only 11%. The ratios of **65c**:**7** formed in the presence and in the absence of external acid are thus 4:1 and 1:2.25, respectively. Further, photolysis of **1** in 2-propanol (**62b**)/trifluoroacetic acid (1.5 equiv) yields **65b** (24%) and **7** (31%) and in glacial acetic acid gives 3-acetoxy-2,5-diphenylpyrrole (**65c**, >20%). Although more optimum conditions and the mechanistic aspects (homolytic and/or heterolytic processes[33]) for acid-catalyzed photolytic decomposition of **1** in alcohols and carboxylic acids have not been studied, it is apparent that such reactions for 3-pyrrolediazonium derivatives have considerable synthetic promise.

Scheme III



Decomposition of aromatic diazonium salts in aromatic substrates is an important arylation method and apparently involves free-radical substitution processes.[34] Photolysis and thermolysis of 2,5-diphenyl-3-pyrrolediazonium trifluoroacetate (**2**, Z = $^-O_2C\text{-}CF_3$) have now been studied as models for pyrrylation of aromatics. Irradiation of **1**, trifluoroacetic acid (1.5 equiv), and benzene (**42a**) proceeds cleanly with formation of **47a** (67%). Similarly, photolysis of **2** (Z = $^-O_2C\text{-}CF_3$) in anisole (**31a**) results in ortho and para substitution to give 3-(*o*-methoxyphenyl)-2,5-diphenylpyrrole (**47d**, 27%; identified by synthesis) and its para isomer **38a** (27%) along with **7** (7%). Further, **2** at 170 °C converts benzonitrile (**42b**) to the ortho and para isomers, **47c** and 3-(*p*-cyanophenyl)-2,5-diphenylpyrrole (**47e**, assigned upon synthesis), in ~1:1 ratio in >50% yield. The above decomposition reactions of **2** lead to a viable pyrrylation method and appear to be of the free-radical type involving **69**. A principal aspect of the present report thus is that there are important differences in the pyrrylation of aromatics as effected by photolysis, thermolysis, and photosensitization of **1** and by irradiation and/or heating of **2** (Z = $^-O_2CCF_3$ and $^-O_2CCH_3$). Such differences may also be significant in the hetarylation of aromatics by other diazo five-membered ring heterocycles and their corresponding diazonium salts.



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To make the structural assignments of the products of reaction of **1** and **2** with various benzene derivatives, it was necessary to prepare a number of new 2,5-diphenyl-3-(substituted-phenyl)pyrroles (**74**). The sequence employed (Scheme III) usually involved conjugate addition of lithium [α,α-bis(phenylthio)benzyl]cuprate (**71**)[35] at −75 °C to an appropriate chalcone (**70**),[35] hydrolysis of the intermediate dithioketals (**72**), and cyclization of the resulting 1,4-diketones (**73**) with ammonium acetate/acetic acid. Synthesis of **36** from 3-benzoyl-2,5-diphenylpyrrole (75)[36] was

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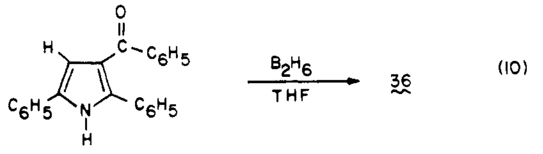
[33] Lee, W. E.; Calvert, J. G.; Malmberg, E. W. *J. Am. Chem. Soc.* **1961**, *83*, 1928 and Lewis, E. S.; Holliday, R. E.; Hartung, L. D. *Ibid.* **1969**, *91*, 430 have reported and discussed the photolysis of aryl diazonium salts in hydroxylic media.

[34] For discussion of homolytic and heterolytic arylation of aromatic compounds by diazonium salts see: (a) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335. (b) Burri, P.; Loewenschuss, H.; Zollinger, H.; Zwolinski, G. K. *Helv. Chim. Acta* **1974**, *57*, 395. (c) Bergstrom, R. G.; Landells, R. G. H.; Wahl, G. H.; Zollinger, H. *J. Am. Chem. Soc.* **1976**, *98*, 3301. (d) References therein.

[35] Mukaiyama, T.; Narasaka, K.; and Furusato, M. *J. Am. Chem. Soc.* **1972**, *94*, 8641.

[36] Sprio, V. *Gazz. Chim. Ital.* **1956**, *86*, 95.

effected by reduction with diborane in tetrahydrofuran (eq 10).



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(10)

Experimental Section

General Methods. Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Microanalysis, Inc., Wilmington, DE, by Galbraith Laboratories, Inc., Knoxville, TN, or by Scandinavian Microanalytical Laboratory, Herlev, Denmark. A Cary recording spectrophotometer (Model 14) was used for the ultraviolet absorption measurements. Infrared spectra were recorded on Perkin-Elmer Model 137 or 457 spectrophotometers calibrated against polystyrene absorption at 1601 cm^{-1}. Samples were prepared as KBr wafers unless otherwise stated. Proton magnetic resonance spectra were obtained with Varian Associates NMR spectrometer Models A-60A, HA-100, and EM-360L, respectively. Bruker instruments (Models HX-90 and WP-80) were used for determining carbon-13 magnetic resonance. All spectra were measured in chloroform-*d* with tetramethylsilane as internal standard. Mass spectra were determined on an AEI-MS-9 mass spectrometer. Gas chromatographic analyses were made with a Wilkins Aerograph unit (Model HI-FY 600-D) with a flame ionization detector. Relative peak areas were obtained by multiplying peak height by peak width at half height. MN Laboratories "Silica Gel", 70–270 mesh, was used for column chromatography.

Decompositions. All decompositions (both thermal and photolytic) of **1** were carried out under nitrogen. Unless otherwise stated, all photolyses were performed with a Hanovia 450-W medium-pressure mercury lamp placed in a Pyrex immersion well. The well itself was fitted to a photochemical reactor containing the solution to be irradiated. All solvents were dried and deoxygenated before use.

3-Diazo-2,5-diphenylpyrrole (1).[37] 2,5-Diphenylpyrrole[8] was nitrosated with sodium ethoxide and isoamyl nitrite in absolute ethanol to give 3-nitroso-2,5-diphenylpyrrole (**4**) in >95% yield, mp 203–204 °C (lit.[6] 204–205 °C). Reduction of **4** with hydrogen and Raney Nickel T-1 in 1:1 acetone:2-propanol afforded 3-amino-2,5-diphenylpyrrole (**5**, 45–50%), mp 184–186 °C (lit.[6] 186–187 °C). Diazotization of **5** in 4:1 acetic acid-water with aqueous sodium nitrite followed by neutralization with sodium carbonate solution at 0–5 °C precipitated orange-red **1**. Diazopyrrole **1** crystallizes from 5:1 petroleum ether (65–110 °C)–benzene as brown-red needles: mp 122–123 °C dec (lit.[6] 122–123 °C); IR 3040 (aromatic C–H), 2100 (diazo), 1600 (aromatic), 1445, 1340, 1310, 1260, 1165, 765, 755, and 690 cm^{-1} (aromatic); NMR δ 6.80 (s, pyrrole 4-*H*, 1) and 7.05–8.10 (m, aromatic *H*, 10); exact mass calcd for $C_{16}H_{11}N_3$, 245.0953; found, 245.0957. The overall yield of **1** from 2,5-diphenylpyrrole ranged from 25 to 30%. Diazopyrrole **1** is a stable and nonexplosive compound at room temperature and can be stored for months as a solid in the dark. Exposure of solutions in various solvents (benzene, chloroform, etc.) to light leads to slow decomposition as indicated by a change in color.

Photolysis of 1 in Cyclohexane. Diazopyrrole **1** (0.490 g, 2.0 mmol) in cyclohexane (145 mL) was irradiated for 2.5 h. Concentration of the mixture gave a red-brown residue which was chromatographed over silica gel (MN) and eluted with 2:3 benzene–hexane. The first product off the column was 3-cyclohexyl-2,5-diphenylpyrrole (**6**, 0.190 g, 32%): mp (hexane), 103–104 °C; IR 3440 (pyrrole N–H), 3030 (aromatic C–H), 2920 and 2845 (aliphatic C–H), 1600 and 1490 (aromatic), 820, 770, 760, and 690 cm^{-1} (aromatic); NMR δ 1.10–2.20 (br m, $-\mathrm{H}\overline{\mathrm{C}(C\mathit{H}_2)_4\mathrm{C}}\mathit{H}_2$, 10), 2.75 (br m, $-\mathit{H}\overline{\mathrm{C}(\mathrm{CH}_2)_4\mathrm{C}}\mathrm{H}_2$, 1), 6.55 (d, *J* = 2.5 Hz, pyrrole 4-H, 1), 7.0–7.60 (m, aromatic H, 10), and 8.0–8.25 (br s, pyrrole N–H, 1); exact mass calcd for $C_{22}H_{23}N$, 301.1830; found, 301.1836.

Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69. Found: C, 87.40; H, 7.82.

Further elution gave 2,5-diphenylpyrrole (**7**, 0.110 g, 25%) identified by comparison with an authentic sample.

Thermolysis of 1 in Cyclohexane. Diazopyrrole **1** (0.490 g, 2.0 mmol) in cyclohexane (200 mL) was heated at 80 °C for 48 h and concentrated. The residue, upon careful chromatography and elution, gave **6** (0.130 g, 22%) and **7** (0.070 g, 16%).

Photolysis of 1 in Cumene. A solution of **1** (0.490 g, 2.0 mmol) in cumene (175 mL) was photolyzed for 0.5 h. The concentrate was chromatographed and eluted with petroleum ether (30–60 °C). Fraction 1 was 2,3-dimethyl-2,3-diphenylbutane (**13**, 0.120 g, 25%): mp 116–118 °C (lit.[12] 119–120 °C); IR 3020 (aromatic C–H), 2980 (aliphatic C–H), 1495 (aromatic), 1440, 1380 and 1365 (geminal dimethyls), 780 and 705 cm^{-1} (aromatic); NMR δ 1.30 (s, CH_3, 12) and 7.10 (s, aromatic H, 10); exact mass calcd for $C_{18}H_{22}$; 238.1721; found; 238.1724. Fraction 2 was identified as 3-(1-methyl-1-phenylethyl)-2,5-diphenylpyrrole (**12**, 0.291 g, 43%): mp (hexane) 122–123 °C; IR 3445 (pyrrole N–H), 2970 (aliphatic C–H), 1600 and 1490 (aromatic), 1380 and 1360 (geminal methyls), 770, 760 and, 700 cm^{-1} (aromatic); NMR δ 1.62 (s, CH_3, 6), 6.70 (d, *J* = 3 Hz, pyrrole 4-*H*, 1), 6.90–7.60 (m, aromatic *H*, 15), and 8.00–8.32 (br s, pyrrole N–H, 1); exact mass calcd for $C_{22}H_{23}N$, 337.1830; found, 337.1836.

Anal. Calcd for $C_{25}H_{23}N$: C, 88.89; H, 6.87; N, 4.15. Found: C, 89.18; H, 7.01; N, 4.22.

The final fraction was **7** (0.20 g, 46%).

Thermolysis of 1 in Cumene. A cumene solution (200 mL) of **1** (0.490 g, 2.0 mmol) was refluxed for 24 h and concentrated in vacuo. The viscous dark residue was chromatographed and eluted with 1:1 hexane–benzene. The first fraction contained **13** (0.110 g, 23%). The second product was **12** (0.295 g, 44%). Finally, **7** was isolated (0.210 g, 48%).

Photolysis of 1 in Cyclohexene. A cyclohexene solution (380 mL) of **1** (0.980 g, 4.0 mmol) was photolyzed 3 h. Chromatography[38] of the concentrate gave 3-(3-cyclohexenyl)-2,5-diphenylpyrrole (**15**, 0.392 g, 33%): mp (hexane) 80–82 °C; IR 3430 (pyrrole N–H), 3010 (aromatic and olefinic C–H), 2920 (aliphatic C–H), 1600 and 1490 (aromatic), 820, 770, 760, and 700 cm^{-1} (aromatic); NMR δ 1.20–2.30 (br m, $\overline{\mathrm{HCH{=}CHC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}}\mathit{H}_2$, 6), 3.35–3.80 (br m, $-\mathit{H}\overline{\mathrm{CCH{=}CH(CH_2)_2C}}\mathrm{H}_2$, 1), 5.75 (br s, olefinic H, 2), 6.40 (d, *J* = 2.5 Hz, pyrrole 4-H, 1), 7.0–7.60 (m, aromatic H, 10), and 7.90–8.23 (br s, pyrrole N–H, 1), exact mass calcd for $C_{22}H_{21}N$, 299.1673, found, 299.1678. Since **15** could not be purified satisfactorily for analysis, it was reduced to 3-cyclohexyl-2,5-diphenylpyrrole (**6**, see below) for confirmation of its structure. A second product isolated was **7** (0.179 g, 21%).

Hydrogenation of 3-(3-Cyclohexenyl)-2,5-diphenylpyrrole (15). Pyrrole **15** (0.110 g, 0.368 mmol) in methanol (30 mL) was hydrogenated for 3 h at 20 psi over 5% Pd/C (10 mg). Filtration through Celite, concentration, filtration through silica gel with 1:1 hexane–benzene, and crystallization yielded **6** (0.101 g, 91%) identical with the previous sample (IR, NMR, mp, and mass spectrum).

Thermolysis of 1 in Cyclohexene. A mixture of **1** (0.490 g, 2.0 mmol) and cyclohexene (200 mL) on heating at 80 °C for 1 week, concentration, and chromatography yielded **15** (0.16 g, 27%) and **7** (0.105 g, 24%) as established from their IR and NMR spectra.

Photolysis of 1 in Allylbenzene. Diazopyrrole **1** (0.490 g, 2.0 mmol) in allylbenzene (175 mL) was photolyzed 15 min. The product was chromatographed on silica gel and eluted. The first product was **7** (0.092 g, 21%) by NMR. The second fraction was a mixture of 2,5-diphenyl-3-(3-phenyl-2-propenyl)pyrrole (**20**) and 2,5-diphenyl-3-(1-phenyl-2-propenyl)pyrrole (**21**, 0.22 g, 32%): IR (neat) 3440 (pyrrole N–H), 3065 and 3040 (aromatic and olefinic C–H), 1605 and 1500 (aromatic), 1270, 1075, 1030, 970 (C–H out of plane bending of trans –CH=CH–), 910 (C–H out of plane bending of $-CH{=}CH_2$), 760 and 695 cm^{-1} (aromatic); NMR δ 2.85–3.63 (m, allylic H), 4.70–5.23 (m, aromatic H), 6.35–6.52 (m,

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[37] A modification of the method of ref 6.

[38] All chromatographic elutions were effected with benzene–hexane unless stated otherwise.

pyrrole 4-H), 6.73–7.62 (m, aromatic H), and 8.05–8.35 (br s, pyrrole N–H); mass spectrum, *m*/*e* 335 (M^+ for $C_{22}H_{21}N$, 335).

Hydrogenation of 20 and 21. The mixture of **20** and **21** (0.211 g, 0.63 mmol) in ethyl acetate (30 mL) was hydrogenated (40 psi) over 5% Pd/C (30 mg). NMR showed the concentrate (0.130 g to be 2,5-diphenyl-3-(3-phenylpropyl)pyrrole (**25**) and 2,5-diphenyl-3-(1-phenylpropyl)pyrrole (**26**) with signals at δ 0.90 (distorted t, $-CH_2CH_3$), 1.85–2.15 (br m, $-CH_2CH_3$ and $-CH_2CH_2CH_2-$), 2.62 (distorted quartet, $-CH_2CH_2CH_2-$), 3.83 (m, methine H), 6.42–6.60 (m, pyrrole 4-H), 6.90–7.62 (m, aromatic *H*), and 8.0–8.33 (br s, pyrrole N–H). NMR integration at δ 0.90 and 2.62 gave a ratio of 3:2 for **20** and **21**.

Oxidative Cleavage of 20 and 21. To **20** and **21** (0.168 g, 0.50 mmol) in 4:1 dioxane–water was added 5% osmium tetraoxide in ether (5 drops) followed by sodium periodate (0.30 g). The suspension was stirred 30 min, poured into water, and extracted with ether. The ether extracts were washed with water and dried. GC analysis of the concentrate (0.115 g) showed the presence of benzaldehyde and the absence of phenylacetaldehyde (20% SE-30 on Chrom W 60–80 mesh, NAW). Pyrrole **7** was unchanged under the above conditions.

Thermolysis of 1 in Allylbenzene. An allylbenzene solution (100 mL) of **1** (0.490 g, 2.0 mmol) was heated at 160 °C for 1 h, concentrated, and chromatographed. The first product removed was **7** (0.135 g, 31%). Further elution yielded **20** and **21** 0.220 g, 33%): IR (neat) 3440 (pyrrole N–H), 3060 and 3040 (aromatic and olefinic C–H), 1605 and 1500 (aromatic), 1275, 1080, 1035, 970 (C–H out of plane bending of trans –CH=CH–), 915 (C–H out of plane bending of $-CH{=}CH_2$), 765, 700, and 690 cm^{-1} (aromatic); NMR δ 2.90–3.60 (m, allylic H), 4.68–5.25 (m, olefinic H), 6.35–6.50 (m, pyrrole 4-H), 6.90–7.55 (m, aromatic H), and 7.97–8.30 (br s, pyrrole N–H); mass spectrum, *m*/*e* 335 (M^+ for $C_{25}H_{21}N$, 335). Hydrogenation of the mixture as described before gave a product whose NMR was similar to that previously described. Integration at δ 0.88 and 2.62 gave a ratio of 5:2 for **20** and **21**. Oxidative cleavage of **20** and **21** with osmium tetraoxide/sodium periodate yielded benzaldehyde (by GC analysis, same conditions as reported earlier).

Photolysis of 1 in 2,3-Dimethyl-2-butene. A solution of **1** (0.980 g, 4.0 mmol) in 2,3-dimethyl-2-butene (380 mL) was photolyzed (4 h). Concentration and chromatography led to only one tractable material, 3-(2,3-dimethyl-2-butenyl)-2,5-diphenylpyrrole (**29**, 0.465 g, 39%): mp (hexane) 96.5–98.0 °C; IR 3435 (pyrrole N–H), 3040 (aromatic C–H), 2900 (aliphatic C–H), 1600 and 1490 (aromatics), 1275, 910, 820, 780, 770, and 690 cm^{-1} (aromatic); NMR δ 1.63 (br s, CH_3), 1.73 (br s, CH_3, together 9), 3.42 (br s, $-CH_2-$, 2), 6.4 (d, *J* = 3 Hz, pyrrole 4-H, 1), 7.08–7.67 (m, aromatic *H*, 10), and 8.0–8.42 (br s, pyrrole N–H, 1), exact mass calcd for $C_{22}H_{23}N$, 301.1830; found, 301.1834.

Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.33; H, 7.57; N, 4.77.

Decomposition of 1 in Anisole (31a). Diazopyrrole **1** (0.490 g, 2.0 mmol) in **31a** (100 mL) was maintained at 160 °C for 45 min. Vacuum distillation left a residue which was chromatographed and eluted. The first fraction was **7** (0.094 g, 16%). Continued elution gave 3-(*p*-methoxyphenyl)-2,5-diphenylpyrrole (**38a**, 0.325 g, 50%): mp (2-propanol) 116–118 °C; IR 3400 (pyrrole N–H), 3030 (aromatic C–H), 1600 and 1485 (aromatic), 1220 (C–O–C), 1165, 945, 830 (aromatic C–H out of plane bending, characteristic of para substitution), 760, and 695 cm^{-1} (aromatic); NMR δ 3.75 (s, $-OCH_3$, 3), 6.62 (d, *J* = 3 Hz, pyrrole 4-*H*, 1), 6.78 (distorted doublet, *J* = 8 Hz, $-\overline{\mathrm{CCHC}H\mathrm{C(OCH_3)C}H\mathrm{C}}\mathrm{H}$, part of an AA′BB′ pattern, 2), 6.93–7.63 (m, aromatic *H*, 12), and 8.17–8.50 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{22}H_{19}NO$, 325.1499; found, 325.1473.

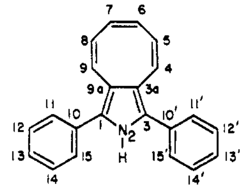
Photolysis of 1 in Anisole (31a). Photolysis (2 h) of **1** (0.490 g, 2.0 mmol) and **31a** (100 mL), concentration, and chromatography afforded **7** (0.038 g, 9%) and **38a** (0.277 g, 43%) identified by comparison with authentic samples.

Photolysis of 1 in Toluene (31b). Photolysis (1 h) and concentration of **1** (0.490 g, 2.0 mmol) and **31b** (175 mL) were effected. Chromatography first gave 1,2-diphenylethane (**40**, 0.014 g, 4%) identified by its NMR signals at δ 2.90 (s, $CH_2C_6H_5$, 4) and 7.18 (s, aromatic *H*, 10) and by comparison of its GC properties with an authentic sample (20% SE-30 on Chrom W).

Crystallization of the second fraction (0.236 g) from hexane yielded **7** (0.024 g, 6%). The filtrate was concentrated to a residue (0.210 g): IR (neat) 3440 (pyrrole N–H), 3060 and 3025 (aromatic C–H), 2920 (aliphatic C–H), 1605 and 1490 (aromatic), 1455, 1270, 1220, 810, 760 and 695 cm^{-1} (aromatic); NMR δ 2.08 (s, Ar–CH_3), 2.28 (s, Ar–CH_3), 3.95 (s, Ar–CH_2), 6.30 (d, *J* = 3 Hz, pyrrole 4-*H*), 6.47 (d, *J* = 3 Hz, pyrrole 4-*H*), 6.58 (d, *J* = 3 Hz, pyrrole 4-*H*), 6.75–7.53 (m, aromatic *H*), and 8.00–8.23 (br s, pyrrole N–*H*); mass spectrum *m*/*e* 309 (M^+ for $C_{22}H_{19}N$, 309). NMR shows that the residue after removal of **7** contained 3-benzyl-2,5-diphenylpyrrole (**39**), 2,5-diphenyl-3-(*p*-tolyl)pyrrole (**38b**), and 2,5-diphenyl-3-(*o*-tolyl)pyrrole (**35**) in 34% yield. Products **38b** and **39** were confirmed by synthesis (see later). Integration of the signals at δ 2.08, 2.28, and 3.95 gives the ratio of **35**:**38b**:**39** as 1:1:1.

Thermolysis of 1 in Toluene (31b). Diazopyrrole **1** (0.490 g, 2.0 mmol) in **31b** (100 mL) was warmed at 110 °C for 14 h. Chromatography of the concentrate yielded **40** (0.008 g, 2%) as identified by GC. Further elution resulted in a product (0.320 g) which, on cooling in hexane, deposited **7** (0.061 g, 14%). The filtrate gave an oil (0.251 g, 41%): IR (neat) 3440 (pyrrole N–H), 3060 and 3030 (aromatic C–H), 1600 and 1495 (aromatic), 1445, 1265, 1220, 760 and 695 cm^{-1} (aromatic); NMR δ 2.12 (s, Ar–CH_3), 2.33 (s, Ar–CH_3), 4.0 (s, Ar–CH_2–), 6.35 (d, *J* = 3 Hz, pyrrole 4-*H*), 6.52 (d, *J* = 3 Hz, pyrrole 4-*H*), 6.63 (d, *J* = 2.5 Hz, pyrrole 4-*H*), 6.85–7.63 (m, aromatic *H*), and 8.05–8.30 (br s, pyrrole N–*H*); mass spectrum, *m*/*e* 309 (M^+ for $C_{23}H_{19}N$ 309). The oil is a mixture of **35**, **38b**, and **39** (by NMR); their ratio by integration of the signals at δ 2.12, 2.33, and 4.0 is ~1:1:1.

Photolysis of 1 in Benzene (42a). Irradiation of **1** (0.980 g, 4.0 mmol) in **42a** (380 mL) for 4 h, concentration, and chromatography yielded a yellow solid as the only isolable product; 1,3-diphenyl-2*H*-cycloocta[*c*]pyrrole (**46a**, 0.366 g, 31%): mp (hexane–benzene) 196.5–197.5 °C; IR 3430 (pyrrole N–H), 3030 (aromatic and olefinic C–H), 1640 (olefinic C=C), 1600 and 1470 (aromatic), 920, 800, 760, and 690 cm^{-1} (aromatic); NMR δ 5.79–6.36 (m, olefinic *H*, 6), 7.12–7.52 (m, aromatic *H*, 10), and 8.07–8.38 (br s, pyrrole N–*H*, 1); ^{13}C NMR (in ppm downfield from Me_4Si) 132.441 (C-1,3 or 10,10′), 131.033 (C-1,3 or 10,10′), 130.451 (C-6,7), 130.062 (C-5,8), 128.703 (C-12,12′,14,14′), 127.198 (C-4,9), 127.101 (C-11,11′,15,15′), 126.907 (C-13,13′), and 119.381 (C-3a,9a); UV (ethanol) λ 221 (28,330) and 330 nm (30,860); exact mass calcd for $C_{22}H_{17}N$, 295.1361; found, 295.1368.



Anal. Calcd for $C_{22}H_{17}N$: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.20; H, 5.75; N, 4.82.

Thermolysis of 1 in Benzene (42a). A solution of **1** (0.490 g, 2.0 mmol) in **42a** (200 mL) at 80 °C for 90 h and workup as above yielded **46a** (0.461 g, 73%) and **1** (0.246 g). Similarly, **1** (0.245 g, 1.0 mmol) in **42a** (50 mL) was rocked in a glass lined autoclave (American Instrument Co., Model 40-1220) at 175 °C for 1 h. Concentration of the mixture followed by chromatography gave **46a** as the only isolable product (0.202 g, 69%).

Thermolysis of 1 in Benzonitrile (42b). A mixture of **1** (0.490 g, 2.0 mmol) and **42b** (100 mL) was heated at 180 °C for 1 h. The yellow solid obtained after concentration and chromatography was shown by ^{13}C NMR to be a mixture of 4-, 5-, and 6-cyano-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles (**46b**, **46b**, and **46b**, 0.30 g, 47%) (see Results and Discussion): mp (hexane–benzene) 176–177 °C; IR 3300 (pyrrole N–H), 3050 and 3020 (aromatic and olefinic C–H), 2220 (–CN), 1640 (olefinic C=C), 1605 and 1485 (aromatic), 900, 805, 765, and 695 cm^{-1} (aromatic); NMR δ 5.50–6.88 (m, olefinic *H*, 5), 7.23–7.60 (m, aromatic *H*, 10), and 8.50–8.90 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{23}H_{16}N_2$, 320.1313; found, 320.1318.

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.75. Found: C, 86.50; H, 5.30; N, 8.26.

Photolysis of 1 in Benzonitrile (42b). The photolysate (**6h**) from **1** (0.490 g, 2.0 mmol) in **42b** (175 mL), after chromatography (benzene), yielded a yellow solid (mp 175–178 °C), a mixture of **46b**, **46b′**, and **46b″** (0.227 g, 36%) having identical properties (IR, NMR, and exact mass) with the previous product from thermolysis of 1 in **42b**.

Thermolysis of 1 in Nitrobenzene (42c). A mixture of **42c** (50 mL) and 1 (0.245 g, 1.0 mmol) was thermolyzed (170 °C) for 25 min, concentrated, and chromatographed (benzene–petroleum ether, 30–60 °C). The first compound eluted was 3-(*m*-nitrophenyl)-2,5-diphenylpyrrole (**47b**, 0.033 g, 10%): mp (2-propanol) 135.5–137 °C; IR 3390 (pyrrole N–H), 3040 (aromatic C–H), 1595 (aromatic), 1530 and 1340 ($-NO_2$), 1110, 810, 765, 750 and 700 cm^{-1} (aromatic); NMR δ 6.60 (d, $J = 2.5$ Hz, pyrrole 4-*H*, 1), 7.0–7.63 (m, aromatic *H*, 12), 7.75–8.20 (m, *H* ortho to the nitro group, 2), and 8.42–8.67 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{22}H_{16}N_2O_2$, 340.1216; found, 340.1220.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.50; H, 4.82; N, 8.26.

The second fraction was a mixture of 4- and 6-nitro-1,3-diphenyl-2*H*-cycloocta[*c*]pyrroles, (**46c** and **46c″**; 0.046 g, 14%) (see Results and Discussion for these assignments): mp (benzene) softens at 154–156 °C, decomposes at 220–223 °C; IR 3420 (pyrrole N–H), 3030 (aromatic C–H), 1610 (aromatic), 1520 and 1335 ($-NO_2$), 855, 770, 755 and 695 cm^{-1} (aromatic); NMR δ 5.75–6.63 (m, olefinic *H*, 3), 7.03–7.67 (m, aromatic and olefinic *H*, 12), and 8.25–8.58 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{22}H_{16}N_2O_2$, 340.1216; found, 340.1220.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.77; H, 4.92; N, 8.21.

The final product was assigned as 5-nitro-1,3-diphenyl-2*H*-cycloocta[*c*]pyrrole (**46c′**, 0.060 g, 18%) (see Results and Discussion): mp (hexene–benzene) 210–211 °C; IR 3350 (pyrrole N–H), 3040 (aromatic and olefinic C–H), 1630 (olefinic C=C), 1600 and 1480 (aromatic), 1300 (nitro), 1015, 910, 770 and 700 cm^{-1} (aromatic); NMR δ 6.0–6.22 (m, olefinic *H*, 2), 7.03–7.67 (m, aromatic and olefinic *H*, 12), 7.85 (s, olefinic *H*, 1), and 8.57–8.93 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{22}H_{16}N_2O_2$: 340.1216; found, 340.1220.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 78.05; H, 4.93; N, 8.28.

Conversion of 47b to Methyl *m*-Nitrobenzoate. A mixture of **47b** (0.204 g, 0.6 mmol), potassium permanganate (0.474 g, 3.0 mmol), and water (10 mL) was heated at 130 °C for 3 h, filtered, and acidified with hydrochloric acid to pH 2. The suspension was extracted with ether; evaporation of the ether gave a crude product containing *m*-nitrobenzoic acid: NMR δ 7.21–7.94 (m, aromatic *H*), 8.94 (s, aromatic *H* at C-2 of $m\text{-}O_2N\text{-}C_6H_4\text{-}CO_2H$ identical with that of an authentic sample) and 10.75 (br s, $-CO_2H$). Reaction of the product with ethereal diazomethane, destruction of excess diazomethane with acetic acid, extraction with sodium bicarbonate, water, and brine, concentration, and analysis by GC revealed the presence of methyl benzoate and methyl *m*-nitrobenzoate as confirmed by co-injection of authentic samples.

Photosensitization of 1 in Benzene (42a) with Thioxanthen-9-one. A solution of 1 (0.245 g, 1.0 mmol), **42a** (90 mL), and thioxanthen-9-one (2.37 g, 11.2 mmol, calculated to absorb at least 95% of the incident light at 380 nm, the λ_{max} for the photosensitizer in **42a**) was photolyzed for 1 h and concentrated. The solid was extracted with **42a** and filtered. The extraction was repeated to remove the thioxanthen-9-one. Finally, chromatography of the residue from the filtrate gave 2,3,5-triphenylpyrrole (**47a**, 0.134 g, 46%), identical with an authentic sample. There was no evidence for **46a**.

Photosensitization of 1 and Benzene (42a) with 4,4′-Bis(dimethylamino)benzophenone. 4,4′-Bis(dimethylamino)benzophenone (Michler's ketone) (1.485 g, 5.53 mmol, calculated to absorb at least 95% of the incident light at 380 nm, the high-wavelength cut-off for a Corning 7-37 filter) and 1 (0.061 g, 0.25 mmol) in **42a** (90 mL) was irradiated through a Corning 7-37 filter (10% transmittance at 335 and 380 nm; greater than 21% at 365 nm) with a Schoeffel Instrument 1000-W high-pressure mercury–xenon lamp for 8 h. Excess **42a** was removed and the residue was dissolved in chloroform and chromatographed (benzene). A mixture (0.022 g) of **7** and **47a** was obtained which was identified and analyzed by NMR, IR, and mass spectral methods. Integration of the NMR signals at δ 6.55 (**7**) and 6.66 (**47a**) indicated that **7** and **47a** are present in 1:1 ratio.

Photosensitization of 1 in Benzonitrile (42b) with Thioxanthen-9-one. A solution of 1 (0.245 g, 1.0 mmol) and thioxanthen-9-one (2.37 g, 11.2 mmol, calculated to absorb >95% of the incident light at 380 nm) in **42b** (175 mL) was photolyzed for 4 h. The mixture was concentrated, extracted with hot benzene, and filtered. The only tractable product, after concentration and chromatography, was a pale yellow solid, 3-(*o*-cyanophenyl)-2,5-diphenylpyrrole (**47c**, 0.062 g, 19%): mp (hexane–benzene) 197.5–198.5 °C; IR 3360 (pyrrole N–H), 3060 (aromatic C–H), 2230 (–CN), 1600 and 1490 (aromatic), 1300, 1275, 1160, 1080, 960, 920, 910, 815, 765, and 700 cm^{-1} (aromatic); NMR δ 6.70 (d, $J = 2.5$ Hz, pyrrole 4-*H*, 1), 7.03–7.70 (m, aromatic *H*, 14) and 8.58–8.83 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{23}H_{16}N_2$, 320.1313; found, 320.1321.

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74. Found: C, 86.05; H, 5.18; N, 8.59.

Thermolysis of 1 in *N*,*N*-Dimethylaniline. *N*,*N*-Dimethylaniline (150 mL) and 1 (0.890 g, 4.0 mmol) were warmed at 185 °C for 2 h. Excess amine was vacuum distilled and the residue chromatographed to give **7** (0.076, 9%), 3-*N*-methyl-*N*-phenylamino)-2,5-diphenylpyrrole (**61b**, 0.132 g, 10%, identical in mp, IR, and NMR to the product from 1 and **59b** as described below) and 3-(*N*-methyl-*N*-phenylaminomethyl)-2,5-diphenylpyrrole (0.266 g, 19%): mp (hexane) 122–123 °C; IR 3435 (pyrrole N–H), 3050 (aromatic C–H), 2900 (aliphatic C–H), 1600, 1515, 1510, 1380, 1350, 1265, 1225, 820, 770, 750, and 695 cm^{-1} (aromatic); NMR δ 2.85 (s, $-N\text{-}CH_3$, 3), 4.55 (s, $-N\text{-}CH_2\text{-}$, 2), 6.43 (d, $J = 3$ Hz, pyrrole 4-*H*, 1), 6.62–6.9 (m, hydrogen at C-2 and C-6 in $N\text{-}C_6H_5$, 2), 7.03–7.50 (m, aromatic *H*, 13) and 8.12–8.35 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{24}H_{22}N_2$, 338.1783; found, 338.1788.

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.28; H, 6.49; N, 8.31.

Thermolysis of 1 in Aniline (59a). A solution of 1 (0.980 g, 4.0 mmol) in **59a** (150 mL) was heated at 180 °C for 2 h. Vacuum concentration and chromatography yielded **7** (0.180 g, 21%) and 2,5-diphenyl-3-(phenylamino)pyrrole (**61a**, 0.361 g, 29%): mp (hexane) 141–142 °C; IR 3425 and 3380 (pyrrole and amino N–H), 3045 and 3020 (aromatic C–H), 1605 and 1495 (aromatic), 1440, 1275, 760, and 695 cm^{-1} (aromatic); NMR δ 5.06 (br s, amino N–*H*, 1), 6.47 (d, $J = 2.5$ Hz, pyrrole 4-*H*, 1), 6.70–6.80 (distorted d, $J = 7$ Hz, H at C-2 and C-6 in $NH\text{-}C_6H_5$, 2), 7.0–7.63 (m, aromatic *H*, 13), and 7.95–8.30 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{22}H_{18}N_2$, 310.1470; found, 310.1476.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.02. Found: C, 85.15; H, 5.87; N, 9.01.

Thermolysis of 1 in *N*-Methylaniline (59b). Diazopyrrole 1 (0.490 g, 2.0 mmol) and **59b** (100 mL) were kept at 185 °C for 1 h. After removal of **59b** at reduced pressure, chromatography yielded **7** (0.155 g, 35%) and **61b** (0.174 g, 27%): mp (hexane) 121–122 °C; IR 3420 (pyrrole N–H), 3040 (aromatic C–H), 2880 (aliphatic C–H), 1600 and 1500 (aromatic), 1440, 1350, 1300, 1275, 995, 770, 755, and 700 cm^{-1} (aromatic); NMR δ 3.13 (s, $-N\text{-}CH_3$, 3), 6.40 (d, $J = 3$ Hz, pyrrole 4-*H*, 1), 6.67–6.90 (m, hydrogen at C-2 and C-6 in $N\text{-}C_6H_5$, 2), 7.0–7.63 (m, aromatic *H*, 13), and 8.13–8.40 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{23}H_{20}N_2$, 324.1626; found, 324.1634.

Anal. Calcd for $C_{23}H_{20}N_2$: C, 85.15; H, 6.21; N, 8.63. Found: C, 85.22; H, 6.27; N, 8.56.

Thermolysis of 1 in Benzyl Alcohol (62a). A solution of 1 (0.245 g, 1.0 mmol) in **62a** (5 mL) was heated (150 °C) for 4 h. Excess **62a** was then distilled into saturated ethanolic 2,4-dinitrophenylhydrazine (15 mL); benzaldehyde 2,4-dinitrophenylhydrazone (0.187 g, 65%) formed: mp (ethanol) 235–237 °C (lit.[39] 237–238 °C). Chromatography of the thermolysis residue afforded **7** (0.154 g, 70%).

Photolysis and Thermolysis of 1 in 2-Propanol (62b). Diazopyrrole 1 (0.490 g, 2.0 mmol) in dry acetone-free **62b** (175 mL) was photolyzed 45 min. Analysis of the photolysate by GC using butanal as an internal standard showed acetone (**64b**, 0.07 g, 64%) to be present (15% Carbowax 20M on Chrom W). Removal of **62b** and chromatography gave **7** (0.293 g, 67%).

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(39) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; Wiley: New York, 1964.

(Photolysis without 1 did not yield **64b**.) Similarly, refluxing 1 (0.245 g, 1.0 mmol) in **62b** (100 mL) led to 7 (0.130 g, 59%) and **64b**.

Photolysis of 1 in Methanol (62c). Diazopyrrole 1 (0.490 g, 2.0 mmol) and **62c** (175 mL) were irradiated 4.5 h, evaporated, and chromatographed. Elution gave 7 (0.120 g, 27%) and then 3-methoxy-2,5-diphenylpyrrole (**65c**, 0.062 g, 12%): mp (hexane) 107.5–109 °C; IR 3450 (pyrrole N-H), 3020, 1600 and 1480 (aromatic), 1180 (C-O-C), 1040, 750, and 690 cm^{-1} (aromatic); NMR δ 3.88 (s, OC*H*$_3$, 3), 6.35 (d, J = 3 Hz, pyrrole 4-*H*, 1), 7.10–7.75 (m, aromatic *H*, 10), and 7.95–8.32 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{17}H_{15}NO$, 249.1153; found, 249.1158.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06. Found: C, 81.79; H, 6.18.

Photolysis of 1 in Acidic Methanol (62c). A mixture of 1 (0.490 g, 2.0 mmol) and trifluoroacetic acid (0.342 g, 3.0 mmol) in **62c** (175 mL) was photolyzed 4.5 h. Workup and chromatography yielded 7 (0.049 g, 11%) and **65c** (0.220 g, 44%).

Photolysis of 1 in Acidic 2-Propanol (62b). A solution of 1 (0.490 g, 2.0 mmol) and trifluoroacetic acid (0.342 g, 3.0 mmol) in **62b** (175 mL) was irradiated for 1 h, stripped, and chromatographed. The eluents were 7 (0.137 g, 31%) and 3-(2-propoxy)-2,5-diphenylpyrrole (**65b**, 0.134 g, 24%): mp (hexane) 108–109 °C; IR 3440 (pyrrole N-H), 3020 (aromatic C-H), 2980 (aliphatic C-H), 1610 and 1500 (aromatic), 1390 and 1375 (-CH-(CH$_3$)$_2$ bending vibrations), 1200, 1110 (C-O-C), 770, and 690 cm^{-1} (aromatic); NMR δ 1.35 (d, J = 6 Hz, -CH(C*H*$_3$)$_2$, 6), 4.37 (septet, J = 6 Hz, -C*H*(CH$_3$)$_2$, 1), 6.28 (d, J = 2.5 Hz, pyrrole 4-*H*, 1), 7.0–7.80 (m, aromatic *H*, 10), and 7.85–8.13 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{19}H_{19}NO$, 277.146; found, 277.147.

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.17; H, 6.98; N, 5.17.

Photolysis of 1 in Acetic Acid. Irradiation of 1 (0.490 g, 2.0 mmol) in glacial acetic acid (175 mL) for 75 min, concentration, and chromatography (benzene) yielded 7 (0.032 g, 7%) and 3-acetoxy-2,5-diphenylpyrrole (**65d**, 0.112 g, 20%): mp (hexane–benzene) 122–123 °C; IR 3380 (pyrrole N-H), 1740 (>C=O of acetate), 1600 (aromatic), 1230, 760, and 695 cm^{-1} (aromatic); NMR δ 2.22 (s, -OCOC*H*$_3$, 3), 6.45 (d, J = 3 Hz, pyrrole 4-*H*, 1), 7.05–7.57 (m, aromatic *H*, 10), and 8.25–8.67 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{18}H_{15}NO_2$, 277.1103; found, 277.1107.

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.98; H, 5.34; N, 4.94.

Photolysis of 1 in Acidic Benzene (42a). Irradiation (2 h) of a mixture of 1 (0.490 g, 2.0 mmol), **42a** (175 mL) and trifluoroacetic acid (0.342 g, 3.0 mmol), concentration, and chromatography afforded 2,3,5-triphenylpyrrole (**47a**, 0.447 g, 76%): mp (hexane) 140–141 °C (lit.[40] 140–141 °C); IR 3420 (pyrrole N-H), 3030 (aromatic C-H), 1600 and 1490 (aromatic), 960, 830, 760, and 695 cm^{-1} (aromatic); NMR δ 6.67 (d, J = 2.5 Hz, pyrrole 4-*H*, 1), 7.14–7.65 (m, aromatic *H*, 15) and 8.10–8.47 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{22}H_{17}N$, 295.1361; found, 295.1368.

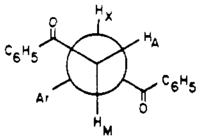
Photolysis of 1 in Acidic Anisole (31a). Chromatography of the concentrate from photolysis (2 h) of 1 (0.490 g, 2.0 mmol) in **31a** (175 mL) and trifluoroacetic acid (0.342 g, 3.0 mmol) gave (1) 7 (0.029 g, 7%), (2) **38a** (0.177 g, 27%) having superimposable IR and NMR with an authentic sample, and (3) 3-(*o*-methoxyphenyl)-2,5-diphenylpyrrole (**47d**, ~0.179 g, 28%): mp (hexane–benzene) 135–136 °C; IR 3370 (pyrrole N-H), 3035 (aromatic C-H), 2920 (aliphatic C-H), 1600 and 1490 (aromatic), 1460, 1250, 1180, 1125, 1030, 760, and 695 cm^{-1} (aromatic); NMR δ 3.50 (s, -OC*H*$_3$, 3), 6.65 (d, J = 3 Hz, pyrrole 4-*H*, 1), 6.70–7.63 (m, aromatic *H*, 14), and 8.20–8.45 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{23}H_{19}NO$, 325.1466; found, 325.1473.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30. Found: C, 85.16; H, 6.07; N, 4.16.

Thermolysis of 1 in Acidic Benzonitrile (42b). From decomposition (1.5 h) of 1 (0.490 g, 2.0 mmol) in **42b** (100 mL) and trifluoroacetic acid (0.342 g, 3.0 mmol), vacuum concentration, and chromatography was obtained a mixture (~1:1) of **47c** and 3-(*p*-cyanophenyl)-2,5-diphenylpyrrole (**47e**) (0.320 g, 50%): mp (hexane–benzene) softens at 163–166 °C, melts at 184–188 °C; IR 3360, 3310 (pyrrole N-H), 3040 (aromatic C-H), 2225 (CN), 1600 and 1490 (aromatic), 1295, 1270, 1975, 960, 915, 845, 815, 765, and 695 cm^{-1} (aromatic); NMR δ 6.57 (d, J = 2.5 Hz, pyrrole 4-*H*), 6.70 (d, J = 2.5 Hz, pyrrole 4-*H* together integrating for 1H), 6.85–7.60 (m, aromatic *H*, 14), and 8.58–8.90 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{23}H_{16}N_2$; 320.1313; found; 320.1321. The composition of **47c** and **47e** was determined by IR comparison with an authentic mixture.

1,4-Diphenyl-2-(*p*-tolyl)-1,4-butanedione (73a). To benzaldehyde diphenyl thioacetal (3.08 g, 10.0 mmol) in tetrahydrofuran (70 mL) was added *n*-butyllithium in hexane (2.4 M, 4.17 mL, 10.0 mmol) at −70 °C under nitrogen. Cuprous iodide (0.955 g, 5.0 mmol) was introduced after 1 h and the mixture was stirred 1 h at −70 °C. Upon adding (*p*-methylbenzylidene)acetophenone[41] (1.11 g, 5.0 mmol) in tetrahydrofuran (15 mL) dropwise at −70 °C, the mixture was stirred at −70 °C for 2 h, then quenched with water (10 mL), and warmed to room temperature. After the copper salts were filtered and the tetrahydrofuran was removed under reduced pressure, the residue was suspended in water and extracted with ether. The extract was dried, concentrated, chromatographed, and eluted with hexane–benzene to give 1,4-diphenyl-4,4-bis(phenylthio)-3-(*p*-tolyl)-1-butanone (**72a**, 1.33 g, 2.5 mmol, 50%).

Thioketal **72a**, upon dissolution in 99% aqueous acetone (50 mL), was stirred at 25–30 °C for 1 h with cupric chloride (0.675 g, 5.0 mmol) and cupric oxide (0.795 g, 10.0 mmol). Filtration of the heterogeneous mixture and concentration and chromatography of the filtrate yielded **73a** (0.68 g, 80%): mp (2-propanol) 88.5–90 °C; IR 3060 and 3040 (aromatic C—H), 2925 (aliphatic C—H), 1680 (>C=O), 1600 (aromatic), 1520, 1455, 1345, 1230, 1010, 1005, 830 (aromatic C—H out of plane bending, characteristic of para substitution), 795, 750 and 695 cm^{-1} (aromatic); NMR δ 2.20 (s, Ar-C*H*$_3$, 3), 3.17 (dd, J_{AM} = 18 Hz, J_{AX} = 3.5 Hz, H_A, 1), 4.17 (dd, J_{AM} = 18 Hz, J_{MX} = 9 Hz, H_M, 1), 5.30 (dd, J_{AX} = 3.5 Hz, J_{MX} = 9 Hz, H_X, 1), 6.90–7.47 (m, aromatic *H*, 10), and 7.83–8.15 (m, aromatic *H*, 4); the NMR spectra of 1,4-diketones **73a–f** are discussed as per the accompanying projection formula; exact mass calcd for $C_{23}H_{20}O_2$, 328.1643; found, 328.1470.



Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.39; H, 6.24.

2,5-Diphenyl-3-(*p*-tolyl)pyrrole (74a). A solution of **73a** (0.328 g, 1.0 mmol), ammonium acetate (0.462 g, 6.0 mmol), and glacial acetic acid (10 mL) was deoxygenated with nitrogen, heated at 130 °C for 5 h under nitrogen, and then poured into ice/ammonia. The ether extract of the precipitate formed was washed with water, dried, and concentrated to yield **74a** (0.292 g, 95%): mp (hexane) 144–145 °C; IR 3420 (pyrrole N-H), 3070 and 3030 (aromatic C-H), 2920 (aliphatic C-H), 1600 (aromatic), 1520, 1495, 1270, 1180, 963, 835 (aromatic C-H out of plane bending, characteristic of para substitution), 800, 770, 765, and 700 cm^{-1} (aromatic); NMR δ 2.30 (s, Ar-C*H*$_3$, 3), 6.65 (d, J = 3 Hz, pyrrole 4-*H*, 1), 6.85–7.67 (m, aromatic *H*, 14), and 8.20–8.48 (br s, pyrrole N-*H*, 1); exact mass calcd for $C_{23}H_{19}N$, 309.1517; found, 309.1526.

Anal. Calcd for $C_{23}H_{19}N$: C, 89.23; H, 6.19; N, 4.53. Found: C, 89.09; H, 6.35; N, 4.51.

2-(*p*-Methoxyphenyl)-1,4-diphenyl-1,4-butanedione (73b).[42] To sodium cyanide (0.049 g, 1.0 mmol) in dry dimethylformamide (5 mL) at 35 °C under nitrogen was added (5 min) benzoin (1.06 g, 5.0 mmol) in dimethylformamide (17 mL). After stirring the suspension for 5 min, (*p*-methoxybenzylidene)acetophenone[43] (1.785 g, 7.5 mmol) in dimethylformamide (10 mL) was introduced (10 min). The mixture was stirred at 35 °C for 20 h, poured into water, and extracted with chloroform. Removal of the chloroform, after washing the extract with water and drying, gave **73b** (1.40 g, 54%): mp (2-propanol) 138–139 °C; IR 3050 (aromatic C—H),

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[40] Angelico, F.; Calvello, E. *Gazz. Chim. Ital.* **1904**, *34* (I), 38.

[41] Davey, W.; Tivey, D. J. *J. Chem. Soc.* **1958**, 1230.

[42] A modification of the general method of Stetter, H.; Schreckenberg, M. *Chem. Ber.* **1974**, *107*, 2453.

[43] Conant, J. B.; Kohler, E. P. *J. Am. Chem. Soc.* **1917**, *39*, 1699.

1670 (>C=O), 1600 (aromatic), 1500, 1440, 1225, 1025, 990, 830 (aromatic C—H out of plane bending characteristic of para substitution), 760, and 700 cm^{-1} (aromatic); NMR δ 3.25 (dd, J_{AM} = 17 Hz, J_{AX} = 4 Hz, 1), 3.72 (s, ArOCH_3, 3), 4.18 (dd, J_{AM} = 17 Hz, J_{MX} = 9 Hz, H_M, 1), 5.30 (dd, J_{AX} = 4 Hz, J_{MX} = 9 Hz, H_X, 1), 6.82 (distorted d, part of AA′BB′ pattern, J = 9 Hz, H ortho to *p*-methoxy, 2), 7.15–7.63 (m, aromatic H, 8), and 7.83–8.16 (m, aromatic H, 4); exact mass calcd for $C_{23}H_{20}O_3$, 344.1412; found, 344.1420.

Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.97; H, 5.98.

3-(*p*-Methoxyphenyl)-2,5-diphenylpyrrole (74b = 38a). A solution of diketone **73b** (0.688 g, 2.0 mmol) and ammonium acetate (0.924 g, 12.0 mmol) in glacial acetic acid (10 mL) under nitrogen was maintained at 130 °C for 3 h. Workup as for **74a** yielded **74b** (**38a**) (0.623 g, 95%): mp (2-propanol) 116–117 °C. The IR and NMR of **74b** are identical to that of the product of para substitution of **31a** by **3** and by **2** ($Z = {}^{-}O_2C-CF_3$). Exact mass calcd for $C_{23}H_{19}NO$, 325.1466; found, 325.1473.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 4.30. Found: C, 84.76; H, 4.27.

2-(*p*-Cyanophenyl)-1,4-diphenyl-1,4-butanedione (73c). Diketone **73c** was prepared by the same method as **73a**. Thus, 3-(*p*-cyanophenyl)-4,4-bis(phenylthio)-1,4-diphenyl-1-butanone (**72c**, 2.0 g, 74%) was obtained starting from *p*-cyanobenzylideneacetophenone[44] (1.165 g, 5.0 mmol). Hydrolysis of crude **72c** (1.084 g, 2.0 mmol) with cupric chloride/cupric oxide in 99% aqueous acetone afforded **73c** (0.572 g, 84%): mp (ethanol) 161.5–162 °C; IR 3060 (aromatic C—H), 2990 (aliphatic C—H), 2240 (-CN), 1670 (>C=O), 1660, 1490 (aromatic), 845 (aromatic C—H out of plane bending, characteristic of para substitution), 760, and 700 cm^{-1} (aromatic); NMR δ 3.32 (dd, J_{AM} = 17.5 Hz, J_{AX} = 5 Hz, H_A, 1), 4.18 (dd, J_{AM} = 17.5 Hz, J_{MX} = 9 Hz, H_M, 1), 5.42 (dd, J_{AX} = 5 Hz, J_{MX} = 9 Hz, H_X, 1), 7.15–7.67 (m, aromatic H, 10), and 7.80–8.15 (m, aromatic H, 4); exact mass calcd for $C_{23}H_{17}NO_2$, 339.1259; found, 339.1265.

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.46; H, 5.17; N, 4.21.

3-(*p*-Cyanophenyl)-2,5-diphenylpyrrole (74c = 47e). Heating **73c** (0.339 g, 1.0 mmol) and ammonium acetate (0.462 g, 6.0 mmol) in glacial acetic acid (4 mL) at 130 °C for 3 h under nitrogen yielded **74c** (0.251 g, 78%): mp (2-propanol) 230.5–231.5 °C; IR 3320 (pyrrole N–H), 3050 (aromatic C–H), 2235 (-CN), 1605 and 1480 (aromatic), 1180, 960, 845 (aromatic C–H out of plane bending characteristic of para substitution), 765, and 695 cm^{-1} (aromatic); NMR δ 6.70 d, J = 2 Hz, pyrrole 4-H, 1), 7.09–7.85 (m, aromatic H, 14) and 8.45–8.60 (br s, pyrrole N–H, 1); exact mass calcd for $C_{23}H_{16}N_2$, 320.1313; found, 320.1321.

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74. Found: C, 85.95; H, 5.16; N, 8.78.

(*m*-Cyanobenzylidene)acetophenone. Aqueous sodium hydroxide (10%; 10 mL) was added to *m*-cyanobenzaldehyde (3.275 g, 25.0 mmol) and acetophenone (3.0 g, 25.0 mmol) in methanol (125 mL) at −10 °C. After the mixture was stirred for 12 h it was diluted with water, cooled, and filtered to yield *m*-cyanobenzylideneacetophenone (4.528 g, 77%): mp (2-propanol) 114–115 °C; IR 3065 (aromatic and olefinic C–H), 2240 (-CN), 1670 (α,β-unsaturated C=O), 1605 (aromatic), 1435, 1375, 1222, 1027, 995, 775, 690, and 670 cm^{-1} (aromatic); NMR δ 7.23–7.90 (m, aromatic and olefinic H, 8) and 7.95–8.17 (m, aromatic H, 3); exact mass calcd for $C_{16}H_{11}NO$, 233.0840; found, 233.0845.

Anal. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.50; H, 4.69; N, 5.94.

2-(*m*-Cyanophenyl)-1,4-butanedione (73d). Conjugate addition of lithium [α,α-bis(phenylthio)benzyl]cuprate (71)[35] to *m*-cyanobenzylideneacetophenone (1.165 g, 5.0 mmol) and hydrolysis of thioketal **72d** as described for **72a** afforded **73d** (0.681 g, 40%): mp (2-propanol) 143–144 °C; IR 3065 (aromatic C–H), 2920 (aliphatic C–H), 2240 (-CN), 1670 (C=O), 1600 (aromatic), 1465, 1260, 1220, 1005, 780, 745, and 690 cm^{-1} (aromatic); NMR δ 3.30 (dd, J_{AM} = 18 Hz, J_{AX} = 4 Hz, H_A, 1), 4.17 (dd, J_{AM} = 18 Hz, J_{MX} = 9 Hz, H_M, 1), 5.40 (dd, J_{AX} = 4 Hz, J_{MX} = 9 Hz, H_X, 1), 7.0–7.77 (m, aromatic H, 10), and 7.85–8.20 (m, aromatic H, 4); exact mass calcd for $C_{23}H_{17}NO_2$, 339.1259; found, 339.1268.

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.43; H, 5.42; N, 4.11.

3-(*m*-Cyanophenyl)-2,5-diphenylpyrrole (74d). Cyclization of **73d** (0.510 g, 1.5 mmol) with ammonium acetate (0.693 g, 9.0 mmol) in glacial acetic acid (15 mL) at 130 °C for 4 h under nitrogen yielded **74d** (0.424 g, 88%): mp (2-propanol) 189–190 °C; IR 3320 (pyrrole N–H), 3060 (aromatic C–H), 2245 (-CN), 1605 and 1490 (aromatic), 1275, 900, 820, 810, 795, 770, 760, and 705 cm^{-1} (aromatic); NMR δ 6.67 (d, J = 2.5 Hz, pyrrole 4-H, 1), 7.23–7.75 (m, aromatic H, 14), and 8.35–8.60 (br s, pyrrole N–H, 1); exact mass calcd for $C_{23}H_{16}N_2$, 320.1313; found, 320.1321.

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74. Found: C, 86.09; H, 5.10; N, 8.62.

2-(*o*-Methoxyphenyl)-1,4-diphenyl-1,4-butanedione (73e). The sequence for preparing **73a** was followed. Thus, starting with *o*-methoxybenzylideneacetophenone[45] (1.19 g, 5.0 mmol), **73e** was obtained (1.03 g, 60%): mp (2-propanol) 119–120 °C; IR 3060 (aromatic C–H), 2920 (aliphatic C–H), 1670 (>C=O), 1600, 1580 (aromatic), 1500, 1450, 1385, 1240, 1000, 965, 760, and 690 cm^{-1} (aromatic); NMR δ 3.15 (dd, J_{AM} = 18 Hz, J_{AX} = 3.5 Hz, H_A, 1), 3.85 (s, -ArOCH_3, 3), 4.30 (dd, J_{AM} = 18 Hz, J_{MX} = 9 Hz, H_M, 1), 5.73 (dd, J_{AX} = 3.5 Hz, J_{MX} = 9 Hz, H_X, 1), 6.80–7.60 (m, aromatic H, 10), and 7.97–8.25 (m, aromatic H, 4); exact mass calcd for $C_{23}H_{20}O_3$: 344.1412; found: 344.1420.

Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.15; H, 5.80.

3-(*o*-Methoxyphenyl)-2,5-diphenylpyrrole (74e = 47d). Condensation of **73e** (0.80 g, 2.32 mmol) and ammonium acetate (1.074 g, 13.9 mmol) in glacial acetic acid (25 mL) under nitrogen at 140 °C for 6 h gave **74e** (0.756 g, 95%): mp (hexane–benzene) 136–137 °C; its IR and NMR were superimposable on that of **74e** (the third product of photolysis of **1** in acidic **31a**); exact mass calcd for $C_{23}H_{19}NO$, 325.1466; found, 325.1473.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30. Found: C, 85.16; N, 6.07; N, 4.16.

2-(*p*-Nitrophenyl)-1,4-diphenyl-1,4-butanedione (73f). By the use of the procedure detailed for **73a**, (*p*-nitrobenzylidene)acetophenone[46] (1.256 g, 5.0 mmol) was converted to 3-(*p*-nitrophenyl)-4,4-bis(phenylthio)-1,4-diphenyl-1-butanone (**72f**, 0.750 g, 60%). Hydrolysis of ketal **72f** (0.280 g, 0.5 mmol) led to **73f** (0.160 g, 89%): mp (ethanol) 146.5–147.5 °C; IR 3060 (aromatic C—H), 1670 (>C=O), 1600 (aromatic), 1510 and 1310 (NO_2), 1240, 1205, 1000, 850 (aromatic C–H out of plane bending characteristic of para substitution), 755, and 695 cm^{-1} (aromatic); NMR δ 3.35 (dd, J_{AM} = 18 Hz, J_{AX} = 4.5 Hz, H_A, 1), 4.22 (dd, J_{AM} = 18 Hz, J_{MX} = 9 Hz, H_M, 1), 5.48 (dd, J_{AX} = 4.5 Hz, J_{MX} = 9 Hz, H_X, 1), 7.23–7.70 (m, aromatic H, 8), and 7.85–8.27 (m, aromatic H, 6); exact mass calcd for $C_{22}H1_7NO_4$, 359.1157; found, 359.1164.

Anal. Calcd for $C_{22}H_{17}NO_4$: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.59; H, 4.92; N, 3.96.

3-(*p*-Nitrophenyl)-2,5-diphenylpyrrole (74f). Ring closure of **73f** (0.255 g, 0.71 mmol) with ammonium acetate (0.445 g, 4.26 mmol) in glacial acetic acid (15 mL) at 140 °C for 6 h under nitrogen resulted in **74f** (0.227 g, 94%): mp (2-propanol) 217.5–219 °C; IR 3400 (pyrrole N–H), 3050 (aromatic C–H), 1600 (aromatic), 1505, 1330 (-NO_2), 1110, 850 (aromatic C–H out of plane bending, characteristic of para substitution), 760, and 695 cm^{-1} (aromatic); NMR δ 6.73 (d, J = 2.5 Hz, pyrrole 4-H, 1), 7.15–8.17 (m, aromatic H, 14), and 11.35–11.50 (br s, pyrrole N–H, 1); exact mass calcd for $C_{22}H_{16}N_2O_2$, 340.1211; found, 340.1217.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.62; H, 4.82; N, 8.10.

3-Benzyl-2,5-diphenylpyrrole (39). 3-Benzoyl-2,5-diphenylpyrrole (**75**, 1.076 g, 3.33 mmol)[36] in dry tetrahydrofuran (10 mL) was added to a solution of diborane (0.96 M) in tetrahydrofuran (30 mL) under nitrogen. The mixture was stirred at room temperature for 16 h and the excess diborane was destroyed with saturated aqueous sodium chloride. Ether extraction, drying ($MgSO_4$), and evaporation gave **39** (1.01 g, 98%): mp (hexane) 82–83 °C; IR 3440 (pyrrole N–H), 3060 and 3035 (aromatic C–H), 1605 and 1500 (aromatic), 1406, 1455, 1275, 770 and 700 cm^{-1} (aromatic); NMR δ 4.0 (s, ArCH_2-, 2), 6.37 (d, J = 3 Hz, pyrrole

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(44) Maclean, I. S.; Widdows, S. T. *J. Chem. Soc.* **1914**, *105*, 2169.

(45) Stobbe, H.; Wilson, F. J. *J. Chem. Soc.* **1910**, *97*, 1722.

(46) Davey, W.; Gwilt, J. R. *J. Chem. Soc.* **1957**, 1008.

4-*H*, 1), 7.13–7.60 (m, aromatic *H*, 15), and 8.15–8.40 (br s, pyrrole N–*H*, 1); exact mass calcd for $C_{23}H_{19}N$, 309.1517; found, 309.1523. Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.41; H, 6.05; N, 4.41.

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Registry No. **1**, 68058-80-0; **4**, 75096-67-2; **5**, 13219-95-9; **6**, 86863-97-0; **7**, 838-40-4; **12**, 86863-98-1; **13**, 1889-67-4; **15**, 86863-99-2; **20**, 86864-00-8; **21**, 86864-01-9; **25**, 86864-02-0; **26**, 86864-03-1; **29**, 86864-04-2; **31a**, 100-66-3; **31b**, 108-88-3; **35**, 70487-20-6; **38a**, 70487-19-3; **38b**, 70487-21-7; **39**, 70487-23-9; **40**, 103-29-7; **42a**, 71-43-2; **42b**, 100-47-0; **42c**, 98-95-3; **46a**, 70487-12-6; **46b** (4-CN), 70487-13-7; **46b′** (5-CN), 70487-14-8; **46b″** (6-CN), 70487-15-9; **46c** (4-NO_2), 70487-16-0; **46c′** (5-NO_2), 70487-17-1; **46c″** (6-NO_2), 70487-18-2; **47a**, 3274-61-1; **47b**, 86864-05-3; **47c**, 70487-22-8; **47d**, 86864-06-4; **47e**, 86864-07-5; **59a**, 62-53-3; **59b**, 100-61-8; **61a**, 86864-08-6; **61b**, 86864-09-7; **62a**, 100-51-6; **62b**, 67-63-0; **62c**, 67-56-1; **64b**, 67-64-1; **65b**, 86864-10-0; **65c**, 86864-11-1; **65d**, 86864-12-2; **72a**, 86864-13-3; **72c**, 86864-14-4; **72d**, 86884-71-1; **72f**, 86864-15-5; **73a**, 86864-16-6; **73b**, 68614-52-8; **73c**, 86864-17-7; **73d**, 86864-18-8; **73e**, 86864-19-9; **73f**, 86864-20-2; **74a**, 70487-21-7; **74d**, 86864-21-3; **74f**, 86864-22-4; **75**, 13220-01-4; cyclohexane, 110-82-7; cumene, 98-82-8; cyclohexene, 110-83-8; allylbenzene, 300-57-2; 2,3-dimethyl-2-butene, 563-79-1; methyl *m*-nitrobenzoate, 618-95-1; thioxanthen-9-one, 492-22-8; 4,4′-bis(dimethylamino)benzophenone, 90-94-8; acetic acid, 64-19-7; benzaldehyde diphenyl thioacetal, 7695-69-4; (*p*-methylbenzylidene)acetophenone, 4224-87-7; benzoin, 119-53-9; (*p*-methyoxybenzylidene)acetophenone, 959-33-1; (*m*-cyanobenzalidine)acetophenone, 62584-53-6; *m*-cyanobenzaldehyde, 24964-64-5; acetophenone, 98-86-2; (*o*-methoxybenzylidene)acetophenone, 5416-70-6; (*p*-nitrobenzylidene)acetophenone, 1222-98-6; *N*,*N*-dimethylaniline, 121-69-7.

S,N Double Rearrangement. 3. Reaction Mechanism

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The mechanism of the "S,N double rearrangement" was studied by ^{13}C labeling and crossover reactions. The results indicate that the condensation is a thiallylic rearrangement of the initial ring-closure product formed from the cyano and mercapto groups of the starting compound and benzoic acid.

In a study of the synthesis of 1,3-thiazin-4-ones from 2-cyano-3-mercapto-3-(methylthio)acrylamide (**1a**), we found that **1a** condensed with benzoic acid in the presence of polyphosphate ester (PPE) to give 5-cyano-4-(methylthio)-2-phenyl-1,3-thiazin-6-one (**3a**) via **2a** (Scheme I). We have termed this novel condensation reaction involving interchange of sulfur and nitrogen atoms an "S,N double rearrangement".[1,2]

In a previous paper,[2] we proposed a reaction pathway via a thiete intermediate for this condensation. However, the following three observations cannot be explained by this postulated mechanism (see Scheme II).

(1) A mixture of **1a** (2.9 mmol), benzoic acid (2.9 mmol), PPE (2 g), and chloroform (12 mL) was refluxed for 60 min to produce **2a**, whereas **5a** was obtained as a main product by employing half that quantity of PPE (eq 1).

(2) The *N*-methyl (**1b**), *N*-ethyl (**1c**), and *N*-benzyl (**1d**) derivatives of **1a** reacted with benzoic acid (2.9 mmol) in the presence of PPE (2 g) to afford the corresponding **5b–d** in 20%, 46%, and 15% yields, respectively (eq 2).

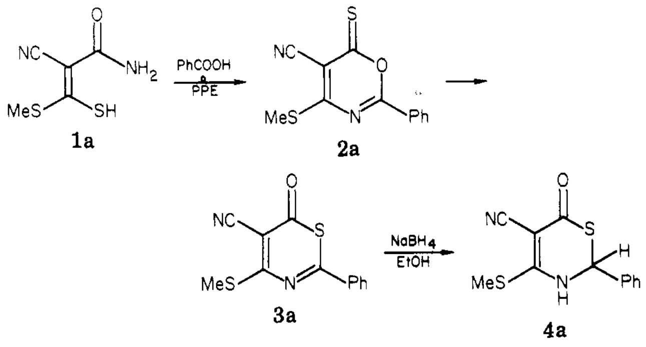
(3) Compounds **1f** and **1g**, having an ethyl or phenyl group, respectively, in place of the SMe group in **1a**, reacted with benzoic acid in the same way to afford unrearranged products, 6-substituted 5-cyano-2-phenyl-1,3-thiazin-4-ones (**6a,b**) in moderate yields (eq 3).

The results of eq 1 and 2 suggest that **5a-d** may be formed by a ring closure involving benzoic acid and the cyano and mercapto groups of **1a**. In this paper we present an alternative to our previous mechanism[2] for the reaction.

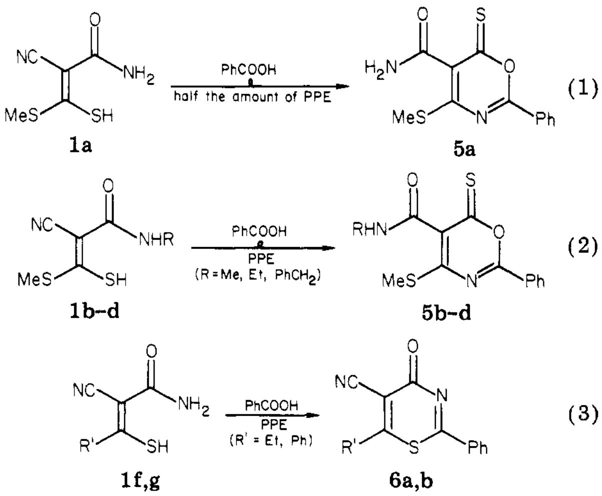
Results and Discussion

First, ^{13}C labeling of the cyano group of **1a** was carried out to elucidate mechanistic features. Compound **2a*** was synthesized from **1a*** and benzoic acid. On being refluxed in ethanol, **2a*** was converted to **3a***,[3] which was reduced

Scheme I



Scheme II



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(1) S,N Double Rearrangement. 1: Yokoyama, M.; Nakamura, M.; Imamoto, T.; Yamaguchi, K. *J. Chem. Soc. Chem. Commun.* **1981**, 560.

(2) S,N Double Rearrangement. 2: Yokoyama, M.; Nakamura, M.; Ohteki, H.; Imamoto, T.; Yamaguchi, K. *J. Org. Chem.* **1982**, 47, 1090.