1-Carbamoyl-2-(5-tetrazolyl)maleimide Monohydrate.—A mixture of 4.0 g of tetramethylammonium 5-tricyanovinyltetrazole and 25 ml of concentrated hydrochloric acid was stirred at 25° for 72 hr. The mixture was poured into 100 g of ice–water. The gray solid (1.6 g, dec pt >275°) was collected on a filter and washed with ice–water. Recrystallization from water (Darco) gave 1.25 g of light yellow microcrystals, dec pt >275°.

Anal. Calcd for $C_6H_6N_6O_4$: C, 31.86; H, 2.68; N, 37.17; mol wt, 226. Found: C, 31.27; H, 2.79; N, 36.79; mol wt (boiling acetone), 217, 213.

Preparation of Salts of 5-(2-Cyano-1,2-di-*p*-toluenesulfonylvinyl)tetrazole.—To a slurry of 1.35 g of lithium azide in 75 ml of dry dimethylformamide cooled to −10° under nitrogen was added in one portion 9.65 g (0.025 mole) of 1,2-di-*p*-toluenesulfonyl-1,2-dicyanoethylene.[10] The mixture became reddish orange, and the azide dissolved rapidly. The mixture was stirred for 1 hr at −10° and filtered cold under nitrogen, and the filtrate was evaporated at 1 mm. The glassy residue was taken up in acetone and added to ice-cold 20% aqueous tetramethylammonium chloride. The resulting oil crystallized on cooling to give 6.9 g of a yellow-orange tetramethylammonium salt (55%), mp 88–92° dec. The salt was sensitive to warm hydroxylic solvents. It was recrystallized from acetone–ether, mp 94–95°, $\lambda_{max}^{CH_2Cl_2}$ 393 mμ (ϵ_{max} 11,300).

Anal. Calcd for $C_{22}H_{26}N_6O_4S_2$: C, 52.57; H, 5.22; N, 16.72. Found: C, 52.67; H, 5.16; N, 17.07.

A reaction carried out on a similar scale and added to cold, 5% aqueous silver nitrate gave the yellow, microcrystalline silver salt in quantitative yield, dec pt >275°.

Anal. Calcd for $C_{19}H_{14}AgN_5O_4S_2$: C, 41.61; H, 2.57; N, 12.78. Found: C, 41.58; H, 2.57; N, 13.34.

A Novel Synthesis of 1,5-Diphenylpyrazolone-3[1]

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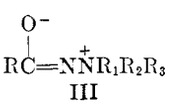
1,5-Diphenylpyrazolone-3 was first synthesized by Knorr,[3] who obtained it in vanishingly small yield by pyrolyzing cinnamoyl phenylhydrazide. Improved yields result from the reaction of monoacetyl phenylhydrazine with benzoylacetic ester in the presence of phosphorus trichloride.[4] We now report a new route to this compound which gives somewhat higher yields than Willert's method. The starting material for this synthesis is N-dimethylanilinophenylpropiolimide (II), a hitherto unreported compound which was prepared by treating N,N-dimethyl-N-phenylamine imine (I) with ethyl phenylpropiolate in an inert, anhydrous solvent such as tetrahydrofuran. The required amine imine (I) was obtained by deprotonation of dimethylphenylhydrazonium chloride with a strong base such as sodium ethylate. The over-all reaction sequence is summarized in the following equations. It was not necessary to isolate the free amine imine (I) before proceeding with the second step. The over-all yield of N-dimethylanilinophenylpropiolimide (II) was about 86%.

$$(PhN(CH_3)_2NH_2)^+Cl^- + NaOEt \longrightarrow \underset{I}{PhN^+(CH_3)_2N^-H} + NaCl + EtOH \quad (1)$$

$$I + PhC{\equiv}CCOOEt \longrightarrow \underset{II}{PhC{\equiv}CCON^-N^+(CH_3)_2Ph} + EtOH \quad (2)$$

It has been previously demonstrated[5,6] that trisubstituted hydrazonium salts deprotonate in the presence of a strong base according to eq 1 to give free amine imines. Analogous reactions have been described for the formation of phosphine imines[7,8] and arsine imines.[9]

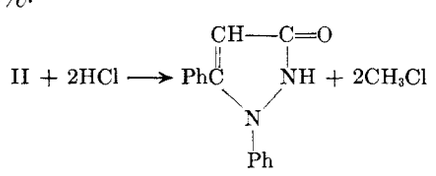
Amine imides of type II have been reported in which the acyl moiety is benzoyl[10] and acetyl.[11] These were obtained by synthetic methods entirely independent of the procedure described here. The structure of N-dimethylanilinophenylpropiolimide (II) was established by chemical analysis, molecular weight, and infrared and nmr proton spectroscopy. An infrared peak at 4.55 μ is due to the acetylenic bond. A very strong peak at 6.35 μ is assignable, according to Wawzonek,[11] to the stretching frequency of the C=N bond as it occurs in the resonance form (III) of amine imides.



III

This mesomeric form (III) is favored by the polar character of the N–N bond in the amine imide and must make a major contribution to the actual structure, since the normal carbonyl vibration is almost completely suppressed. A single peak in the nmr spectrum for methyl protons indicates that there had been no wandering of methyl groups during the reaction. The position of the methyl groups was further verified by the formation of dimethylaniline in the reductive cleavage of II.

To form 1,5-diphenylpyrazolone-3 (IV) from N-dimethylanilinophenylpropiolimide, the latter was heated at reflux with 6 *N* hydrochloric acid for several hours in an inert atmosphere. During this time, diphenylpyrazolone separated as a crystalline precipitate. Simultaneously, a gas was evolved and the reaction mixture turned green, owing to the formation of an unidentified by-product. The gas was identified by mass spectrometry as methyl chloride. The reaction, therefore, proceeded primarily according to eq 3. The yield of 1,5-diphenylpyrazolone-3 was about 80%.



IV

(3)

It was of interest to elucidate the mechanism of this rather surprising cyclization, involving as it does the loss of two methyl groups and the addition of two protons in the 2 and 4 positions of the pyrazolone ring.

(1) This work is part of a thesis submitted by H. W. Schiessl in partial fulfillment of the requirements for the degree of Doctor of Sciences.

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(3) L. Knorr, *Ber.*, **20**, 1107 (1887).

(4) W. Willert, *Ann.*, **358**, 159 (1907).

(5) G. Wittig and M. Rieber, *ibid.*, **562**, 177 (1949).

(6) R. Schöllhorn, Doctoral Dissertation, University of Heidelberg, Germany, 1963.

(7) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

(8) R. Appel and A. Hauss, *Angew. Chem.*, **71**, 626 (1959).

(9) R. Appel and D. Wagner, *ibid.*, **72**, 209 (1960).

(10) R. Hinman and M. Flores, *J. Org. Chem.*, **24**, 660 (1959).

(11) S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).

The acid hydrolysis (reaction 3) was repeated in deuterium oxide, using 6 *N* deuterium chloride. Mass spectrometric examination of the methyl chloride confirmed the complete absence of deuteration. The mass spectrum of the diphenylpyrazolone was consistent with deuteration in the 2 and 4 positions of the ring. Therefore, the methyl groups are not eliminated as carbene. They are expelled intact, either as methyl cations or through a concerted attack by the chloride ion with elimination of the nitrogen function. It seems likely that the first step in the hydrolysis is formation of the amine imide hydrochloride salt. This is suggested by dissolution of the water-insoluble amine imide (II) upon acidification, as well as by deuteration in the ring. The hydrochloride might be expected to split out one methyl group as methyl chloride, much the same as tetramethylammonium chloride decomposes thermally to trimethylamine and methyl chloride. Loss of the second methyl group would be thermodynamically favored by formation of the aromatic pyrazolone ring.

Experimental Section

Dimethylphenylhydrazonium Chloride.—Anhydrous, gaseous chloramine, generated in an apparatus similar to that described by Sisler,[12] was bubbled through pure anhydrous dimethylaniline at 25° to yield a thick slurry of the hydrazonium salt in unreacted dimethylaniline. The crystals were separated by vacuum filtration and washed with benzene, then with ether. To remove ammonium chloride from the product, the solids were extracted in a Soxhlet apparatus with an anhydrous mixture of ethyl acetate–methanol (90:10), in which ammonium chloride is practically insoluble. Dimethylphenylhydrazonium chloride precipitated from the extract upon cooling. Recrystallization from methanol with ether yielded a pure product, mp 188–189° (lit.[13] mp 187–188°).

Anal. Calcd for $C_8H_{13}ClN_2$: Cl, 20.5. Found: Cl (Volhard), 20.8.

N-Dimethylanilinophenylpropiolimide (II).—Dimethylphenylhydrazonium chloride (12.6 g, 0.073 mole) was added to a stirred suspension of freshly prepared sodium ethylate (4.9 g, 0.072 mole) in 150 ml of anhydrous tetrahydrofuran and maintained for several hours at −20° under a nitrogen atmosphere. Ethyl phenylpropiolate (6.3 g, 0.036 mole) was then added and the mixture was allowed to warm to room temperature. After stirring for 48 hr at room temperature, most of the solvent was removed by distillation under reduced pressure; the solid residue was collected by suction filtration and washed with ether and then with cold water. There was obtained 8.1 g (86%) of a white solid, mp 157–158° dec.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; mol wt, 264.3. Found: C, 76.92; H, 6.01; N, 10.90; mol wt (cryoscopic in nitrobenzene), 259.

Infrared bands (KBr disk) were found at 4.5 (C≡C) and 6.35 (C=N) μ. The nmr spectrum ($CDCl_3$, against tetramethylsilane) showed the usual peaks for aromatic protons in the region of τ 2.5, and also a single peak at 6.4 for methyl protons. The ratio of aromatic to methyl protons was the expected 10:6.

1,5-Diphenylpyrazolone-3.—A solution of N-dimethylanilinophenylpropiolimide (4.7 g, 0.018 mole) in 30 ml of 6 *N* hydrochloric acid was subjected to reflux for 2 hr in a helium atmosphere. The evolved gas was found by mass spectrometric analysis to be methyl chloride. The precipitate formed during reaction was collected by suction filtration, washed with acetone, and recrystallized from ethanol to give 3.2 g (76%) of a white solid which sublimed at 254°. An analytically pure sample was obtained by vacuum sublimation, mp 257° (closed capillary lit.[14] mp 256°).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.35; H, 5.14; N, 12.09.

The infrared spectrum was identical with that of an authentic sample of 1,5-diphenylpyrazolone-3 prepared by the method of Willert.[4] A mixture melting point determination with the authentic sample showed no depression.

When the above hydrolysis was carried out with 6 *N* deuterium chloride in deuterium oxide, no deuterated methyl chloride was formed. The deuterium appeared, instead, in the diphenylpyrazolone.

(12) H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3906 (1954).

(13) G. M. Omietanski (Ohio State University), German Patent 1,056,140 (April 30, 1959).

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Friedländer Syntheses with *o*-Aminoaryl Ketones. II. Structure of the Product Formed in the Condensation of *o*-Aminobenzophenone with Acetylacetone[1]

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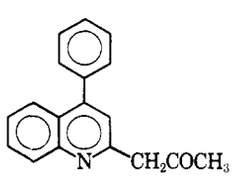
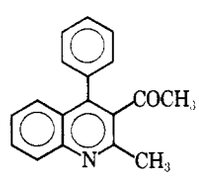
In 1939 Borsche and Sinn[2] described a compound, $C_{18}H_{15}NO$, which they obtained as the product of a Friedländer-type condensation between *o*-aminobenzophenone and acetylacetone and to which they assigned structure **1**. No evidence was offered to support the proposed structure, and no consideration seems to have been given to the possibility that an alternative (and more likely) course of reaction would lead to structure **2**. Since their observations on the behavior of other



1



2

ketones had led Borsche and Sinn to conclude that only methyl ketones are capable of undergoing normal Friedländer-type condensations with *o*-aminobenzophenone, their assignment of structure **1** to this product seems to have been based on the tacit assumption that the α-methyl group of the ketone must be directly involved in ring formation and must consequently provide C-3 in the resultant 4-phenylquinoline. In view of the results described in the preceding paper in this series,[3] however, it seemed to us most unlikely that acetylacetone would undergo this type of condensation at a methyl group rather than at the much more reactive methylene group,[4] and we have therefore reinvestigated the Friedländer condensation of this β-diketone with *o*-aminobenzophenone. We are now able to report that the product of this reaction is indeed 3-acetyl-4-phenylquinaldine (**2**) and not, as originally assumed, 2-acetonyl-4-phenylquinoline (**1**).

(1) This investigation was supported in part by Public Health Service Research Grant CY-2726(C3) from the National Cancer Institute of the National Institutes of Health.

(2) W. Borsche and F. Sinn, *Ann.*, **538**, 283 (1939).

(3) E. A. Fehnel, *J. Org. Chem.*, **31**, 2899 (1966).

(4) The condensation of acetylacetone with *o*-aminobenzaldehyde yields the expected 3-acetylquinaldine: J. Eliasberg and P. Friedländer, *Ber.*, **25**, 1752 (1892).