# The Reaction of Diazomethane with 2-Phenylazo-1,3-diketones

BY PETER B. RUSSELL

RECEIVED JUNE 25, 1953

Diazomethane reacts with 2-phenylazo-1,3-diketones in ether containing a little methanol to give mainly simple methylene derivatives. These yellow compounds contain no methoxyl group and are formulated as epoxides. On treatment of these epoxides with acidic reagents 3-acyl-1-phenylpyrazoles are formed, the methylene derivative from α-phenylazoacetylacetone giving the known 3-acetyl-5-methyl-1-phenylpyrazole. The mode of formation of the various products is discussed and conclusions regarding the structure of the original "mixed azo compounds" are reached.

The coupling of aromatic diazonium compounds with ethyl acetoacetate in alkaline solution to give colored products was first observed by Meyer and Ambuhl[1] in 1876. Since that time many compounds containing reactive methylene groups have been found to react in a similar manner giving rise to the so-called "mixed azo compounds."[2,3] When the reactive methylene component is a β-diketone, a β-ketoester or the like, the product may have one of the potentially tautomeric structures I, II or III. From time to time various workers have produced
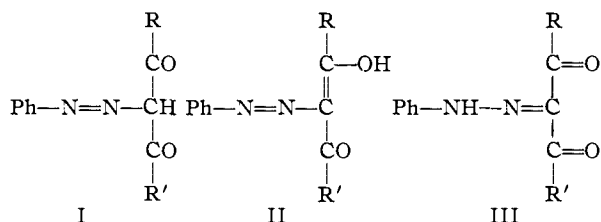

evidence in favor of one or the other of these forms or of the existence of a tautomeric equilibrium involving two or more of them. However, it cannot be said that the question of the structure of these compounds is satisfactorily settled.

The structures of I, II and III differ only in the position of a hydrogen atom and the consequent difference in the position of the double bonds. In recent times Arndt and his school[4,5] have used the reaction with diazomethane to detect the position of hydrogen atoms in potentially tautomeric systems such as those formed by the above structures. A study of the reaction of 2-phenylazo-1,3-diketones with this reagent was undertaken. The products obtained are shown not to be derived from I, II and III by the simple replacement of a hydrogen atom by a methyl group but nevertheless the nature of these products allows an insight into the structure of the original mixed azo compounds.[6]

The phenylazodiketones, α-phenylazoacetylace-

tone (IV, pentan-2,3,4-trione-3-phenylhydrazone),[7] α-phenylazobenzoylacetone (V, 1-phenylbutan-1,-2,3-trione-2 phenylhydrazone),[8] α-phenylazobenzoylacetaldehyde (VI, 1-phenylpropan-1,2-dione-3-al-2-phenylhydrazone),[8] α-phenylazodibenzoylmethane (VII, 1,3-diphenylpropan-1,2,3-trione-2-phenylhydrazone)[8] and phenylazodimethyldihydroresorcinol (VIII, 5,5-dimethylcyclohexan-1,2,3-trione-2-phenylhydrazone)[9] were all treated with diazomethane in ethereal solution containing about ten parts per hundred of methanol. The first four compounds reacted with the reagent, the evolution of nitrogen being rather slow in the cases of IV, V and VII but quite rapid in the case of VI. The cyclic derivative VIII, however, failed to react under the conditions described.
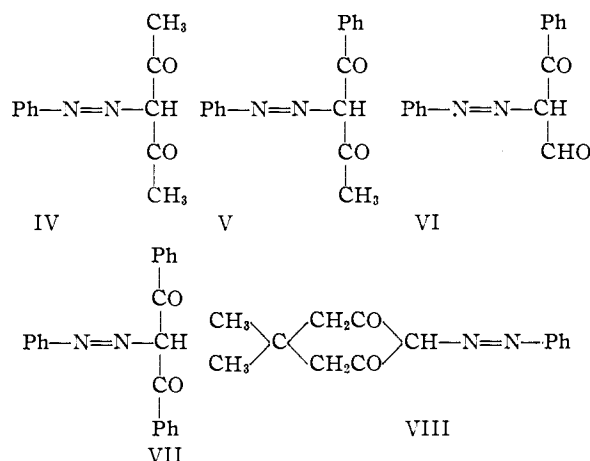
No pure compound was isolated from the gummy product of the reaction of VII with diazomethane despite many attempts. The reaction products of IV, V and VI all yielded one or more crystalline products. In each case the total yield of crystalline products isolated was some 90% of the amount of the starting material not recovered. In no case was a methoxyl containing compound isolated but in each instance the chief product was a simple methylene derivative of the starting material. These products were yellow in color and when treated with ferric chloride in acetic anhydride all gave rise to colorless compounds with the loss of a molecule of water. The methylene derivatives from IV and V, but not that from VI, were also dehydrated on treatment with dilute acetic or hydrochloric acids.

The colorless dehydration products gave car-

(1) V. Meyer and G. Ambuhl, Ber., 9, 384 (1876); 11, 2418 (1878); 17, 1928 (1884).

(2) K. Holzach, "Die aromatischen Diazoverbindungen," Enke, Stuttgart, 1947, p. 141.

(3) K. H. Saunders, "The Aromatic Diazo-compounds and Their Technical Applications," 2nd Ed., Edward Arnold and Co., London, 1949, p. 209.

(4) F. Arndt, Rev. Faculte sci. univ. Istanbul, No. 4, 7 (1936). "Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1953, Vol. I, p 197.

(5) B. Eistert, "Syntheses with Diazomethane" in "New Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 513.

(6) 2-Phenylazo-1,3-diketones will be referred to as azo compounds throughout in accordance with general usage and despite the fact that the conclusion is reached that these compounds exist in a modified hydrazone form. The systematic name of each compound will be given in parentheses when it is first mentioned.

(7) C. Bülow and F. v. Schlotterbeck, Ber., 35, 2188 (1902).

(8) C. Beyer and L. Claisen, ibid., 21, 1705 (1888).

(9) J. Lipschitz, ibid., 47, 1407 (1914).

bonyl reactions. The compound $C_{12}H_{12}N_2O$ (m.p. 89–90°) obtained by dehydration of the reaction product of α-phenylazoacetylacetone and diazomethane gave both a semicarbazone (m.p. 228°) and an oxime (m.p. 174°). With iodine in alkali iodoform was obtained. From its mode of formation, its ultraviolet spectrum and its chemical properties the compound $C_{12}H_{12}N_2O$ was believed to be an acetylmethyl-1-phenylpyrazole. Since it was derived from α-phenylazoacetylacetone (IV) it is reasonable to assume that both the acetyl group and the hydrazine residue are attached to the same carbon atom, i.e., carbon 3 of the pyrazole ring. Both the possible methyl-3-acetyl-1-phenylpyrazoles are reported in the literature. 4-Methyl-3-acetyl-1-phenylpyrazole (IX) was obtained as a degradation product of penicillic acid by Birkenshaw, Oxford and Raistrick[10] while the 5-methyl-3-acetyl-1-phenylpyrazole (X) was obtained, as the oxime, from the reaction of phenylazo-2,5-dimethylpyrrole with hydroxylamine in sodium hydroxide solution by Castellana.[11] The melting point of the ketone $C_{12}H_{12}N_2O$ and its oxime were in good agreement with the melting points recorded by Castellana for X and its oxime. The structure X for this ketone was confirmed by its oxidation with sodium hypobromite to bromoform and 5-methyl-1-phenylpyrazole 3-carboxylic acid (XI).[12] Treatment of the original methylene derivative $C_{12}H_{14}N_2O_2$ with semicarbazide hydrochloride in sodium acetate solution gave the semicarbazone of X.
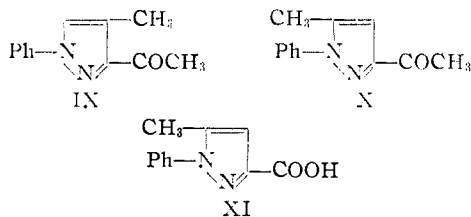

The compounds $C_{16}H_{12}N_2O$ and $C_{17}H_{14}N_2O$ from the reaction product of VI and V, respectively, gave neither iodoform reactions nor semicarbazones. However, the ketonic nature of these substances was demonstrated by the formation of 2,4-dinitrophenylhydrazones and oximes. The ketones were formulated as 3-benzoyl-1-phenylpyrazole (XII) and its 5-methyl homolog (XIII), respectively. The formulation explains the failure of the iodoform test and the reluctance to give a semicarbazone, this latter reaction being rather sensitive to steric influences.[13]

The ultraviolet absorption spectra of the pyrazole ketones offer support for the constitutions XII and XIII assigned to them. In alcoholic solution X shows only one peak in its spectrum (λ_{max} 257 mμ) as does the pyrazole ketone $C_{17}H_{14}N_2O$ (λ_{max} 270 mμ). The pyrazole ketone $C_{16}H_{12}N_2O$, however, shows three maxima (λ_{max} 240 mμ, 260 mμ (broad low peak) and 290 mμ). If these last two compounds are formulated as XIII and XII, re-

(10) J. H. Birkenshaw, A. E. Oxford and H. Raistrick, *Biochem. J.*, **30**, 394 (1936).

(11) V. Castellana, *Gazz. chim. ital.*, **36**, 11, 50 (1906); *Atti R. Accad. Lincei*, [5] **14**, II, 242 (1905); [5] **16**, II, 772 (1907).

(12) L. Claisen and P. Roosen, *Ann.*, **278**, 274 (1894).

(13) H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," 6th Ed., Springer, Vienna, 1938, p. 563.

spectively, then the complexity of the spectrum of the compound $C_{16}H_{12}N_2O$ as compared with those of the other two compounds may be explained as being due to the coplanar configuration of the pyrazole and benzene rings which in X and XIII is prevented by the 5-methyl group.
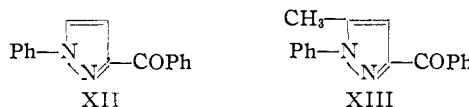
The nature of the original yellow methylene derivatives which give rise to X, XII and XIII on acid treatment calls for some discussion. Obviously these final products could be pictured as being formed by the cyclization of the three carbonyl compounds XIV–XVI, respectively. These carbonyl compounds are simple homologs of the parent compounds IV, VI and V and the reaction of diazomethane with carbonyl compounds to give the simple homologs is well known.[5] However, the structures XIV–XVI represent monophenylhydrazones of 1,3-diketones and such compounds cyclize with great ease to give pyrazole derivatives.[12,14] The yellow methylene derivatives obtained from diazomethane and the 2-phenylazo-1,3-diketones are, on the other hand, quite stable except in the presence of acidic reagents. They are thus assigned the epoxide structures XVII–XIX. Evidence in support of the epoxide structures for these reaction products could not be obtained by chemical means. Attempts to add secondary amines to give the am-
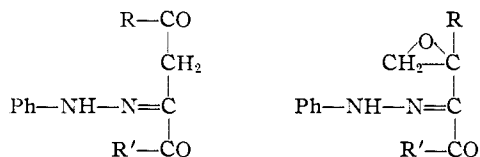
XIV, R = R' = CH$_3$	XVII, R = R' = CH$_3$
XV, R = H, R' = Ph	XVIII, R = H, R' = Ph
XVI, R = CH$_3$, R' = Ph	XIX, R = CH$_3$, R' = Ph

ino alcohols resulted in the recovery of the starting material while attempts to demonstrate the presence of the epoxide ring by cleavage and acylation with ferric chloride in acetic anhydride[15] or benzoyl chloride in pyridine[16] gave the previously described pyrazole ketones. An infrared spectroscopic examination of both forms (see below) of the reaction product of diazomethane and α-phenylazobenzoylacetone (V) offers confirmation of this structure however. Both forms in chloroform solution have similar spectra in the infrared, differing only slightly in the 10.6–11.0 μ region. They show absorption at 2.8 μ, 3.0 μ (m), 6.15 μ (s), 6.25 μ (s), 7.9–8.1 μ (n) and 12.15 μ (m) noting only a few characteristic frequencies. The absence of a carbonyl band below 6.0 μ together with the absorption at 7.9–8.1 μ and 12.15 μ, the frequencies of absorption of the ethylene oxide ring, would seem to be in better accord with XIX than XVI.

The conversion of the epoxides XVII, XVIII and XIX to the ketopyrazoles X, XIII and XII by acid reagents must involve a rearrangement. The

(14) L. Claisen and R. Meyerowitz, *Ber.*, **22**, 3276 (1889).

(15) F. Arndt and B. Eistert, *ibid.*, **61**, 1118 (1928); F. Arndt, B. Eistert and W. Ender, *ibid.*, **62**, 44 (1929).

(16) F. Arndt, B. Eistert and W. Partale, *ibid.*, **61**, 1107 (1928).

possible course of this rearrangement is shown below. Ring closure without rearrangement is conceivable but need not be considered since here the pyrazole IX rather than X would result from XVII. Somewhat similar rearrangements of epoxides under the influence of Lewis-type acids have been recorded by Stevens, Dykstra and Scherr.[17]

R = H or CH₃   X⁺ = H⁺ or FeCl₂⁺
R' = COCH₃ or COPh   Y⁻ = Cl⁻ or OAc⁻
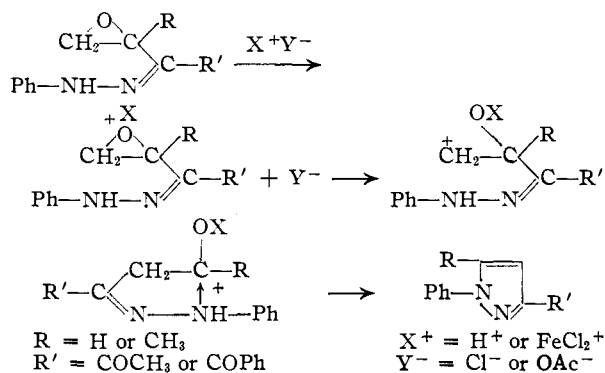
In addition to the methylene derivative XVII the reaction of diazomethane with phenylazoacetylacetone (IV) gave rise to an ether insoluble compound. This appeared to be a simple addition product of the two reactants $C_{12}H_{14}N_4O_2$, it melted at 204° with the evolution of gas, presumably nitrogen. Diazomethane is known to add to carbon–carbon[5] and carbon–nitrogen[18] double bonds to give the corresponding five-membered heterocyclic ring system. Addition products with carbonyl groups have also been obtained[19] which are believed to be diazonium betaines, $RR'{=}CO^{-}{-}CH_2N_2^{+}$. In the present case the point of addition was not determined. It is worth noting that similar addition products were not encountered with other phenylazodiketones.

The main product from the reaction of V with diazomethane was isolated in two forms A (m.p. 104°) and B (m.p. 130°). These two compounds both give rise to the same pyrazole XIII on treatment with ferric chloride in acetic anhydride or with acid, further they have identical spectra in the ultraviolet and very similar infrared spectra. The proportions of the two forms varied from experiment to experiment but the total yield was roughly constant. The relationship between A and B is obscure but both appear to be represented by the formula XVIII.

The application of chromatography on alumina to the separation of the ether soluble products of the action of diazomethane on the phenylazodiketones resulted in the isolation of degradation products of the components of the mixture or the isolation of compounds resulting from further reactions of the methylene derivatives. Thus from the ether soluble portion of the product from α-phenylazoacetylacetone and diazomethane pyruvicaldehyde ω-phenylhydrazone (XX) and the pyrazole X were isolated in addition to some starting material. From the residues obtained from the reaction product of α-phenylazobenzoylacetone and diazometh-

ane, after removal of the main product by crystallization, chromatography yielded a new compound $C_{17}H_{18}N_2O_3$ in some 20% yield. This product is a carbonyl compound giving rise to a semicarbazone. The spectrum of the compound resembles that of XVII rather than XIX and on these grounds it is believed to be the glycol XXI. Possibly it is derived from the corresponding epoxide by addition of water. The structure of this·compound was not rigidly established. It did not give rise to a pyrazole under the usual conditions and neither could it be obtained by mild hydrolysis of XIX.
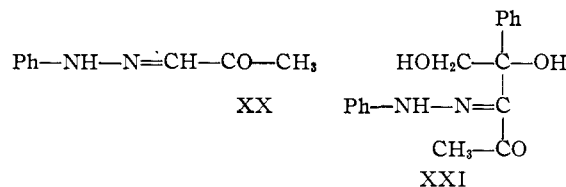
An attempt was made to combine the monophenylhydrazones of several 1,2-diketones with diazomethane, these compounds were XX and its N-methyl homolog cyclopentan-1,2-dione-2-phenylhydrazone and the corresponding cyclohexane derivative. In every case the starting material was recovered in almost quantitative amount after prolonged contact with the reagent.

It is recognized that a ketone which enolizes gives an enol ether with diazomethane. The extent to which an epoxide accompanies this ether is an inverse function of the acidity and degree of enolization of the parent ketone.[20] Accordingly if a carbonyl compound, potentially capable of enolization gives an epoxide exclusively with diazomethane it is believed that enolization does not take place.[21] Thus the isolation of epoxides and the failure to demonstrate the formation of enol ethers in the present work indicates that the α-phenylazodiketones do not undergo simple enolization, that is, they do not exist in the form II, at least in ethereal solution.

It is well known that certain chelate compounds, o-hydroxyacetophenone or salicylic ester for example, are unattacked by diazomethane in absolute ether but give methyl ethers in ethereal methanol solution.[22] It is reported that o-hydroxyazo compounds are not attacked by diazomethane in ether[23] nor is the anil of 2-acetylcyclohexane-1,3-dione (XXII).[24] It has also been found that the anil of formyldesoxybenzoin, to which Wislicenus[25] gave the structure XXIII, does not react with the reagent in absolute ether or in ethereal methanol. Both the anils (XXII, and XXIII) are represented in the ketimine form, they are of course potentially capable of existing in the enamine forms, for example XXIIIa.

The chelate enols of β-diketones are considered as resonance hybrids of structures such as XXIVa

(17) C. L. Stevens, S. Dykstra and A. E. Sherr, Abstracts of Papers 123 Meeting American Chemical Society, Los Angeles, California, March 1953, p. 31 M.

(18) R. Rotter and E. Schaudy, Monatsh., 58, 245 (1931).

(19) H. Meerwein, T. Bersin and W. Burneleit, Ber., 62, 999 (1929).

(20) F. Arndt, L. Loewe, T. Severge and P, Türegün, ibid., 71, 1640 (1938); F. Arndt, L. Loewe and B. Beyer, ibid., 74, 1460 (1941).

(21) F. Arndt, M. Özansoy and H. Üstünyar, Rev. faculte sci. univ. Istanbul, 4, No. 1–2, 83 (1939).

(22) A. Schönberg and R. Moubasher, J. Chem. Soc., 366 (1944); A. Schönberg and A. Mustafa, ibid., 746 (1946).
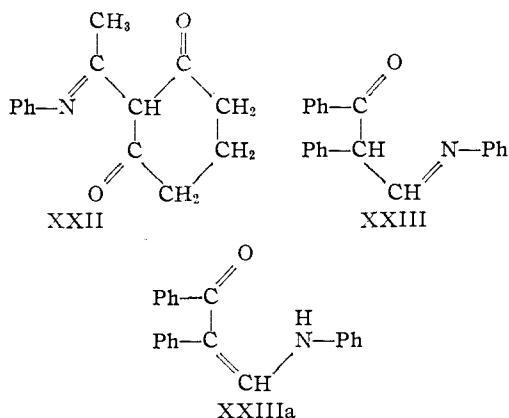
(23) C. Smith and A. D. Mitchell, ibid., 93, 843 (1908).

(24) H. Smith, ibid., 803 (1953).

(25) W. Wislicenus and A. Ruthing, Ann., 319, 229 (1911).

XXII   XXIII

XXIIIa

and b. The chelate XXIV can also be in a proto-tropic equilibrium with XXV which again can be a hybrid of the forms XXVa and b. In the past it has been believed that in a chelate compound of this type the hydrogen was coördinated between the oxygen atoms and had the same relationship to both. Thus XXIV (a and b) and XXV (a and b) were all considered as resonances structures contributing to the same hybrid.[26] Modern views on the nature of the hydrogen bond,[27] however, are in better accord with the view that the hydrogen atom is associated with one member of the bond more than with the other and thus the system XXIV and XXV becomes the prototropic equilibrium described above.

XXIV

XXV
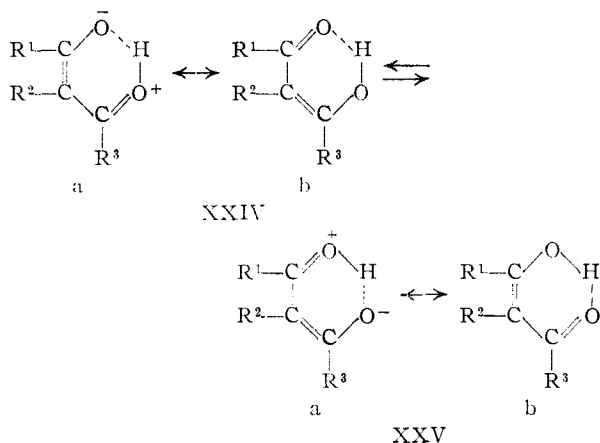
When one oxygen in the above system is replaced by a nitrogen as in the anils of β-dicarbonyl compounds (XXII, XXIII or XXIIIa) or in the phenyl hydrazones of 1,2-diketones then the equilibrium between the corresponding forms XXVI and XXVII (for the hydrazones in this case) might be expected to be displaced almost completely in one direction or the other. Since with diazomethane in methanolic ether no ethers are formed the structure XXVI is unlikely. Further it should be mentioned that the failure to form an enol ether with diazomethane rules out structures such as XXIV and XXV (R² = —N=N—Ph) for the phenylazodiketones. The structure XXVII (R⁴ and

(26) N. V. Sidgwick, *Ann. Rep. Chem. Soc. (London)*, **30**, 113 (1933); **31**, 37 (1934).

(27) (a) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 209; (b) C. A. Coulson, "Valence," Oxford University Press, 1952, p. 298 ff.

XXVI   a
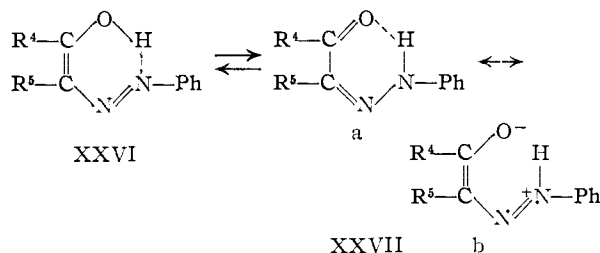
XXVII   b

R⁵ = Ar, Alk or H) seems the best representation of the phenylhydrazones of 1,2-diketones except that the structure XXVIIa alone does not give any reason for the failure to form an epoxide with diazomethane. However, if the phenylhydrazone is looked upon as a hybrid of XXVIIa and b then it is noted that the ketone group is considerably modified and would not be expected to form an epoxide with the reagent. If the structure XXVIIb is to make any considerable contribution to the hybrid the protonated azo group —N=NH—Ar should be a stable entity; that it is was shown by Slotta and Franke[28] in their researches on α-naphthol orange. If the hydrogen on the nitrogen in XXVII is replaced by a methyl group resonance of the type a ⟷ b should still be possible. The contributions of such structures as XXVIIb (with N=N—Ph) to the N-phenyl-N-methylhydrazone of pyruvicaldehyde is indicated since this substance gives no epoxide with diazomethane.

In the phenylazodiketones only one carbonyl group is bound in the resonating system XXVIIa and b. The other carbonyl group, R⁵ in XXVII, is free and it is this group that gives the epoxide with diazomethane. In this it reacts like a carbonyl group attached to an aromatic nucleus which is negatively substituted.[5] When one of the carbonyl groups in the phenylazodiketone is a benzoyl group the other being a formyl or an acetyl group, it would appear from the previously described experiments that the benzoyl group is held in the resonating system, at least mainly, and is not attacked by diazomethane. Thus V may be written XXVII (R⁴ = Ph, R⁵ = COCH₃) and VI as XXVII (R⁴ = Ph, R⁵ = CHO). The phenyl group may conjugate with the resonating system thereby lowering the energy of these forms. Zwitterionic structures similar to XXVIIb were considered by Kuhn[29] to account for the properties of o-hydroxyazo compounds.

Ethyl phenylazoacetoacetate reacts with diazomethane to give a simple methylene derivative containing no methoxyl. While the description of this and similar compounds must be reserved for a further communication it would appear that the structures of the product and starting material are analogous to those described above.

Experimental

All melting points are uncorrected.

The Reaction of α-Phenylazoacetylacetone with Diazomethane.—α-Phenylazoacetylacetone (10.5 g.) in ether (100 ml.) containing methanol (10 ml.) was treated with a solu-

(28) K. H. Slotta and W. Franke, *Ber.*, **64**, 86 (1932).

(29) R. Kuhn, *Naturwiss.*, **20**, 622 (1932).

tion of diazomethane (from 10 g. of nitrosomethylurea[30]) in ether (200 ml.). Nitrogen was evolved slowly and the reaction appeared to be complete in 18 hours. The crystalline material which separated during this time was filtered off. Evaporation of the solution to half-volume at room temperature gave a further quantity of the same substance and dilution of the filtrate with an equal volume of ligroin ("Skelly A") gave a further small amount. In all 1.5 g. of yellow plates, m.p. 190–193°, was collected. After several recrystallizations from methanol it formed bright yellow plates, m.p. 205–206° (gassing).

Anal. Calcd. for $C_{12}H_{14}N_4O_2$: C, 58.5; H, 5.7; N, 22.8. Found: C, 58.2; H, 5.9; N, 22.9; OCH$_3$, 0.0.

The ether–ligroin mother liquors after the separation of the above compound were evaporated under reduced pressure at room temperature. The semicrystalline oil was dissolved in benzene (15 ml.) and the resulting solution, after filtration, was diluted with ligroin (50 ml.). After standing in the ice-box for four days the crystals (3.8 g., m.p. 88°) were filtered, the liquors after evaporation to half bulk yielded a further quantity (0.2 g.) of the same substance. This material after several recrystallizations from hexane formed yellow plates, m.p. 88°.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.1; H, 6.4; N, 12.8; 1 OMe, 13.8. Found: C, 66.1; H, 6.1; N, 13.2; OMe, 0.0.

Ultraviolet spectrum in ethanol: λ_{max} 246 mμ, ϵ 10 $\times$ 10³; λ_{min} 274 mμ, ϵ 2 $\times$ 10³; λ_{max} 354 mμ, ϵ 18 $\times$ 10³.

The combined mother liquors were evaporated to dryness. The resulting yellow oil was taken up in a little Skelly A and on standing deposited pale yellow needles (3 g.). These melted at 88° and this melting point was undepressed on admixture with starting material, mixed with the compound $C_{12}H_{14}O_2N_2$ the melting point was 55–70°. The mother liquors from the above crystallization were chromatogramed on a column of alumina. The chromatogram was developed with hexane containing benzene (5%) to yield a further 0.7 g of starting material and nothing else.

Separation of the Total Ether Soluble Products from the Above Reaction by Chromatography on Alumina.—The reaction was carried out as above using half the quantities. After removal of the compound, m.p. 205–206°, the ethereal solution was evaporated to dryness and the residual oil taken up in benzene (50 ml.). The benzene solution was placed on a column of alumina (12 $\times$ 1.5 inches) and the bands developed with benzene, the first band yielded yellow needles, m.p. 88° (3 g.), identified as the starting material. The second band after elution with ether was rechromatographed, this gave colorless prisms, m.p. 89–90° (2 g.).

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 72.0; H, 6.0; N, 14.0. Found: C, 72.2; H, 5.9; N, 13.7.

Absorption spectrum in ethanol: λ_{min} 233 mμ, ϵ 10.5 $\times$ 10³, λ_{max} 255 mμ, ϵ 14 $\times$ 10³.

After removal of the compound, m.p. 89–90°, elution of the column with chloroform gave a yellow substance which after recrystallization from benzene–ligroin melted at 150°. This compound was identified as pyruvicaldehyde ω-phenylhydrazone by comparison with an authentic sample.[31]

Treatment of the Compound $C_{12}H_{14}N_4O_2$ with Acid.—The compound (100 mg.) was dissolved in methanol (2 ml.) and water (2 ml.) added. To this solution was added glacial acetic or concentrated hydrochloric acid (2 drops). After a few minutes the solution was colorless and crystals began to separate. These crystals melted at 90° and were identical in every respect with the compound $C_{12}H_{12}N_2O$ described above.

Treatment of the Compound $C_{12}H_{14}N_2O_2$ with Ferric Chloride in Acetic Anhydride.—The compound (100 mg.) was dissolved in acetic anhydride (1.5 ml.) and several small crystals of ferric chloride were added. The mixture warmed at once. After warming on a steam-bath for 10 minutes the mixture was poured into water. Colorless crystals (85 mg.), m.p. 90°, separated. These were identical in every respect with the product described above.

Properties of the Compound $C_{12}H_{12}N_2O$, m.p. 89–90°.—With iodine in potassium iodide solution and strong sodium hydroxide the compound gave iodoform. The compound

on treatment with semicarbazide hydrochloride and sodium acetate in aqueous methanol gave a semicarbazone, m.p. 228°.

Anal. Calcd. for $C_{13}H_{15}N_5O$: N, 27.2. Found: N, 26.9.

The same semicarbazone was obtained when the original methylene derivative $C_{12}H_{14}O_2N_2$ was treated under the same conditions.

With hydroxylamine in aqueous alcoholic solution an oxime was obtained which crystallized from methanol as colorless needles, m.p. 174°.

Anal. Calcd. for $C_{12}H_{13}N_3O$: N, 19.5. Found: N, 19.3.

Oxidation of the Compound $C_{12}H_{12}N_2O$ with Sodium Hypobromite.—The ketone (475 mg.) was dissolved in a little methanol and added to a solution of bromine (600 mg.) in 2 N sodium hydroxide (3.6 ml.) and water (2.5 ml.). After the mixture had stood overnight there was a strong smell of bromoform. The solution was heated on a steam-bath for one hour and finally evaporated to half bulk and made acid to congo red with 2 N sulfuric acid. The product separated as colorless needles which after several recrystallizations from hot water melted at 103° before and at 134–135° after drying in a vacuum desiccator. These melting points were not depressed on admixture with the hydrated and anhydrous forms of 5-methyl-1-phenylpyrazole-3-carboxylic acid,[12] respectively.

The Reaction of a Phenylazobenzoylacetone with Diazomethane.—The phenylazodiketone (7.5 g.) was dissolved in ether (100 ml.) containing methanol (10 ml.) and this solution treated with diazomethane (*ca.* 2.8 g.) (from 10 g. of nitrosomethylurea) in ether (100 ml.) at 0–2°. Nitrogen was evolved slowly and the solution darkened slightly. After 16 hours the solution was evaporated at room temperature *in vacuo*, to give a semisolid mass. This yellow mass on washing with ligroin (Skelly A) gave a crop of yellow crystals (4.2 g.), m.p. 118°. By repeated crystallizations of this material from ligroin two crystalline compounds were isolated, the more soluble A, m.p. 104° (2.4 g.) and the less soluble B, m.p. 130° (1.5 g.). Both these compounds crystallized as yellow needles, mixtures melted between the melting points of the pure compounds.

Anal. Calcd. for $C_{17}H_{18}O_2N_2$: C, 72.9; H, 5.7; N, 10.0. Found: A. C, 72.6; H, 5.6; N, 10.1; OCH$_3$, 0.0. B. C, 73.1; H, 5.4; N, 10.4; OCH$_3$, 0.0.

Absorption spectra of A and B in ethanol: λ_{max} 252 mμ, ϵ 17 $\times$ 10³; λ_{min} 310 mμ, ϵ 2 $\times$ 10³; λ_{max} 385 mμ, ϵ 21 $\times$ 10³.

The original ligroin washings of the yellow crystalline material were run through a column of alumina (10 $\times$ 1.5 in.) and the chromatogram developed with ligroin–benzene (9:1). The first runnings gave pure starting material, m.p. 102°. Elution of the column with benzene or with chloroform yielded oily material which crystallized slowly but completely (1.5 g.). Recrystallization of this substance from benzene–ligroin gave yellow plates, m.p. 126°.

Anal. Calcd. for $C_{17}H_{18}N_2O_3$: C, 68.9; H, 6.01; N, 9.3. Found: C, 68.8; H, 6.1; N, 9.3; OCH$_3$, 0.0.

Ultraviolet absorption spectrum in ethanol: λ_{max} 247 mμ, ϵ 15 $\times$ 10³, λ_{min} 310 mμ, ϵ 4 $\times$ 10³; λ_{max} 357 mμ, ϵ 16 $\times$ 10³.

With semicarbazide hydrochloride in aqueous ethanolic sodium acetate the compound gave a semicarbazone, m.p. 180° (after changing color at 120°).

Anal. Calcd. for $C_{18}H_{21}N_5O_3$: C, 60.8; H, 5.9. Found: C, 61.1; H, 5.5.

Conversion of the Compounds A and B to the Dehydration Product. (a) With Ferric Chloride in Acetic Anhydride.—The compound A (0.1 g.) was dissolved in acetic anhydride (1.5 ml.) and treated with a few crystals of ferric chloride as previously described. The dehydration product was isolated as before, it formed colorless needles from aqueous methanol, m.p. 91°. Compound B gave the same substance on similar treatment.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 78.0; H, 5.3; N, 10.7. Found: C, 78.2; H, 5.5; N, 10.3.

Ultraviolet spectrum in ethanol: λ_{min} 242, ϵ 12 $\times$ 10³; λ_{max} 270, ϵ 16 $\times$ 10³.

With 2,4-dinitrophenylhydrazine the above compound gave a hydrazone which, after recrystallization from ethanol melted at 210° (after softening at 195–197°).

Anal. Calcd. for $C_{23}H_{18}N_6O_4$: N, 19.0. Found: N, 19.4.

(30) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(31) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **53**, 519 (1888).

The compound, m.p. 91°, gave an oxime with hydroxylamine hydrochloride in aqueous alcoholic solution containing sodium acetate. This oxime formed colorless needles, m.p. 154°, from aqueous methanol.

Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.8; H, 5.4. Found: C, 74.1; H, 5.6.

(b) **With Acid.**—Compound A (50 mg.) was dissolved in methanol (1 ml.) and water (1 ml.) added. To this solution acetic or concentrated hydrochloric acid (2 drops) was added. The solution rapidly became colorless. Colorless crystals, m.p. 91°, identical with those described above were deposited.

(c) **With Benzoyl Chloride in Pyridine.**—Compound B (100 mg.) was dissolved in pyridine (3 ml.) and benzoyl chloride (0.3 ml.) added. After warming on the steam-bath for 10 minutes the mixture was poured onto crushed ice. Crystals, m.p. 91°, identical with those described above were deposited.

The compound, m.p. 91°, gave no semicarbazone nor did it give the iodoform reaction.

The Reaction of α-Phenylazobenzoylacetaldehyde with Diazomethane.—The phenylazo compound (4 g.) was dissolved in absolute ether (100 ml.) and methanol (10 ml.). To this solution was added a solution of diazomethane (from 10 g. of nitrosomethylurea) in ether (100 ml.). Reaction commenced at once and nitrogen was evolved rapidly. The solution was allowed to stand overnight in the ice-box and then the ether and excess diazomethane were evaporated at room temperature. The resulting oil crystallized on standing in ligroin. After recrystallization from ether–ligroin it formed yellow prisms (2.5 g.), m.p. 120–121°. The mother liquors were evaporated to small bulk to give a further amount of the same substance. In all 3.6 g. was obtained.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.2; H, 5.3; N, 10.5. Found: C, 72.5; H, 5.2; N, 10.9; OCH_3, 0.0.

Ultraviolet spectrum in ethanol: λ_{max} 254 mμ, ϵ 18.3 × 10^3; λ_{min} 310 mμ, ϵ 1 × 10^3; λ_{max} 390 mμ, ϵ 23 × 10^3.

The residues from the above separation yielded no more crystalline material but on treatment with ferric chloride in acetic anhydride a small amount of 1-phenyl-4-benzoylpyrazole (see below) was isolated at its 2,4-dinitrophenylhydrazone.

Treatment of Compound $C_{16}H_{14}N_2O_2$ with Ferric Chloride in Acetic Anhydride.—The compound (1 g.) was dissolved in acetic anhydride (10 ml.) and ferric chloride (0.1 g.) added. Heat was evolved and when the mixture began to cool it was heated on the steam-bath for 10 minutes and poured onto ice. When all the acetic anhydride had been destroyed the solid material was filtered off. After recrystallization from ligroin it formed colorless prisms, m.p. 52° (0.6 g.).

Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.4; H, 4.8. Found: C, 77.1; H, 5.0.

Ultraviolet spectrum in ethanol: λ_{max} 238 mμ, ϵ 16 × 10^3, λ_{max} *ca.* 260 mμ ϵ 14 × 10^3; λ_{max} 242 mμ, ϵ 16.2 × 10^3.

The compound gave no semicarbazone in the cold but with 2,4-dinitrophenylhydrazine it gave a hydrazone which after recrystallization from acetic acid formed brick red needles, m.p. 264° dec.

Anal. Calcd. for $C_{22}H_{16}N_6O_4$: N, 19.6. Found: N, 19.8.

Reaction of Ethyl α-Phenylazoacetoacetate with Diazomethane.—Ethyl α-phenylacetoacetate[32] (7 g.) in ether (100 ml.) containing methanol (10 ml.) was treated with diazomethane (*ca.* 2.8 g.) in ether (100 ml.) at 0°. The mixture was allowed to stand at room temperature for 16 hours. The evolution of nitrogen was slow. The ether and excess of diazomethane were evaporated at room temperature. The resulting oil on standing with a mixture of ether and ligroin gave yellow crystals (1.1 g.). After recrystallization from the same solvent the compound formed bright yellow prisms, m.p. 114–115°.

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.9; H, 6.5; N, 11.4; OC_2H_5, 18.1. Found: C, 62.6; H, 6.2; N, 11.2; OC_2H_5, 18.3.

The original ether–ligroin mother liquors on evaporation gave several crops of starting material, m.p. 80–81° (*ca.* 3.0 g.), together with an oil (*ca.* 0.2 g.) which was not examined further.

Absorption Spectra.—The spectra were determined with a Beckman model DU quartz spectrophotometer (cell length 1 cm.). Spectra not previously reported are given in Table I.

Table I

ABSORPTION SPECTRA OF α-PHENYLAZODIKETONES IN ETHANOL (CONCD. 10 MG./L.)

Compd.	Spectra (wave lengths are given in mμ. The values for ϵ are multiplied by 10^{-3})
IV	λ_{max} 245, ϵ 12; λ_{min} 294, ϵ 1.5; λ_{max} 365, ϵ 21
V	λ_{max} 235, ϵ 15; step out λ 367–389, ϵ *ca.* 8; λ_{min} 305, ϵ 5; λ_{max} 362, ϵ 22
VI	λ_{max} 234, ϵ 15; step out λ 260–290, ϵ 7.6–8.3; λ_{min} 310, ϵ 4.5; λ_{max} 373, ϵ 20

(32) C. Bülow and P. Weber, *Ber.*, **45**, 3732 (1912).