TABLE V

PYRAZOLES FROM 2-PYRAZOLINES

Substituent(s), 2-pyrazoline	Substituent(s), pyrazole	Yield (purified), %	M.p., °C.	Lit.,[23c] m.p., °C.
5-Carbethoxy-	3(5)-Carbethoxy-	40	160–162[a]	160
3-Carbethoxy-	3(5)-Carbethoxy-	30	157–160	
4-Methyl-5-carbethoxy-	4-Methyl-3(5)-carbethoxy-	25	80–83	82–83
3-Methyl-5-carbethoxy-	5(3)-Methyl-3(5)-carbethoxy-	25	158–159.5	156–158
5,5-Diphenyl-	1,3-Diphenyl-[b]	80	84–86	84–85

[a] Identity confirmed by infrared. [b] Infrared shows no N—H.

pared from hydrazine hydrate, the sodium salt of diethyl oxalacetate, and acetic acid in ethanol. Treatment of 0.31 g. of **4,5(3)-diphenylpyrazole-3(5)-boronic acid** (IX) in 10 ml. of boiling ethanol with 0.25 ml. of 30% hydrogen peroxide for 5 min. and three crystallizations from ethanol-water yielded 0.11 g. of **3(5),4-diphenylpyrazol-5(3)-one,** m.p. 232–237°.

Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.38; H, 5.38; N, 11.85.

Heating 0.10 g. of **4,5(3)-diphenylpyrazole-3(5)-boronic acid** (IX) with 4 ml. of 10% aqueous potassium hydroxide dissolved the boronic acid, then led immediately to crystallization of **4,5(3)-diphenylpyrazole,** completed by boiling about 3 min., yield 0.06 g. (85%), m.p. 155–157.5° (lit. m.p. 154–155°[23a]; 3,5-diphenylpyrazole, m.p. 199–200°,[23b] is excluded). The first attempt at preparation of the boronic acid IX, in which the boronic ester was hydrolyzed with water and methanol and solutions were allowed to stand for prolonged periods, yielded 0.7 g. of 4,5(3)-diphenylpyrazole as a by-product. The ultraviolet spectrum of 4,5(3)-diphenylpyrazole, λ_{max} 252 mμ, ϵ 1.19 × 10^4, λ_{max} 227 mμ, ϵ 1.94 × 10^4, ϵ rising steeply below 218 mμ (not taken below 210 mμ), closely resembled that of the boronic acid IX, which had plateaus at 250 mμ, ϵ 2.23 × 10^4, and 224 mμ, ϵ 3.38 × 10^4, λ_{max} 202 mμ, ϵ 6.98 × 10^4 (in abs. ethanol).

Pyrazoles for structure proof of pyrazolines were obtained by oxidizing the pyrazoline in ether with an equimolar amount of pyridine hydrobromide–bromine complex in water, neutralizing with sodium bicarbonate, extracting with ether, and recrystallizing or subliming the product as necessary. Results are tabulated in Table V. The infrared spectrum was consistent with the assigned structure in each case.

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[23] (a) "Beilstein's Handbuch der Organischen Chemie," 4th ed., vol. 23, 1st supp., Julius Springer, Berlin, 1936, p. 67; (b) *ibid.*, vol. 23, p. 253; (c) *ibid.*, vol. 23, p. 178; vol. 25, pp. 116, 117, 120.

Reaction of the Silver Salt of Phenylnitroacetonitrile with Triphenylmethyl Chloride[1]

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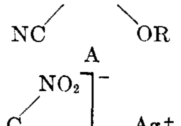
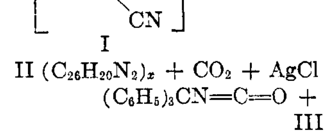
The product II from the reaction of the silver salt I of phenylnitroacetonitrile with triphenylmethyl chloride, originally reported[5] to be tetraphenyldiazoethane (B) has now been found to be α,α'-bis(triphenylmethaneazo)stilbene (D). More detailed aspects of the structure such as stereochemistry and the possibility of valence tautomerism remain to be investigated. The substance II has been reduced with lithium aluminum hydride, phenyllithium, or phenylmagnesium bromide to benzilbis(triphenylmethylhydrazone) (V) which can be reoxidized to II with silver oxide. The bisazoethylene II, when heated, is converted to diphenylacetylene, nitrogen, and triphenylmethyl radicals which are found as triphenylmethyl peroxide. With mild acid treatment bisazoethylene II is converted to 1-triphenylmethylamino-4,5-diphenyltriazole (VII) which reacts with benzoyl chloride to give the known 1-benzoylamino-4,5-diphenyltriazole. Attempts to carry out Diels-Alder reactions with II were unsuccessful.

The reactions of the silver salt I of phenylnitroacetonitrile with halides such as methyl iodide,[3] benzyl chloride,[3] or benzhydryl bromide[4] generally lead to the nitronic ester (A) produced by alkylation on an oxygen atom or to secondary products resulting from further reaction of the nitronic ester. Triphenylmethyl chloride has been shown to be unique, however.[5] It reacts with the silver salt I



A



I

II $(C_{26}H_{20}N_2)_x$ + CO_2 + AgCl +
$(C_6H_5)_3CN{=}C{=}O$ + IV $(C_{14}H_{11}N_3O)$
III

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[1] We gratefully acknowledge partial support of this research by a grant from the Petroleum Research Fund administered by the American Chemical Society.

This work is described principally in the Ph.D. thesis submitted by Donald Keith Wedegaertner to the University of Illinois, 1962. Preliminary results are described in the Ph.D. thesis of Robert James Crawford, University of Illinois, 1956. Both will be available on microfilm from University Microfilms, Ann Arbor, Mich.

[2] Allied Chemical Fellow, 1959–60; Charles Pfizer Fellow, Summer, 1960; Union Carbide Plastics Fellow, 1960–61.

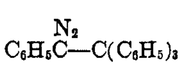
[3] J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

[4] R. L. Shriner and G. B. Brown, *ibid.*, **2**, 560 (1938).

[5] H. Wieland and A. Höchtlen, *Ann.*, **505**, 237 (1933).

in an inert solvent such as benzene at 10° under a nitrogen atmosphere to yield a red product (II), melting at 145°, with the empirical formula $C_{26}H_{20}N_2$ together with carbon dioxide, triphenylmethyl isocyanate (III), and a substance (IV) with the empirical formula $C_{14}H_{11}N_3O$. When the reaction is conducted in air triphenylmethyl peroxide is also obtained.

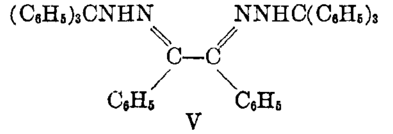
The red product II was found[5] to be converted in hot toluene solution to diphenylacetylene in unspecified yield and triphenylmethyl peroxide (40% yield). Concentrated sulfuric acid decomposed II with the formation of nitrogen gas. On the basis of this evidence the substance II was considered to be tetraphenyldiazoethane (B). It will be seen that the formation of the diazo compound B from the starting materials I and triphenylmethyl chloride requires that at least five covalent bonds be broken and four new ones formed. The complexity of this reaction and the absence of processes analogous to those required for its formulation prompted a reinvestigation.



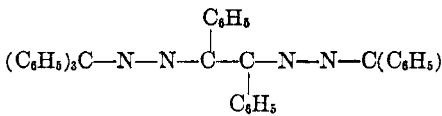
$C_6H_5\overset{N_2}{C}\text{—}C(C_6H_5)_3$

B

Repetition of the reaction of the silver salt I with triphenylmethyl chloride yielded the red compound II. Its molecular weight, however, corresponded not to the formula $C_{26}H_{20}N_2$ but to twice this or $C_{52}H_{40}N_4$.[6] Attempts to carry out catalytic hydrogenation of the product II in ethanol or tetrahydrofuran failed, possibly because of its low solubility, but lithium aluminum hydride reduced it to a dihydro compound V. The same dihydro compound was obtained by treatment of compound II with phenyllithium or phenylmagnesium bromide. The dihydro compound V was hydrolyzed by aqueous sulfuric acid to benzil (95%), triphenylcarbinol (44%), and hydrazine (50%, isolated as benzaldehyde azine). These results and the similarity of the ultraviolet spectrum in ether (λ_{max} 298 mμ, ϵ 2.60 $\times$ 10^4) to that of a benzil bisacetylhydrazone ($\lambda_{max}^{ethanol}$ 283 mμ, ϵ 3.70 $\times$ 10^4) (of unknown stereochemistry) suggested that the dihydro compound V was one of the stereoisomeric bistriphenylmethylhydrazones of benzil. This assignment was confirmed by synthesis of the bishydrazone V from benzil bishydrazone and triphenylmethyl chloride in ether containing pyridine. The structural relationship of the red product II to the reduction product V was further demonstrated by the oxidation of V to II with silver oxide in tetrahydrofuran.



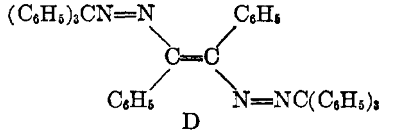
V



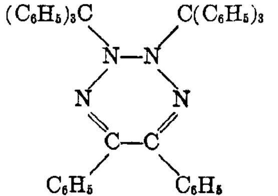
$(C_6H_5)_3C\text{—}N\text{—}N\text{—}\overset{C_6H_5}{C}\text{—}\underset{C_6H_5}{C}\text{—}N\text{—}N\text{—}C(C_6H_5)_3$

C

These observations establish the order of attachment of atoms in the product II as that shown in formula C. The two structures which seem to deserve major consideration are the bisazoethylene D and the tetrazine E. The choice between such structures, which it will be noted are valence tautomers, has been a matter of concern to organic chemists for over seventy years.[7,8]



D



E

Compounds which present this structural problem have been divided into two families: A group having absorption in the visible region of the spectrum has been given the bisazoethylene structure and a group of colorless compounds the tetrazine skeleton.[7] The red product II was found to have a broad absorption maximum at 450 mμ (ϵ 560) with shoulders at 317 (ϵ 8600) and 257 mμ (ϵ 14,000). Such a spectrum is suggestive of a bisazoethylene structure C and may be compared with the spectrum[9,10] of 1,2-bisbenzeneazoethylene which has a shoulder at 490 mμ (ϵ 3200) and a maximum at 363 mμ (ϵ 28,000). It must be added that

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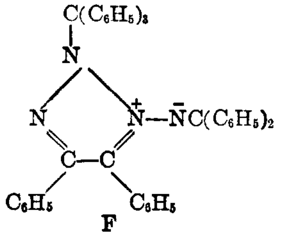
[6] The molecular weight determination might have been difficult because of the low solubility of II had not the vapor pressure osmometer made possible the determination in tetrahydrofuran.

[7] For reviews of the subject see J. G. Erickson, P. F. Wiley, and V. P. Wystrach, "The Chemistry of Heterocyclic Compounds, The 1,2,3- and 1,2,3,4-Triazines, Tetrazines and Pentazines," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. III, and E. Hoggarth, "Chemistry of Carbon Compounds," Vol. IVC, E. H. Rodd, ed., Elsevier Publishing Co., Amsterdam, 1960, pp. 1576 ff.

[8] Other structures with charge separation, for example, the triazole structure F, can also be considered but have no known prototype and little to recommend them, except, perhaps as reaction intermediates present in very small concentrations.



F

[9] S. Bodforss, *Svensk Kem. Tidskr.*, **53**, 183 (1941).

[10] P. Grammaticakis, *Compt. rend.*, **224**, 1509 (1947).

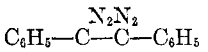
the structural problem of the compound II and its relatives previously reported is not completely solved. In addition to the question of stereochemistry which has not been determined in any of these examples, a final solution may require a knowledge of the ease of interconversion of the valence tautomers and the position of the equilibrium which may depend in specific cases on whether the substance is in the crystalline form or dissolved and, if the latter, on the solvent. For example, the presence of absorption at 450 mμ, characteristic of azo compounds, does not exclude the possibility that a solution of II contains an equilibrium mixture of compounds with structures D and E. Throughout the remainder of this paper the substance II will be referred to as a bisazoethylene with the implicit assumption of these possible complications.

The chemical reactions of the product II are in agreement with either formulation D or E but do nothing to solve the more subtle structural problems. Re-examination of the thermal decomposition[5] mentioned earlier of the substance II in cyclohexane at 80° indicated that diphenylacetylene was formed in nearly quantitative yield. Trityl peroxide was also isolated in agreement with the previous work.[5] This reaction is much more readily explained in terms of the structure D (or E) than with the diazo structure B previously proposed.[5]

$$\mathrm{II\ (C\ or\ D)} \longrightarrow 2(C_6H_5)_3C\cdot + C_6H_5C{\equiv}CC_6H_5 + 2N_2$$

$$2(C_6H_5)_2C\cdot + O_2 \longrightarrow (C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3$$

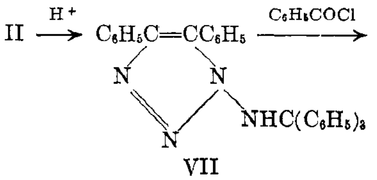
An intermediate may well be the bisdiazo compound VI which has been presumed to be formed and to lose nitrogen readily during the oxidation of benzil bishydrazone to diphenylacetylene.[11]



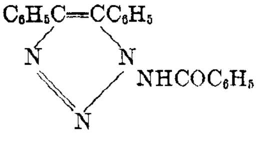
$$C_6H_5{-}\overset{N_2}{C}{-}\overset{N_2}{C}{-}C_6H_5$$

VI

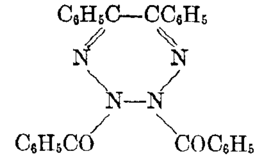
The bisazoethylene II was found to be stable to refluxing methanolic potassium hydroxide but very sensitive to acid. Treatment with 90% acetic acid or even suspension in unpurified aged chloroform caused decomposition to 1-triphenylmethylamino-4,5-diphenyl-1,2,3-triazole (VII). Evidence for this structural assignment included, in addition to carbon, hydrogen, and nitrogen analyses and the molecular weight determination, the presence of absorption at 3400 cm.$^{-1}$ (N—H) in the infrared spectrum. Confirmation of the structure was provided by conversion of the triphenylmethylamine VII to the corresponding benzoyl compound, 1-benzoylamino-4,5-diphenyl-1,2,3-triazole (VIII), which had been previously prepared.[12]



VII

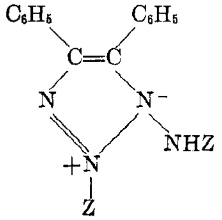


VIII



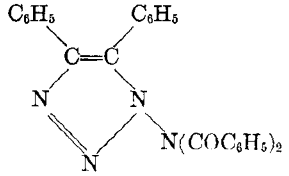
IX

The ease of such a rearrangement to the aminotriazole system appears to be readily explained by the ring closure of a protonated bisazoethylene to an intermediate with the structure X. It will



X

$Z = {-}C(C_6H_5)_3$



XI

be seen that the ion X may be formulated as an aromatic system with six π-electrons,[13] the triazole serving as a good leaving group in the subsequent nucleophilic replacement severing the triphenylmethyl or benzoyl group from the heterocyclic nitrogen atom.

Attempts to carry out Diels–Alder reactions in which the bisazoethylene II participated as the diene were unsuccessful. Treatment with dimethyl acetylenedicarboxylate at room temperature led to no reaction and in boiling tetrahydrofuran solution the only detectable products were diphenylacetylene and bistriphenylmethyl peroxide. Treatment of the bisazoethylene II with tetracyanoethylene in tetrahydrofuran containing potassium carbonate gave only the triphenylmethylaminotriazole in 46% yield.

While it is not possible at present to describe the detailed mechanism of the conversion of I to II certain observations of interest have been made which bear on the mechanism. First, it was found that the reaction could be carried out stepwise. Thus, when the silver salt I and the halide were mixed in toluene at −20°, silver chloride precipitated and, after filtration, a clear solution resulted. When the solution was allowed to warm to 0° carbon dioxide was evolved, the solution turned red, and eventually the red bisazoethylene precipitated. The carbon dioxide amounted to about 50% of the theoretical quantity. In an

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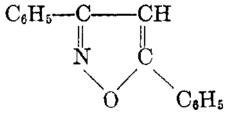
[11] T. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 161 (1891).

[12] R. Stollé, E. Münch, and W. Kind, *J. prakt. Chem.*, [2] **70**, 433 (1904); R. Stollé, *ibid.*, [2] **78**, 545 (1908); *Ber.*, **59**, 1743 (1926). NOTE ADDED IN PROOF: Unpublished work of Dr. N. Alexandrou suggests that compounds previously assigned a tetrazine structure such as IX are probably aminotriazole derivatives.

[13] See G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 136 ff.

effort to trap possible intermediates phenylacetylene was added to the clear solution at −20° and the solution allowed to stand at 0° for several hours. There was obtained, in addition to the bisazoethylene II, which was formed in only 54% of the usual amount, a 15% yield of 3,5-diphenylisoxazole (XII). A 6% yield of triphenylmethylamine was also obtained. The formation of the isoxazole suggests that the benzonitrile oxide XIII is an intermediate in the formation of the bisazoethylene II since the nitrile oxide XIII has been shown[14] to react with phenylacetylene to give the isoxazole XII. A second intermediate is suggested by the isolation by Wieland and Höchtlen[5] of triphenylmethyl isocyanate (III) from the reaction of the silver salt I and triphenylmethyl chloride.[15] It is apparent that further study is required before any additional conclusions can be drawn as to the mechanism of the change of I to II. Such a study is being continued.[16]



XII

$C_6H_5C\equiv\overset{+}{N}-\overset{-}{O}$

XIII

Experimental[17]

α,α′-Bis(triphenylmethaneazo)stilbene (II).—The procedure employed by Wieland and Höchtlen[5] was modified by adding 13.9 g. (0.050 mole) of triphenylmethyl chloride in 100 ml. of toluene slowly to a stirred suspension of 13.3 g. (0.050 mole) the silver salt I of phenylnitroacetonitrile in 50 ml. of toluene at −20° under a nitrogen atmosphere. After completion of addition the mixture was stirred for 3 hr. at −20° and then filtered cold. The clear filtrate was allowed to stand at 10° for 12 hr. after which the red solid which had formed was filtered and washed with benzene to give 2.9 g. (16%) of the red crystalline bisazoethylene II, m.p. 144–145° dec. (reported[5] m.p. 145°, dec.). Although the preliminary investigation (RJC) indicated that the substance was soluble to the extent of 10% in chloroform and had infrared absorption at 2260 cm.$^{-1}$, samples prepared later (DKW) were insoluble or very slightly soluble in all the common solvents examined in agreement with the observation of Wieland and Höchtlen[5] and showed only a very slight absorption maximum at 2240 cm.$^{-1}$ when the infrared absorption in a potassium bromide disk was measured. It seems likely that in each case the absorption at 2240 cm.$^{-1}$ was due to triphenylmethyl isocyanate present as an impurity. The solubility in tetrahydrofuran (1.6×10^{-3} *M*) was sufficient to permit the determination of the ultraviolet-visible spectrum which had λ_{max} 450 mμ (ε 560) and shallow maxima at 317 (ε 8600) and 257 mμ (ε 14,000) and also a molecular weight determination.[17] The tetrahydrofuran employed in making these solutions was pretreated with potassium carbonate in order to prevent decomposition of II by traces of acid.

Anal. Calcd. for $C_{52}H_{40}N_4$: C, 86.6; H, 5.6; N, 7.8; mol. wt., 721. Found: C, 86.9; H, 5.6; N, 7.7; mol. wt., 800.

When the filtrate from an experiment like that described above (but with four times the quantities of reagents) was allowed to stand for 3 months in a refrigerator a yellow solid which had formed was filtered and recrystallized from benzene–ligroin to give 5.7 g. of product, m.p. 176–181°. Further recrystallization from the same solvent mixture gave 5.1 g. of white crystals, m.p. 171.5–173°; soluble in 5% aqueous sodium carbonate solution but insoluble in 5% hydrochloric acid.

Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.7; N, 17.7; O, 6.7; mol. wt., 237. Found: C, 70.9; H, 4.7; N, 17.5; O, 6.7; mol. wt. (Rast in camphor), 243.

In another reaction (0.05-molar scale) there was obtained from the filtrate which had stood for a shorter time 1.5 g. of a product which after recrystallization from benzene–ligroin had m.p. 216–219°.

Anal. Calcd. for $C_{33}H_{25}N_3O$: C, 82.7; H, 5.3; N, 8.8. Found: C, 82.6, 82.8; H, 5.1, 5.4; N, 8.9, 8.8.

Reduction of the Bisazoethylene II to Benzil Bis(triphenylmethylhydrazone) (V).—To finely powdered II (6.0 g., 0.0083 mole) suspended in 500 ml. of absolute ether was added under reflux 150 ml. of a 0.2 *M* solution of lithium aluminum hydride in tetrahydrofuran. After 10 hr. the reaction mixture was cooled in an ice bath and hydrolyzed with the addition of ice. After decantation of the ether solution, the white solid remaining was extracted with ether and the combined ether extracts washed with 5% hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water. After drying over magnesium sulfate the ether was evaporated under reduced pressure to give 5.6 g. of crude product from which was obtained after recrystallization from benzene-ethanol 2.7 g. 46% of bishydrazone (V), m.p. 208–212° dec. The infrared, ultraviolet, and n.m.r. spectra agreed with the authentic V described below. From the filtrate above was isolated 0.25 g. (6%) of triphenylmethane, m.p. 94.5–95° (lit.,[19] m.p. 92°), characterized by a comparison of the infrared spectrum with that of an authentic sample.

Anal. Calcd. for $C_{52}H_{42}N_4$: C, 86.4; H, 5.9; N, 7.8. Found: C, 86.5; H, 5.8; N, 7.9.

The bishydrazone V was also obtained in 53% yield of product, m.p. 207.5–211° dec., by treatment of the bisazo-

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(14) A. Quilico and G. Speroni, *Gazz. chim. ital.*, **76**, 148 (1946).

(15) A mechanism can be formulated in terms of a reaction between benzonitrile oxide (XIII) and the isocyanate III which could lead to carbon dioxide and a nitrilimine which might then dimerize to the bisazoethylene II. Unpublished work by Dr. N. Alexandrou in our laboratories, however, has shown that the nitrile oxide XIII does not react with the isocyanate III to give II at temperatures employed for the formation of II from the silver salt I and triphenylmethyl chloride.

(16) In addition to the product IV ($C_{14}H_{11}N_3O$), m.p. 158°, mentioned earlier, there have been obtained in the reaction of the silver salt I with triphenylmethyl chloride during the present investigation, small amounts of a by-product, m.p. 219°, with the composition $C_{33}H_{25}N_3O$ and a second substance, m.p. 173°, with the composition $C_{14}H_{11}N_3O$ (obtained in the present investigation by storage of the reaction mixture remaining after removal of II for three months). Wieland and Hochtlen[5] reported that their product IV isomerized when treated with base to a substance, m.p. 182°, which may be identical with our product, m.p. 173°. Although the structures of none of these products have been established they may ultimately have a bearing on the nature of the formation of the product II.

(17) All melting points are corrected. Microanalyses were determined by Mr. J. Nemeth, Mr. G. Callahan, Mrs. M. Weatherford, Mrs. A. Bay, and Miss J. Liu. Infrared spectra were measured with a Perkin-Elmer Model 21 or Model 137 spectrophotometer. N.m.r. spectra, reported in τ units[18] were obtained with a Varian Associates V-4300-C high resolution spectrophotometer with a VK-3606 flux stabilizer and calibrated with a Hewlett-Packard 200-CD oscillator or with a Varian Associates A-60 spectrophotometer, all at 60 Mc. Ultraviolet spectra were determined with a Cary Model 14M or a Bausch and Lomb Spectronic 505 spectrophotometer using 1-cm. quartz cells. We are indebted to Mr. Dick Johnson and Mr. Oliver Norton and their assistants for the n.m.r. spectra and many of the infrared spectra and to Miss C. Juan and Mr. Ping-Kay Hon for many ultraviolet spectra. Molecular weights unless otherwise indicated were determined by Mr. J. Nemeth with a Mechrolab vapor pressure osmometer, Model 301A. Ultraviolet, infrared, and n.m.r. spectra are available in the Ph.D. theses referred to in ref. 1.

(18) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(19) N. D. Zelinsky and M. W. Gawerdowskaja, *Ber.*, **61**, 1050 (1928).

ethylene II with excess phenyllithium in tetrahydrofuran-ether and in 61% yield of product, m.p. 203.5–209.5° dec., from II with excess phenylmagnesium bromide. These products showed no melting point depression when mixed with V obtained from lithium aluminum hydride and the infrared and ultraviolet spectra of the three samples were identical.

Benzil Bis(triphenylmethylhydrazone) (V) from Benzil Bishydrazone.—A solution of 14.6 g. (52.6 mmoles) of triphenylmethyl chloride, 4.44 g. (18.7 mmoles) of benzil bishydrazone,[20] and 4.6 ml. (58 mmoles) of pyridine in 200 ml. of absolute ether containing 3.0 g. (25 mmoles) of magnesium sulfate was heated under gentle reflux in a nitrogen atmosphere with stirring for 13 hr. Extraction of the ether solution with water, 5% hydrochloric solution, saturated sodium carbonate solution, and water followed by extraction of the combined aqueous phases with benzene and a similar series of extractions of the benzene solution gave after combination of the ether and benzene solutions dried over magnesium sulfate and evaporated a light yellow solid purified by chromatography over alumina (elution with benzene). The product, further purified by crystallization from benzene–ethanol, amounted to 12.0 g. (89%) of solid, m.p. 205.5–209.5°. Recrystallization of 2.25 g. twice from benzene–ethanol yielded 1.35 g. of white crystalline bishydrazone V, m.p. 205.5–209.5° dec.

Anal. Calcd. for $C_{52}H_{42}N_4$: C, 86.4; H, 5.9; N, 7.8. Found: C, 86.1; H, 6.1; N, 8.0.

Hydrolysis of the Bistriphenylmethylhydrazone V.—Hydrolysis of 1.052 g. (1.45 mmoles) of the product V from the lithium aluminum hydride reduction of II was accomplished by dissolving it in 60 ml. of concentrated sulfuric acid–water (5:1) and then steam distilling to give a liquid product, distilled at 0.1 mm. (pot temperature 100–140°). Analysis of the distillate with vapor phase chromatography (20% Apiezon L on fire brick) by comparing areas and retention times of known benzil solutions indicated that 290 mg. (95%) of benzil had formed. Extraction with benzene of the acidic residue remaining from the steam distillation gave 0.668 g. (88%) of triphenylcarbinol, m.p. 152–159°, which after recrystallization from carbon tetrachloride amounted to 0.334 (44%) of product, m.p. 162.5–163.5° (lit.,[21] 161°). A melting point of a mixture with authentic triphenylcarbinol showed no depression. Addition of 0.8 ml. of benzaldehyde to the remaining acidic solution which had been made basic gave after 1 week 0.522 g. (86%) of benzaldehyde azine, m.p. 92–95° (lit.,[22] 93°), which after crystallization from ethanol gave 0.300 g. (50%) of product, m.p. 92.5–93.5; m.p. of mixture with authentic sample, 92.5–93.5°.

Benzil Bisacetylhydrazone. (a) From the Triphenylmethylhydrazone V.—A solution of 1.01 g. of V in 250 ml. of glacial acetic acid was subjected to slow distillation over a period of 112 hr. After the addition of 0.5 ml. of water and cooling, 0.606 g. of triphenylcarbinol, m.p. 155.5–160°, was obtained. Recrystallization from carbon tetrachloride gave 0.494 g. (68%) of product, m.p. 162–163°. After 3 more days 0.139 g. (31%) of bisacetylhydrazone, m.p. 243–244°, was obtained. Recrystallization from ethanol gave an analytical sample, m.p. 243–244°.

Anal. Calcd. for $C_{18}H_{18}N_4O_2$: C, 67.1; H, 5.6; N, 17.4. Found: C, 67.3; H, 5.7; N, 17.3

(b) **From Benzyl Bishydrazone.**—Acetylation of benzil bishydrazone[20] (1.92 g., 0.008 mole) with 2 ml. (0.02 mole) of acetic anhydride and 3 ml. of pyridine in 120 ml. of benzene under reflux for 24 hr. gave, on cooling, 2.1 g. (81%) of the bisacetylhydrazone, m.p. 242.5–243.5°, identical with the product described above. The product could also be obtained in 58% yield by heating the bishydrazone with glacial acetic acid under reflux in a nitrogen atmosphere for 118 hr.

Oxidation of the Bistriphenylmethylhydrazone V to the Bisazoethylene II.—A mixture of 0.540 g. (0.747 mmole) of hydrazone V, 2.03 g. (8.75 mmoles) of silver oxide, and 10 drops of saturated ethanolic potassium hydroxide in 40 ml. of tetrahydrofuran was stirred at 32° for 6 hr. After removal of undissolved solid by filtration the volume was reduced by evaporation in a stream of nitrogen to 10 ml., 30 ml. of benzene was added and the volume again reduced to 10 ml. The red bisazoethylene which crystallized was filtered and washed with benzene. There was obtained 10.9 mg. with m.p. 136–137° dec. A mixture with II prepared as described previously showed no depression. The infrared spectrum was identical with samples obtained by the previous route except that there was no trace of the weak absorption at 2240 cm.$^{-1}$ which had been attributed to the presence of a trace of impurity.

Thermal Decomposition of the Bisazoethylene II.—When 1.866 g. of II was suspended in benzene (50 ml.) and heated on a steam bath for 30 min. the solid disappeared to give a light red-orange solution. Evaporation of the benzene under reduced pressure gave 1.83 g. of orange, oily solid. Treatment with 150 ml. of ether and filtration of the undissolved solid gave 1.0 g. (75%) of triphenylmethyl peroxide, m.p. 176–180°, from which was obtained by recrystallization from benzene 0.36 g. (38%) of product, m.p. 176–177° (lit.,[23] 186–187°). It was impossible to separate the diphenylacetylene satisfactorily from other products by chromatography on alumina. An estimation of the amount of diphenylacetylene present by comparison of its highly characteristic ultraviolet spectrum with that of an authentic sample suggested that the yield of diphenylacetylene in the fractions collected was 86%. A determination of the amount of diphenylacetylene in these fractions by vapor chromatography with a 4-ft. column (20% silicone Dow 11 on Chromosorb) using a comparison of the area with that of a standard sample gave a value of 63%. In another reaction of 0.0015 g. in 80 ml. of cyclohexane, a clear solution was obtained after 5 hr. of heating on the steam bath. Cyclohexane which had evaporated was replaced quantitatively and the ultraviolet spectrum determined. It showed the characteristic spectrum of diphenylacetylene and a comparison of the absorbances at 288.5 and 281.5 mμ with those of a standard sample gave as the calculated yield 99.5 and 103%.

Triphenylmethyl peroxide was also obtained (52% yield, m.p. 183–198°) together with spectral evidence for diphenylacetylene when the bisazoethylene II (0.27 g., 0.37 mmole) and 0.17 g. (1.2 mmoles) of dimethyl acetylenedicarboxylate in 10 ml. of tetrahydrofuran were stirred at room temperature for 1.5 hr. and then heated under reflux for 1 hr. Treatment of II (0.27 g. 0.75 mmole) with sodium methoxide from 0.72 g. (31.5 mmoles) of sodium and 7 ml. absolute methanol in 20 ml. of tetrahydrofuran for 19.5 hr. at room temperature and then under reflux for 2 hr. gave an 80% yield of diphenylacetylene, as estimated from the ultraviolet spectrum of the product.

Acid Decomposition of the Bisazoethylene II. 1-Triphenylmethylamino-4,5-diphenyltriazole (VII).—A suspension of 0.50 g. of II in 10 ml. of 90% acetic acid was evaporated to one half of the original volume on a hot plate. The solid dissolved with disappearance of the red color in a few minutes. Upon cooling there separated 0.30 g. (90%) of the white crystalline aminotriazole VII, m.p. 255–260° dec. Recrystallization from petroleum ether–benzene raised the m.p. to 265–267°. When the compound was melted on a microscope hot stage it showed highly characteristic behavior. Above 250° sublimation occurred with the formation on the cover glass of crystals which finally melted with decomposition at 270–271°. This same product was obtained when the bisazoethylene II was suspended in ordinary unpurified chloroform for several days. Addition

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(20) W. Schlenk and E. Bergmann, *Ann.*, **463**, 76 (1928).

(21) K. Elbs, *Ber.*, **16**, 1275 (1883).

(22) T. Curtius and R. Jay, *J. prakt. Chem.*, [2] **39**, 27 (1889).

(23) H. Wieland, A. Hintermaier, and I. Dennstedt, *Ann.*, **452**, 9 (1927).

of potassium carbonate to the chloroform prevented the reaction. Treatment of II (0.853 g., 1.11 mmoles) with 0.452 g. (3.5 mmoles) of tetracyanoethylene in 40 ml. of tetrahydrofuran containing a crystal of potassium carbonate for 10 hr. under a nitrogen atmosphere gave a yellow-orange solution from which evaporation of the tetrahydrofuran and trituration with ethanol gave 0.530 g. (1.11 mmoles, 95%) of crude triazole VII, m.p. 244–256°. Recrystallization from tetrahydrofuran–petroleum ether (b.p. 30–60°) gave 0.15 g. of product with m.p. 255–257°. This sample showed the same characteristic sublimation behavior on a microscope hot stage and a mixture with VII prepared from the acetic acid reaction above showed no melting point depression. When the triphenylmethylaminotriazole VII (0.5 g.) was warmed for a few minutes on a steam bath with 60% sulfuric acid and the mixture poured into 50 ml. of ice-water there was obtained after recrystallization from ethanol 0.33 g. of triphenylcarbinol, m.p. 162–163°, identified by its melting point when mixed with an authentic sample and by the identity of the infrared spectra.

The structure of the triazole VII was confirmed by heating 0.096 g. (0.20 mmole) with 0.2 ml. of benzoyl chloride for 5 min. just below the boiling point. Concentrated aqueous ammonia was added to convert excess benzoyl chloride to benzamide and the 8% aqueous sodium hydroxide was added and the solution extracted with ether. A solid fraction (0.040 g.) insoluble in both the ether and base layers was filtered and found to be unchanged starting material, m.p. 255–257°. The clear aqueous alkaline solution was neutralized with aqueous hydrochloric acid to give, after digestion with 5 ml. of ether to remove a small amount of benzoic acid, 0.01 g. (15% or 26% based on unrecovered starting material) of 1-benzoylamino-4,5-diphenyltriazole, m.p. 250–252° dec., (lit.,[12] needles from ethanol, m.p. 248°, soluble in dilute base). Recrystallization from ethanol gave fine needles, m.p. 255.5–257°. The infrared spectrum showed absorption at 3440 (NH) and 1670 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{33}H_{26}N_4$: C, 82.8; H, 5.5; N, 11.7; mol. wt., 479. Found: C, 82.8, 82.4; H, 5.7, 6.3; N, 10.6, 11.5; mol. wt., 416.

Trapping of Benzonitrile Oxide (XIII) in the Reaction of the Silver Salt I with Triphenylmethyl Chloride. 3,5-Diphenylisoxazole. (XII).—A suspension of 13.4 g. (0.05 mole) of the silver salt I in 50 ml. of toluene at −20° was treated with 13.9 g. (0.05 mole) of triphenylmethyl chloride in 100 ml. of toluene. The silver chloride which formed was filtered with a pre-cooled funnel and aliquots of the solution which had been stored for 2 days at −80° was added 1.0 ml. of phenylacetylene and the solution was then allowed to stand in a refrigerator overnight. The resulting yellow solution was evaporated under reduced pressure to give a yellow semisolid which on trituration was petroleum ether became a brownish yellow solid (0.251 g.), m.p. 95–135°. Recrystallization from benzene–ethanol yielded 20.9 mg. of white crystalline isoxazole XII, m.p. 141–146°. The infrared and ultraviolet spectra were nearly identical with those of the authentic sample, m.p. 142.5–143.5°, prepared by the method of Posner[24] (lit.,[24] m.p. 141–142°). An additional fraction of 22.3 mg., m.p. 142–143°, crystallized from the filtrate remaining above. The total amount was 5% of the theoretical.

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.4; H, 5.0; N, 6.3. Found: C, 81.7; H, 5.0; N, 5.6.

A 20-ml. aliquot treated as a control with no added interception agent gave 0.219 g. (8%) of bisazoethylene II, with melting point and infrared spectrum identical to that described previously. An aliquot treated with 3.5 g. of aniline gave an immediate white precipitate of a product which was not identified. Formation of the red product II was completely prevented, however. The formation of the red product II was also prevented or seemed to be greatly reduced by the addition of bicyclo[2.2.1]hept-2-ene (2.0 g. in 5 ml. of toluene) of 3.0 g. of maleic anhydride, in each case to 20-ml. aliquots of the cold reaction mixture, but the products of these reactions were not investigated.

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[24] T. Posner, *Ber.*, **34**, 3985 (1901).

Synthesis and Characterization of Isomeric Methylphenylisoxazole-4-carboxylic Acids

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Various methods of synthesis of 5-methyl-3-phenylisoxazole-4-carboxylic acid (IIa) and 3-methyl-5-phenylisoxazole-4-carboxylic acid (IIIa) are described. On the basis of chemical synthesis and absorption spectra data, unambiguous structures are assigned to the isomers.

The literature concerned with the isoxazole acids IIa and IIIa prepared as illustrated in reaction schemes A and C of the chart fails to present convincing evidence for the assignment of isomeric structure IIIa rather than IIa to the product of reaction C.[2–4] The ambiguity is largely a consequence of the remarkable similarity of melting points of the isomeric isoxazole esters IIb (m.p. 44–46°) and IIIb (m.p. 54–55°), the acids IIa (m.p. 189°) and IIIa (m.p. 189°), and their respective amides IIc (m.p. 206–208°) and IIIc (m.p. 205–207°).

On the basis of crystal structure differences, Quilico[3] concluded that the isoxazole acid prepared by Betti[4] from ethyl benzoylacetoacetate (I) by reaction series C, is isomeric with the acid prepared from α-chlorobenzaldehyde oxime by reaction series A.

The tenuous nature of this conclusion was exemplified by the similarity of crystalline form of the isomeric amides, their failure to exhibit mixed melting point depression,[3] and by the designation

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[1] The author to whom communications should be directed.

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