(2), 193 (17), 192 (100), 177 (24), 121 (7), 107 (8), 42 (15).

Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.3; H, 9.3; N, 5.6. Found: C, 72.1; H, 9.7; N, 5.5.

1,1′-(1-Methyl-1*H*-pyrrole-2,4-diyl)bis(ethanone) (11). 2-Acetyl-1-methylpyrrole (12) (0.56 g), acetyl chloride (0.47 g), and tin(IV) chloride (3.12 g) were refluxed in anhydrous benzene (15 mL) for 20 min. The reaction mixture was quenched with sodium hydroxide (3 M) and extracted with ether in the usual manner to give a yellow solid which was recrystallized (light petroleum) to yield 11 (0.31 g, 41%): white needles, mp 86–87 °C; ^{1}H NMR δ 2.43 (s, 3 H, $COCH_3$(2)), 2.47 (s, 3 H, $COCH_3$(4)), 3.97 (d, 3 H, N-Me, $J_{Me,5}$ = 0.5 Hz), 7.34 (d, 1 H, H3, $J_{3,5}$ = 1.9 Hz), 7.39 (dq, 1 H, H5, $J_{3,5}$ = 1.9 Hz, $J_{Me,5}$ = 0.5 Hz); ^{13}C NMR δ 26.9 (q, 2 × $COCH_3$, ^1J = 127 Hz), 38.0 (qd, N-Me, ^1J = 140.6 Hz, $^3J_{Me,H5}$ = 2.9 Hz), 118.8 (dd, C3, $^1J_{C3,H3}$ = 172.9 Hz, $^3J_{C3,H5}$ = 6.5 Hz), 124.1 (m, C4), 131.5 (m, C2), 133.2 (ddd, C5, $^1J_{C5,H5}$ = 185.5 Hz), 188.9 and 192.3 (m, 2 × C=O); IR ($CHCl_3$) 3015, 1658, 1547, 1391, 1261, 1202, 1192 cm^{-1}; UV (EtOH) 236 nm (ϵ 2.33 × 10^4), 288 (1.50 × 10^4); mass spectrum, m/z (relative intensity) 165 (M^+, 80), 150 (100), 108 (16), 43 (15).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.4; H, 6.7; N, 8.5. Found: C, 65.3; H, 6.5; N, 8.7.

1,1′-(1-Methyl-1*H*-pyrrole-2,5-diyl)bis(ethanone) (10). 1-Methylpyrrole (1) (2.0 g, 24.7 mmol) and acetic anhydride (20 g, 0.2 mol) were heated in an autoclave for 18 h at 225 °C. The reaction mixture was worked up with ether in the ususal manner to give a crude product (1.21 g), which was purified by chromatography on silica using 20% ethyl acetate/light petroleum as eluent. The products in order of polarity were **10** (0.29 g, 7%) (recrystallized from light petroleum) [mp 132–134 °C (lit.[12] mp 133–134 °C); ^{1}H NMR δ 2.43 (s, 6 H, 2 × $COCH_3$), 4.10 (s, 3 H, N-CH_3), 6.77 (s, 2 H, H3(4)); ^{13}C NMR δ 28.2 (q, $COCH_3$, ^1J = 127.5 Hz), 35.0 (q, N-Me, $^1J_{Me,H}$ = 142 Hz), 117.1 (dd, C3(4), $^1J_{C3(4),H3(4)}$ = 173.9 Hz, $^2J_{C3(4),H4(3)}$ = 2.9 Hz), 134.7 (m, C2(5)), 190.0 (q, 2 × C=O, $^2J_{CO,Me}$ = 5.9 Hz); UV (EtOH) 232 nm (ϵ 9.10 × 10^3), 304 (2.16 × 10^4)] and **11** (0.42 g, 10%).

Four Novel Phenyldithienoindole Isomers from the Oxidative Photocyclization of Dithienylpyrroles

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Received October 8, 1986

The Stetter reaction with thiazolium catalysis was used to prepare diones **20** and **22–24** in high yield. From these were prepared the four isomeric 2,3-dithienyl-1-methyl-5-phenylpyrroles **1**, **7**, **9**, and **11**. From **20** were prepared phenylterthiophene **5** and furan **3**. The diarylpyrroles are the first reported to undergo oxidative photocyclization, forming four novel phenyldithienoindole isomers, **2**, **8**, **10**, and **12**. However, neither **3** nor **5** (in contrast to the unsubstituted terthiophene **6**) would undergo photocyclization; it is suggested that this anomaly has its origin in perturbation of the underlying hexatriene MOs.

Interest in the phototoxic properties of polythiophenes such as α-terthienyl[2] has led us to the synthesis of the substituted terthiophene **5**, the related furan **3**, and the *N*-methylpyrroles **1**, **7**, **9**, and **11** (Scheme I) and to the study of their photoreactivity. We report that the pyrroles undergo oxidative photocyclization to form the novel phenyldithienoindoles **2**, **8**, **10**, and **12**. An examination of Mallory's exhaustive review[3] and of the more recent literature indicates that these are the first oxidative photocyclizations of diarylpyrroles to be reported. The four dithieno-fused indole ring systems formed in these cyclizations are likewise unprecedented and are of further interest because of their similarity to several compounds recently synthesized by Cava as thiophene congeners of two phosphodiesterase inhibitors related to antitumor agent CC-1065.[4] (However, Cava's palladium photocyclization protocol did not improve yields with our compounds.[5])

In surprising contrast to **1**, the analogous thiophene **5** and furan **3** are photoinert. A still more striking contrast in photoreactivity is afforded by **5** and its unsubstituted parent terthiophene **6**, whose synthesis in this laboratory was recently reported:[6] whereas **5** is inert, **6** readily undergoes oxidative photocyclization under the same conditions as **1** to form the as-yet unreported benzotrithiophene **4**[7] in good yield (72%).

This pattern of reactivity gives rise to several mechanistic considerations. All cyclizations proceed upon irradiation of a benzene solution with 350-nm light in the presence of air, with yields improved when a catalytic quantity of iodine is present as well: these are the standard conditions for the oxidative photocyclization of *o*-terphenyl to triphenylene. There is extensive evidence[3] that the latter reaction, as well as analogous photocyclizations of diaryl heteroaromatics like **1**, **7**, **9**, and **11**, proceeds by a concerted conrotatory process from the lowest excited singlet state to form a *trans*-dihydrotriphenylene intermediate. This intermediate must be trapped by an effective oxidant such as iodine if the desired product is to be formed, since it can otherwise readily revert to the starting material by either a thermal or a photochemical process, thereby regenerating three aromatic rings.[8]

When one or both of the cyclizing aryl groups is 3-thienyl, as in **7**, **9**, and **11**, considerations advanced by Wynberg would suggest that the yield of cyclized product

(1) Authors to whom inquiries concerning X-ray analysis should be directed.

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(3) Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 1–456.

(4) (a) Cava, M. P.; Jones, R. J. *J. Chem. Soc., Chem. Commun.* **1986**, 826–827. See also: (b) Cava, M. P.; Rawal, V. H. *J. Am. Chem. Soc.* **1986**, *108*, 2110–2112.

(5) Cava, M. P.; Rawal, V. J.; Jones, R. J. *Tetrahedron Lett.* **1985**, *26*, 2423–2426.

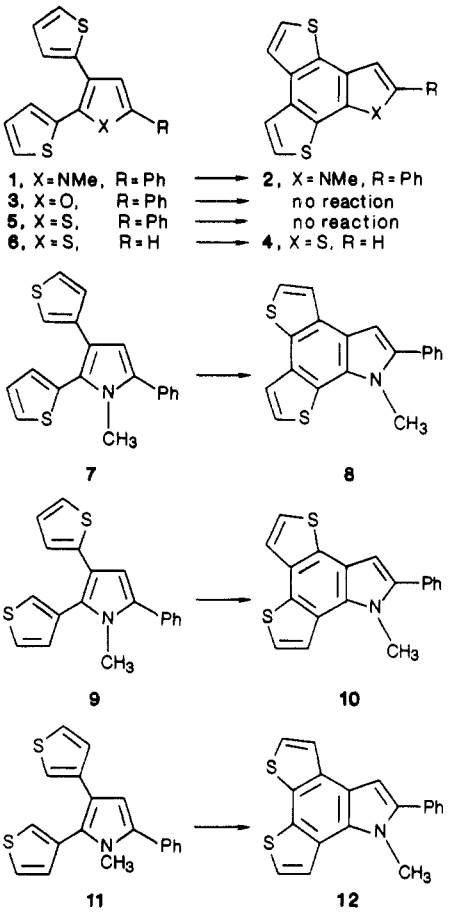
(6) Jayasuriya, N.; Kagan, J. *Heterocycles* **1986**, *24*, 2261–2264.

(7) (a) Jayasuriya, N.; Kagan, J., unpublished results. The synthesis of the C_3-symmetric benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene by high-pressure trimerization of 4-thiobutyrolactone has been reported: (b) Proetzsch, R.; Bieniek, D.; Korte, F. *Tetrahedron Lett.* **1972**, 543–544. See also the synthesis of the isomeric "exocyclic benzene", a trithiahexaradialene, benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene: (c) Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326–4327.

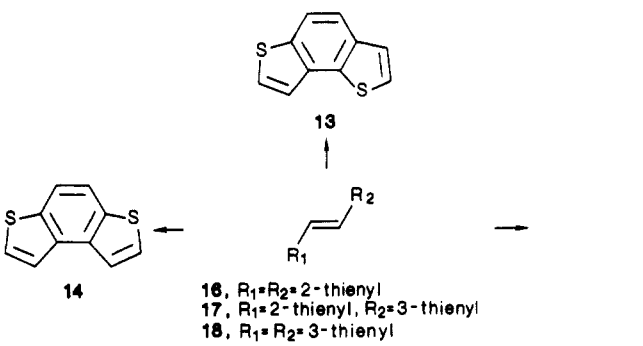
(8) (a) Muszkat, K. A. *Top. Curr. Chem.* **1980**, *88*, 89–143. See also (b) Somers, J. B. M.; Couture, A.; Lablanche-Combier, A.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1387–1394.

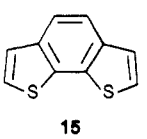
0022-3263/87/1952-2213$01.50/0

Scheme I



Scheme II





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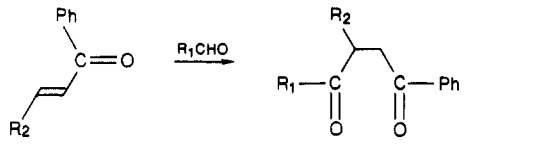
should be markedly less than with **1** due to the formation and subsequent decomposition of unstable thiyl radicals during oxidation of the 3-thienyl-substituted dihydro intermediate. Wynberg offered this explanation for his finding (Scheme II) that **16** underwent oxidative photocyclization to **14** in 90% and **17** to **13** in 47% yield, while **18** failed to form the expected **15** at all but underwent slow photodecomposition instead.[9] Contrary to this expectation, we found that photoproducts **2**, **8**, **10**, and **12** were formed (albeit with noticeable attendant decomposition)

Scheme III



19, R_2 = 2-thienyl
21, R_2 = 3-thienyl

20, $R_1 = R_2$ = 2-thienyl
22, R_1 = 2-thienyl, R_2 = 3-thienyl
23, R_1 = 3-thienyl, R_2 = 2-thienyl
24, $R_1 = R_2$ = 3-thienyl

in approximately the same (28–47%) yield. (On the basis of simple HMO calculations of free valence numbers, Klasing and Volkert[10] provided an alternative explanation for Wynberg's data; however, later extended HMO calculations by Muszkat of the first excited-state electronic overlap population appear to confirm Wynberg's hypothesis.[11])

Since no 3-thienyl groups are involved, formation of thiyl radicals during the oxidation step cannot account for the surprising contrast in photoreactivity between pyrrole **1** and the analogous furan **3** and thiophene **5** nor for the still more surprising contrast between **5** and **6**, where the 5′-phenyl substituent appears to render the terthiophene photoinert. The nearest analogy in the literature to the contrasting reactivity of **5** and **6** is that afforded by 2,3-diphenylfuran, which has been reported to undergo oxidative photocyclization in 70% yield,[12] and 2,3,5-triphenylfuran, which fails to cyclize. A substituent-induced perturbation of the relevant MOs is the only explanation which has been offered to date for this phenomenon.[13] (Clearly, the phenyl substituent in **5** can offer no steric hindrance to the cyclization process, as has been plausibly proposed[14] as the cause of the photoinactivity[15,16a] of tetraphenylthiophene and tetraphenylfuran, where the C-3 phenyl group is forced out of plane by the two neighboring phenyl groups.[16]) Work continues in this laboratory in conjunction with Laarhoven's group to further test this hypothesis.

Any assignment of structure to the product of a photolysis reaction involving thiophenes must give due consideration to Wynberg's well-known studies of the photoisomerization of substituted thiophenes,[17] which indicated that 2-methyl-5-phenylthiophene irreversibly photoisomerized to its 2-methyl-4-phenyl isomer. (However, 2,5-diphenylthiophene did not photoisomerize nor have studies in this laboratory found 2,5-di-2-thienylthiophene [α-terthienyl] to do so.) Since **1**, **7**, **9**, and **11** each give a unique and distinct isomeric photoproduct, it seems unlikely that any interconversion of these substrates by a process like

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(10) (a) Guesten, H.; Klasinc, L.; Volkert, O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1969**, *24B*, 12–15. See also: (b) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 1069–1083, 4865–4881.

(11) (a) Laarhoven, W. H.; Tinnemans, A. H. A.; Sharafi-Ozeri, S.; Muszkat, K. A. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 239–243. (b) Muszkat, K. A.; Seger, G.; Sharafi-Ozeri, S. *J. Chem. Soc., Faraday Trans. 2* **1975**, 1529–1544.

(12) Padwa, A.; Hartman, R. *J. Am. Chem. Soc.* **1966**, *88*, 3759.

(13) (a) Anderson, D. T.; Horspool, W. M. *J. Chem. Soc., Chem. Commun.* **1971**, 615; (b) *J. Chem. Soc., Perkin Trans. 1* **1972**, 532–536.

(14) Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 96.

(15) Wynberg, H.; van Driel, H.; Kellogg, R. M.; Buter, J. *J. Am. Chem. Soc.* **1967**, *89*, 3487–3494. The authors also report here that 2,3-diphenylthiophene photocyclizes in 40% yield.

(16) The failure of these compounds to cyclize has also been rationalized on MO grounds: (a) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Recl. Trav. Chem. Pays-Bas* **1968**, *87*, 687–698. Similar electronic factors have been suggested as the explanation for the failure of tetraphenylpyrrole to undergo oxidative photocyclization: (b) Blackburn, E. V.; Timmons, C. J. *J. Chem. Soc. C* **1970**, 172–175.

(17) (a) Wynberg, H.; Beekhuis, G. E.; van Driel, H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 3498–3505. (b) Wynberg, H. *Acc. Chem. Res.* **1971**, *4*, 65–73.

that observed by Wynberg could be taking place prior to cyclization. The less likely possibility of a migration of the phenyl group from the 2-pyrrole to the 3-indole position upon photolysis would also seem to be ruled out, since the position of the indole H singlet in the NMR spectra of **2**, **8**, **10**, and **12** is more consistent with a 2- than a 3-phenyl substituent.[18] In any case, all doubt as to the structure of **2** was removed by a single-crystal X-ray diffraction analysis (Figure 1, supplementary material), which showed it to be the expected product of the photocyclization of **1**. (The geometry of **2** has no unexpected features: the dithienoindole ring exhibits a slightly distorted planarity, with the indole ring at an approximately 4° dihedral angle to each thiophene ring; the phenyl substituent is at a 25° angle to the rest of the molecule.)

The ready accessibility of photosubstrates **1**, **3**, **5**, **7**, **9**, and **11** was due in large measure to the excellent yields and facile procedure afforded by the Stetter reaction,[19] which was used to synthesize the requisite 1,4-diones **20** and **22–24** (Scheme III). From these, pyrroles, thiophenes, and furans were prepared by modifications of known procedures.

Experimental Section

Melting points are uncorrected. HPLC was carried out with a reverse-phase 25-cm Alltech C-18 column with $MeOH/H_2O$ (9:1) eluant. Elemental analyses were by Micro-Tech Laboratories, Skokie, IL.

General Procedure for Synthesis of Diones 20 and 22–24. Enones **19**[20] and **21**[21] were made following the standard chalcone synthesis.[22] Following Stetter,[23] 62 mmol each of the respective enone and aldehyde, 12 mmol of 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (Aldrich), and 36 mmol of Et_3N were stirred with 90 mL of EtOH (absolute) at gentle reflux under dry N_2 for 12–16 h, until HPLC showed disappearance of starting enone. On cooling of the reaction mixture in ice and neutralization with methanolic HCl, a product crystallized, which was 97–99% pure by HPLC. Analytic materal was obtained by one recrystallization from 1:3 $CHCl_3$/MeOH or MeCOEt/*n*-PrOH.

4-Phenyl-1,2-di-2-thienyl-1,4-butanedione (20). From **19** and 2-thiophenecarboxaldehyde, a 94% yield of crude product was obtained. Recrystallization gave white crystals: mp 106–108 °C; NMR ($CDCl_3$) ABX (3 H) δ 3.37 (H_A, J_{AB} = 18 Hz), 4.20 (H_B, J_{BX} = 10 Hz), 5.43 (H_X, J_{AX} = 4 Hz), 6.80–8.13 (m, 11 H). Anal. Calcd for $C_{18}H_{14}O_2S_2$: C, 66.23; H, 4.32; S, 19.46. Found: C, 66.16; H, 4.38; S, 19.67.

4-Phenyl-1-(2-thienyl)-2-(3-thienyl)-1,4-butanedione (22). From **21** and 2-thiophenecarboxaldehyde, a 91% yield of crude product was obtained. Recrystallization gave white crystals: mp 119–120 °C; NMR ($CDCl_3$) ABX (3 H) δ 3.25 (H_A, J_{AB} = 18 Hz), 4.12 (H_B, J_{BX} = 10 Hz), 5.28 (H_X, J_{AX} = 4 Hz), 6.95–8.07 (m, 11 H). Anal. Calcd as for **20**. Found: C, 66.07; H, 4.41; S, 19.72.

4-Phenyl-2-(2-thienyl)-1-(3-thienyl)-1,4-butanedione (23). From **19** and 3-thiophenecarboxaldehyde, an 81% yield of crude product was obtained. Recrystallization gave white crystals of analytical purity: mp 99–100 °C; NMR ($CDCl_3$) ABX (3 H) δ 3.35 (H_A, J_{AB} = 18 Hz), 4.18 (H_B, J_{BX} = 10 Hz), 5.40 (H_X, J_{AX} = 4 Hz), 6.80–8.30 (m, 11 H). Anal. Calcd as for **20**. Found: C, 66.06; H, 4.34; S, 19.75.

4-Phenyl-1,2-di-3-thienyl-1,4-butanedione (24). From **21** and 3-thiophenecarboxaldehyde, a 72% yield of crude product was obtained. Recrystallization gave white crystals: mp 86–87 °C; NMR ($CDCl_3$) ABX (3 H) δ 3.25 (H_A, J_{AB} = 18 Hz), 4.13 (H_B, J_{BX} = 10 Hz), 5.28 (H_X, J_{AX} = 4 Hz), 7.00–8.28 (m, 11 H). Anal. Calcd as for **20**. Found: C, 66.50; H, 4.48; S, 19.80.

1-Methyl-5-phenyl-2,3-di-2-thienyl-1*H*-pyrrole (1). Following Stetter,[24] 8.0 g of **20**, 150 mL of EtOH, and 70 mL of 40% $MeNH_2$ (aqueous) were refluxed for 18 h. On cooling, 6.8 g (85%) of crystals formed, 99% pure by HPLC. Recrystallization from MeCOEt/*n*-PrOH (1:4) gave analytically pure yellow crystals: mp 132.0–133.5 °C; NMR ($CDCl_3$) δ 3.47 (s, 3 H, NMe), 6.53 (s, 1 H, 4-pyrrole), 6.83–7.60 (m, 11 H); UV (MeOH) 208, 270 nm (log ϵ 4.32, 4.30), shoulder at 295 nm. Anal. Calcd for $C_{19}H_{15}NS_2$: C, 70.99; H, 4.70; N, 4.36; S, 19.95. Found: C, 71.17; H, 4.65; N, 4.28; S, 20.10.

General Procedure for the Preparation of Pyrroles 7, 9, and 11. In a modified Paal–Knorr procedure,[24b] a solution of 5–10 g of $MeNH_3Cl$ in 75–100 mL of 40% (aqueous) $MeNH_2$ was added to a solution of 5.0 g of the appropriate dione in 150 mL of *n*-PrOH maintained at the boiling point. The solution was refluxed until HPLC showed complete conversion to product. Usually the product began to crystallize directly from the reaction mixture after 1 h. On cooling, crystallization was complete; the product was collected, washed with water and cold MeOH and recrystallized from *n*-PrOH/MeCOEt (3:1).

1-Methyl-5-phenyl-2-(2-thienyl)-3-(3-thienyl)-1*H*-pyrrole (7). From 4.0 g of **22** was obtained 3.8 g (97%) of **7**, 100% pure by HPLC. Recrystallization from heptane/benzene (1:6) gave colorless crystals of analytic purity: mp 149.5–150.5 °C; NMR ($CDCl_3$) δ 3.47 (s, 3 H, NMe), 6.50 (s, 1 H, 4-pyrrole), 6.92–7.58 (m, 11 H); UV (MeOH) 209, 262 nm (log ϵ 4.54, 4.30), shoulder at 290 nm. Anal. Calcd as for **1**. Found: C, 71.28; H, 4.79; N, 4.17; S, 20.06.

1-Methyl-5-phenyl-3-(2-thienyl)-2-(3-thienyl)-1*H*-pyrrole (9). From 5.0 g of **23** was obtained 4.3 g (90%) of **9**, 100% pure by HPLC. Recrystallization gave analytically pure colorless crystals: mp 147–148 °C; NMR ($CDCl_3$) δ 3.43 (s, 3 H, NMe), 6.55 (s, 1 H, 4-pyrrole), 6.80–7.63 (m, 11 H); UV (MeOH) 208, 268, 300 nm (log ϵ 4.40, 4.30, 4.30). Anal. Calcd as for **1**. Found: C, 71.14; H, 4.69; N, 4.34; S, 20.11.

1-Methyl-5-phenyl-2,3-di-3-thienyl-1*H*-pyrrole (11). From 4.0 g of **24** was obtained 3.9 g (100%) of **11**, 99% pure by HPLC. Recrystallization gave colorless crystals of analytic purity: mp 163–164 °C; NMR ($CDCl_3$) δ 3.47 (s, 3 H, NMe) 6.50 (s, 1 H, 4-pyrrole), 6.87–7.60 (m, 11 H); UV (MeOH) 207, 260, 294 nm (log ϵ 4.61, 4.23, 4.24). Anal. Calcd as for **1**. Found: C, 71.10; H, 4.81; N, 4.30; S, 20.11.

5-Phenyl-2,3-di-2-thienylfuran (3). A solution of 3.0 g of **20** in 100 mL of 10% methanolic HCl was refluxed for 20 min, at which time HPLC indicated complete consumption of starting material. The reaction mixture was cooled to ambient temperature and poured cautiously into a well-stirred, ice-cooled, saturated $NaHCO_3$ solution. The mixture was extracted with $CHCl_3$, and the extracts were dried ($MgSO_4$), filtered through Celite, and reduced to a dense yellow oil. This was recrystallized from a few milliliters of 95% EtOH. The yield of **3** was 2.6 g (93%), 98% pure by HPLC. Analytic material could be obtained by dissolving these crystals in boiling hexane and filtering the hot solution under pressure through a silica gel plug; cooling gave pale yellow crystals: mp 72–73 °C; NMR ($CDCl_3$) δ 6.77 (s, 1 H, 4-furyl), 6.90–7.83 (m, 11 H); UV (MeOH) 206, 231, 272, 338 nm (log ϵ 4.34, 4.14, 4.24, 4.25). Anal. Calcd for $C_{18}H_{12}OS_2$: C, 70.10; H, 3.92; S, 20.79. Found: C, 70.23; H, 4.02; S, 20.94.

5′-Phenyl-2,2′:3′,2″-terthiophene (5). Following Shridhar,[25] a solution of 3.0 g of **20** in 30 mL of PhMe was added dropwise to a refluxing mixture of 20.0 g of Lawesson's reagent[26] in 100 mL of PhMe and reflux continued for 0.5 h. The mixture was then passed through a 20-cm column of silica gel and further eluted with CCl_4. HPLC showed that the first few fractions contained

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(21) Mihailovic, M.; Tot, M. *J. Org. Chem.* **1957**, *22*, 652–654.

(22) Kohler, E. P.; Chadwell, H. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 78–80.

(23) Stetter, H. *Chem. Ber.* **1985**, *118*, 3172–3187 and references cited therein.

(24) Stetter, H.; Krasselt, J. *J. Heterocycl. Chem.* **1977**, *14*, 573–581. (b) We have found that the use of the added amine salt and the higher boiling solvent with diones **7**, **9**, and **11** markedly improved both the rate and yield of the reaction.

(25) (a) Shridhar, D. R.; Jogibhukta, M.; Rao, P. S.; Handa, V. K. *Synthesis* **1982**, 1061–1062; (b) *Indian J. Chem., Sect. B* **1983**, *22B*, 1187–1190.

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5; they were reduced to dryness, extracted into heptane, filtered hot through Celite, and cooled. The resulting crystals (1.1 g, 37% yield) were contaminated with about 4% of 3. After five recrystallizations from heptane, analytically pure material was obtained as pale olive-green crystals: mp 98–99 °C; NMR ($CDCl_3$) δ 6.90–7.73 (m); UV (MeOH) 206, 276, 330 nm (log ε 4.42, 4.36, 4.11). Anal. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.79; H, 3.67; S, 29.85.

General Procedure for Photolysis of 1, 7, 9, and 11. A solution of 1.5 g of the pyrrole and 10–20 mg of I_2[27] in 500 mL of PhH was placed in a quartz vessel in a 350-nm Rayonet reactor and stirred magnetically while a slow stream of air was passed through the solution by means of a bubbler. Irradiation was continued until HPLC showed virtual disappearance of starting pyrrole. In all cases, a single product peak emerged on HPLC, but the mixture became turbid from the formation of intractable decomposition products over the course of the irradiation, which required 8–14 h. The reaction mixture was filtered through Celite and reduced to a black oil, which was exhaustively extracted with boiling heptane. The hot extracts were forced through a 2-cm layer of silica gel, whereupon the product crystallized in high purity on cooling or concentrating.

1-Methyl-2-phenyl-1*H*-dithieno[2,3-*e*:3′,2′-*g*]indole (2). From 1.5 g of 1 was obtained 0.6 g (40%) of 2, 98% pure by HPLC. Recrystallization from *n*-PrOH/MeCOEt (9:1) gave analytically pure colorless crystals: mp 131–133 °C; NMR ($CDCl_3$) δ 4.00 (s, 3 H, NMe), 6.77 (s, 1 H, 3-indole), 7.23–7.77 (m, 9 H); UV (MeOH) 204, 218, 277, 317 nm (log ε 4.47, 4.44, 4.55, 4.21); MS, *m/e* (relative intensity) 319 (M^+, 100). Anal. Calcd for $C_{19}H_{13}NS_2$: C, 71.44; H, 4.10; N, 4.39; S, 20.07. Found: C, 71.54; H, 4.01; N, 4.32; S, 20.32.

9-Methyl-8-phenyl-9*H*-dithieno[3,2-*e*:3′,2′-*g*]indole (8). From 1.5 g of 7 was obtained 0.4 g (28%) of 8, 98% pure by HPLC. Recrystallization from *n*-PrOH/MeCOEt (9:1) gave analytically pure colorless crystals: mp 152–153 °C; NMR ($CDCl_3$) δ 4.03 (s, 3 H, NMe), 6.88 (s, 1 H, 3-indole), 7.30–7.73 (m, 9 H); UV (MeOH) 205, 256, 278, 326 nm (log ε 4.58, 4.38, 4.43, 4.32), shoulder at 342 nm; MS, *m/e* (relative intensity) 319 (M^+, 100). Anal. Calcd as for 2. Found: C, 71.54; H, 4.11; N, 4.31; S, 20.34.

7-Methyl-8-phenyl-7*H*-dithieno[2,3-*e*:2′,3′-*g*]indole (10). From 1.5 g of 9 was obtained 0.7 g (47%) of 10, 99% pure by HPLC. Recrystallization gave analytically pure colorless crystals: mp 169–170 °C; NMR ($CDCl_3$) δ 3.98 (s, 3 H, NMe), 6.78 (s, 1 H, 3-indole), 7.26–7.90 (m, 9 H); UV (MeOH) 205, 237, 270, 312, 341 nm (log ε 4.42, 4.36, 4.67, 4.13, 4.02); MS, *m/e* (relative intensity) 319 (M^+, 100). Anal. Calcd as for 2. Found: C, 71.55; H. 4.04; N, 4.39; S, 20.35.

4-Methyl-5-phenyl-4*H*-dithieno[3,2-*e*:2′,3′-*g*]indole (12). From 1.5 g of 11 was obtained 0.5 g (33%) of 12 as yellow crystals of 98% purity. Several recrystallizations and filtrations through silica gel in hot heptane resulted in colorless crystals, mp 179–180 °C; however, a persistent cocrystallizing contaminant of <0.01% could be detected with HPLC. NMR ($CDCl_3$) δ 4.05 (s, 3 H, NMe), 6.88 (s, 1 H, 3-indole), 7.33–7.93 (m, 9 H); UV (MeOH) 209, 242, 292, 323, 336, 350 nm (log ε 4.45, 4.45, 4.24, 4.18, 4.22, 4.21, 4.18); MS, *m/e* (relative intensity) 319 (M^+, 100). Anal. Calcd as for 2. Found: C, 71.40; H, 4.02; N, 4.35; S, 20.21.

Attempted Photocyclization of 3 and 5. A dilute solution of 3 in PhH with I_2 showed no change by HPLC after 3 h in a 350-nm Rayonet reactor. A catalytic amount of I_2 was added to 0.426 g of 3 dissolved in 1.5 L of PhH, and the solution was irradiated with a 450-W Hanovia probe in a water-cooled quartz jacket. Within 20 min all of 3 had decomposed with no discrete product formation. Similarly, 5 in PhH with I_2 and a slow stream of air through a bubbler showed no change after irradiation in a 350- or 300-nm Rayonet reactor. During more than 6 h of exposure to a 450-W Hanovia probe in a quartz vessel, 0.414 g of 5 in 300 mL of PhH with 0.013 g of I_2 underwent slow decomposition to 25% of its initial concentration with no evidence of discrete product formation.

Single-Crystal X-ray Analysis of 2. The crystal structure of compound 2 was determined from three-dimensional X-ray diffraction data collected on an Enras-Nonius CAD4 four-circle diffractometer using copper radiation at room temperature. Lp and decay corrections were applied to the data; no absorption was done. The contour of the structure was solved by direct methods using the SDP program. Refinement of positional and anisotropic thermal parameters was carried out by full-matrix least-squares methods for all 22 non-hydrogen atoms; a final difference Fourier revealed no missing or misplaced electron density. Pertinent crystal, data collection, and refinement parameters are summarized in Table I (supplementary material).

Acknowledgment. We are grateful to Dr. Kurt L. Loening of Chemical Abstracts Service for help in assigning the systematic names to 2, 8, 10, and 12. D.M.P. gratefully acknowledges support from the Chicago Province Jesuit Graduate Scholarship Fund.

Supplementary Material Available: Crystallographic data, including Figure 1 and Table I, and tables of atomic positional and thermal parameters and bond angles for 2 (6 pages). Ordering information is given on any current masthead page.

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Intramolecular [2 + 2] Cycloadditions of Ketene Iminium Salts to Carbon–Carbon Double Bonds

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Received December 9, 1986

Intramolecular [2 + 2] cycloadditions of ketene iminium salts with carbon–carbon double bonds are compared with the corresponding intramolecular [2 + 2] ketene cycloadditions. The ketene cycloaddition process provides better yields than the ketene iminium salt method for ketoketenes. However, the aldoketene iminium salts give much better yields than the corresponding aldoketenes.

Several recent reports on the intramolecular [2 + 2] cycloaddition of ketenes and ketene iminium salts to carbon–carbon double bonds and carbonyl groups have demonstrated the power and versatility of these reactions

0022-3263/87/1952-2216$01.50/0