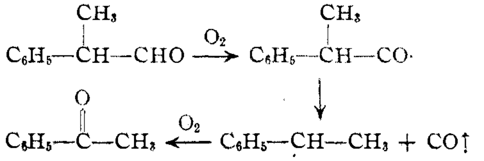

$$C_6H_5-\overset{\overset{CH_3}{|}}{C}H-CHO \xrightarrow{O_2} C_6H_5-\overset{\overset{CH_3}{|}}{C}H-CO\cdot \;\downarrow\; C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \xleftarrow{O_2} C_6H_5-\dot{C}H-CH_3 + CO\uparrow$$

Carbon monoxide was detected in the effluent gases. In several trials, no 2-phenylpropionic acid could be isolated.

Loss of CO from an acyl radical is a common phenomenon.[3] Work in these Laboratories has indicated that branching at the alpha carbon atom facilitates this reaction, at the expense of the normal formation of the acid, in oxidation of aldehydes with gaseous oxygen.[4]

Experimental

OXO.—To a 500-cc. rocking bomb was charged 165 cc. of commercial grade styrene, 50 cc. benzene and 15–18 cc. of cobalt carbonyl solution (10% cobalt carbonyl content).[5] The bomb was pressurized to 2700 p. s. i. g. with a 50-50 carbon monoxide, hydrogen mixture and heated. At 110° gas absorption started. The pressure was maintained at 3000–3400 p. s. i. g. by recharging the bomb when necessary. The temperature was maintained at 115°. After 55 minutes, gas absorption became quite slow. The bomb was cooled to room temperature and the contents discharged. The crude aldehyde analyzed 9% $-\overset{\overset{O}{/\!/}}{C}-H$ or a conversion of 50%. The aldehyde was removed from the catalyst by rapid distillation at about 0.5 mm. from a Claisen flask. The distillate was then redistilled and the material boiling from 70–100° at 1.0 mm. taken as product. The yield was 46% of distilled material which on the basis of carbonyl content[6] contained 95% phenylpropionaldehydes.

Oxidation.—Two hundred and thirty grams of the aldehyde mixture was poured into a Pyrex column wrapped with heating wire and equipped with a water-jacketed side-arm for circulation and cooling, a sintered glass oxygen inlet at the bottom, and a thermometer and reflux condenser at the top. The flow of oxygen and the flow of cooling water were adjusted to bring the temperature up to 50° in one hour. The reaction was exothermic for about the first two hours, and then small amounts of heat were applied to maintain the temperature at 50°. The % COOH was checked every hour, and leveled off at about 14.5 after six hours. The calculated % COOH for phenylpropionic acid is 30.0. Carbon monoxide[7] was detected in the effluent gases.

The column was drained and the product distilled through an 8-inch helix-packed column, giving the following fractions

Fraction	G.	B. p., °C.	CHO, %	COOH %
Trap	9.0	(Acetophenone)		
I	37.9	55–64/2 mm.	16.1	..
II	17.6	64–76/2	12.1	..
III	3.0	76–103/1.5	..	23.3
IV	50.4	103–13/1.5	..	28.0
V	22.8	113–17/1.5	..	26.7
Residue	41.6	....	..	3.1
Total	182.3			

The carbonyl component was identified as acetophenone through the semicarbazone (m. p. 193–195.5°) and 2,4-dinitrophenylhydrazone (m. p. 243–246°). The melting point of a mixture of this latter derivative with an authentic sample of acetophenone 2,4-dinitrophenylhydrazone was 244–247°. The acid was identified as 3-phenylpropionic acid by neutral equivalent and m. p. (47–48.5°). From these data, it may be calculated that the product contained 44.4 g. of acetophenone and 72.5 g. of 3-phenylpropionic acid, equivalent to 49.5 g. and 64.8 g. of the 2- and 3-phenylpropionaldehydes, respectively.

Summary

Oxidation of the phenylpropionaldehyde produced by the OXO reaction with styrene gives a mixture of acetophenone and 3-phenylpropionic acid. This indicates that both 2- and 3-phenylpropionaldehydes are formed in the OXO reaction.

PHILADELPHIA, PA. RECEIVED MARCH 9, 1950

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[3] *E. g.*, Winstein and Seubold, THIS JOURNAL, **69**, 2916 (1947).

[4] McKeever, unpublished results.

[5] McKeever, U. S. Patent No. 2,477,553; 2,476,263.

[6] Ref. 1b, p. 3053.

[7] Carbon monoxide was detected by an immediate blue coloration when a tube packed with a molybdate compound was placed in the gas stream. The tube was obtained from the late Professor Adkins, and we have been unable to ascertain the details of its preparation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Reactions of 1,4-Diphenyl-1-bromo-3-butene-2-one. I. A Synthesis of 1-Aryl-2,5-diphenyl-3-pyrrolidones

BY PHILIP L. SOUTHWICK, DAVID I. SAPPER AND L. A. PURSGLOVE[1]

The preparation of 1,4-diphenyl-1-bromo-3-butene-2-one (I) by the action of N-bromosuccinimide on benzyl styryl ketone was described in a recent communication from this Laboratory.[2] Since this compound appears to offer unusual possibilities as a synthetic intermediate, an investigation of its reactions has been undertaken. The reactions to be described here, those with primary aromatic amines, have afforded a means of preparing an interesting new type of unsaturated arylamino ketone and have led to a new synthesis of 3-pyrrolidones. Only a few derivatives of 3-pyrrolidone have previously been described, and all of these were made by the use of the Dieckmann condensation or related methods.[3]

Contrary to the original expectation, 1,2,5-

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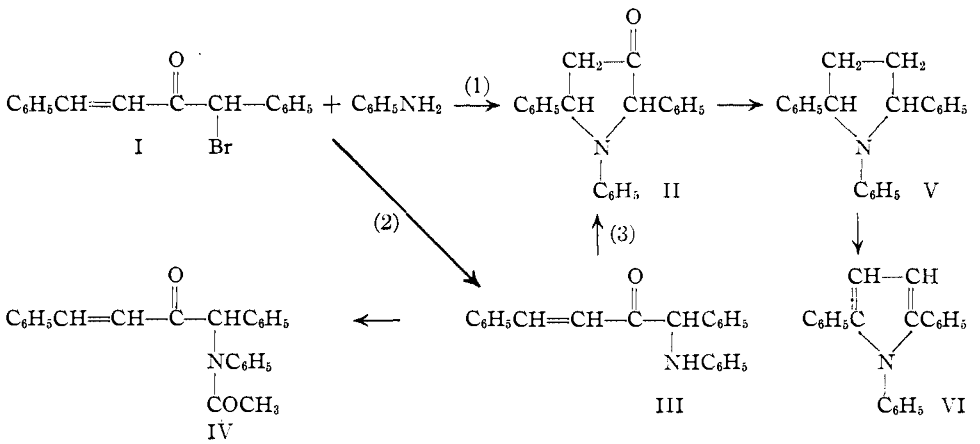
[1] Institute Graduate Fellow in Organic Chemistry, 1948–1949.

[2] Southwick, Pursglove and Numerof, THIS JOURNAL, **72**, 1604 (1950).

[3] (a) Prill and McElvain, *ibid.*, **55**, 1233 (1933); (b) De-Mouilpied, *J. Chem. Soc.*, **87**, 435 (1905); (c) Ruzicka and Seidel, *Helv. Chim. Acta*, **5**, 715 (1922); (d) Cook and Reed, *J. Chem. Soc.*, 399 (1945).



triphenyl-3-pyrrolidone (II) did not result directly (reaction 1) from the reaction of the bromo ketone (I) with aniline. Although the initial reaction product has the composition $C_{22}H_{19}ON$, which corresponds to formula II, it was obtained in the form of needles, m. p. 139.5–140°, of a definite lemon-yellow color not in conformity with that structure. The yellow color suggested that in this product the conjugated system of the α,β-unsaturated bromo ketone is retained. The ultraviolet absorption spectrum of the compound (Fig. 1, Curve A) confirmed this view. It corresponds rather closely in its principal features to a curve (Fig. 1, Curve B) obtained by a summation of the spectra of benzyl styryl ketone (Fig. 2, Curve B) and N-methylaniline.[4] The substance readily reduces potassium permanganate solutions. The presence of a keto group was shown by preparation of a 2,4-dinitrophenylhydrazone, the presence of a secondary amino group by acetylation with acetyl chloride. It is apparent from Fig. 2 that the ultraviolet absorption spectrum of the acetyl derivative (Curve A) closely approximates a summation of the spectra of benzyl styryl ketone (Curve B) and N-methylacetanilide (Curve C). This spectrum is therefore in agreement with the structure IV for the acetyl derivative, and all of the above observations are fully in accord with the conclusion that the parent compound is not the 3-pyrrolidone (II), but 1-anilino-1,4-diphenyl-3-butene-2-one (III), formed as shown in reaction 2.

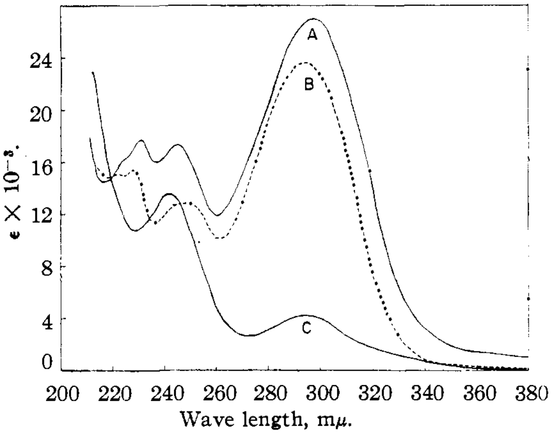


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: A, 1-anilino-1,4-diphenyl-3-butene-2-one (III); B, calculated curve for (III); C, 1,2,5-triphenyl-3-pyrrolidone (II).

The ring closure (reaction 3) of the unsaturated anilino ketone (III) was accomplished by heating with dilute sulfuric acid.[5] The product obtained by this means is a colorless compound, m. p. 186.5–187.5°, which was found to exhibit the properties expected of 1,2,5-triphenyl-3-pyrrolidone (II). Thus, it failed to reduce potassium permanganate solutions at room temperature, and did not yield an acetyl derivative when treated with acetyl chloride, but readily formed a 2,4-dinitrophenylhydrazone and an oxime. The ultraviolet absorption spectrum of the com-

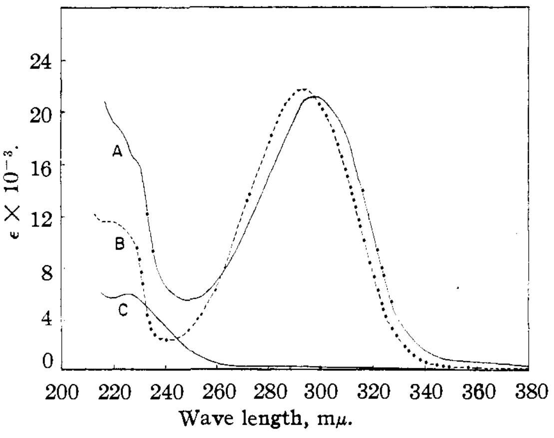


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol: A, N-acetyl-1-anilino-1,4-diphenyl-3-butene-2-one (IV); B, benzyl styryl ketone; C, N-methylacetanilide.

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(4) The data for N-methylaniline used in constructing Curve B, Fig. 1, were obtained from a spectrum measured in ethanol. However, this spectrum did not differ significantly from that measured in isoöctane solution by Tunnicliff, *Anal. Chem.*, **20**, 828 (1948).

(5) There was some evidence, as noted in the Experimental section, that the 2,4-dinitrophenylhydrazone of III slowly changes into the corresponding derivative of the pyrrolidone (II) upon standing.

pound (Fig. 1, Curve C) indicates the disappearance of the α,β-unsaturation present in the uncyclized anilino ketone (III). The strong band associated with benzyl styryl ketone (Fig. 2, Curve B) is no longer observed and the spectrum resembles that of N,N-dimethylaniline,[6] as would be expected if the substance has the structure of the 3-pyrrolidone (II).

Further support for the assignment of the pyrrolidone structure II to the product of the acid treatment was obtained by conversion of the substance into the known 1,2,5-triphenylpyrrole (VI) by a two-step process. Reduction of the keto group by the Wolff–Kishner method yielded a mixture from which was separated two substances, melting at 138–139.5° and 204.5–206°, which have the composition of 1,2,5-triphenylpyrrolidine (V). These products are evidently the *meso* and racemic forms of the pyrrolidine.[7] No effort was made to establish the configurations of the individual diastereoisomers. A mixture containing both of them was dehydrogenated by treatment with chloranil in boiling *p*-cymene to yield 1,2,5-triphenylpyrrole (VI).

The bromo ketone (I) was treated with two other primary aromatic amines, *p*-toluidine and *p*-chloroaniline, with results entirely similar to those obtained with aniline. Thus, the initial reaction products were 1-*p*-toluidino-1,4-diphenyl-3-butene-2-one (VII) and 1-*p*-chloroanilino-1,4-diphenyl-3-butene-2-one (VIII), respectively. The nature of these products was deduced from their composition, their yellow color, and their ultraviolet absorption spectra (Fig. 3). The spectra are clearly those of α,β-unsaturated ketones closely related to the anilino derivative (III). However, when these compounds were heated with dilute sulfuric acid, they were converted into the colorless 3-pyrrolidones, 1-*p*-tolyl-2,5-diphenyl-3-pyrrolidone (IX) and 1-*p*-chlorophenyl-2,5-diphenyl-3-pyrrolidone (X), with the expected changes in absorption spectra (Fig. 3).

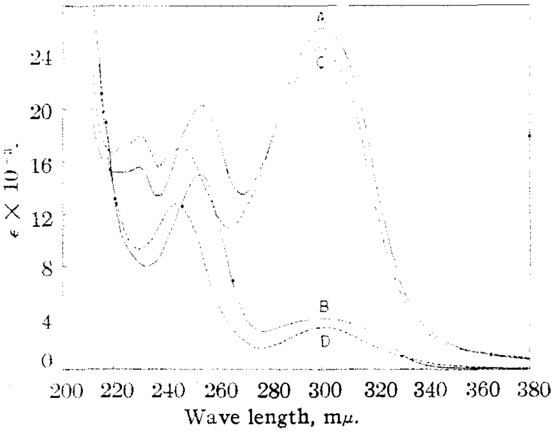

Fig. 3.—Ultraviolet absorption spectra in 95% ethanol: A, 1-*p*-chloroanilino-1,4-diphenyl-3-butene-2-one (VIII); B, 1-*p*-chlorophenyl-2,5-diphenyl-3-pyrrolidone (X); C, 1-*p*-toluidino-1,4-diphenyl-3-butene-2-one (VII); D, 1-*p*-tolyl-2,5-diphenyl-3-pyrrolidone (IX).

That acid conditions should be needed for the ring closure of the unsaturated arylamino ketones to pyrrolidones is perhaps not surprising, since it has recently been shown that the addition of aromatic amines to a similar conjugated system, that of the acrylic esters, is promoted by acetic acid.[8] The presence of a positive charge on the β-carbon atom of the α,β-double bond, which might be expected to result from the acquisition of a proton by the carbonyl oxygen, should facilitate the nucleophilic attack of the amino nitrogen by which the ring closure is presumably accomplished. This effect apparently outweighs the reduction in the nucleophilic activity of the amino nitrogen normally to be expected in an acid solution, possibly because in this instance the nitrogen atom is so weakly basic that the equilibrium may favor the free amine over the corresponding ammonium salt even in solutions which are strongly acid. Qualitative observations indicate that concentrated acids are needed to form salts from compound III in aqueous media.

Further work is in progress on the preparation and reactions of unsaturated amino ketones related to compound III and on 3-pyrrolidones derived from these substances.

Experimental[9,10]

Reactions of 1,4-Diphenyl-1-bromo-3-butene-2-one (I) with Primary Aromatic Amines.—Three procedures were employed in conducting reactions of the bromo ketone I with aromatic primary amines. These procedures differed in the basic reagent used to remove hydrogen bromide formed in the condensation, and in the presence or absence of water in the solvent. In the preparation of the compounds described below is illustrated an example of each of these procedures; the use of a second mole of the amine in absolute ethanol, of sodium hydroxide in aqueous ethanol, and of sodium bicarbonate in aqueous ethanol. The bromo ketone employed was prepared by the action of N-bromosuccinimide on benzyl styryl ketone as described previously.[2] It was used in the partially purified form in which it separates from petroleum ether extracts of the crude product.

(A) 1-Anilino-1,4-diphenyl-3-butene-2-one (III).—Three grams (0.01 mole) of the bromo ketone (I) was dissolved in 10 ml. of absolute ethanol with gentle warming. Aniline (1.9 g., 0.02 mole) was added, and the mixture was allowed to stand for several minutes until it developed a deep red color. When the mixture was seeded with crystals from a previous run, crystallization proceeded rapidly until a solid mass was formed. An additional 5 ml. of ethanol was added, and the mixture was stirred, then allowed to stand for forty-five minutes. The yellow product was removed by filtration, washed thoroughly with

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[6] The spectrum of N,N-dimethylaniline as measured in isooctane solution by Remington, THIS JOURNAL, **67**, 1838 (1945), differs from Curve C, Fig. 1, chiefly in a shift of the position of the principal maximum, which is found at 250 mμ with N,N-dimethylaniline.

[7] There was no definite evidence of the formation of more than one diastereoisomer of the 3-pyrrolidone (II), although two racemic forms are possible.

[8] (a) Elderfield, Gensler, Bembry, Kremer, Brody, Hageman and Head, THIS JOURNAL, **68**, 1259 (1946); (b) Johnson, Woroch and Buell, *ibid.*, **71**, 1901 (1949).

[9] Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[10] Melting points are corrected.

water and dried over phosphorus pentoxide. The yield was 2.15 g. (69%) of material melting at 132–134°. Two recrystallizations from ethanol gave an analytical sample in the form of light yellow needles, m. p. 139.5–140°.

Anal. Calcd. for $C_{22}H_{19}ON$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.05; H, 5.99; N, 4.76.

The compound is insoluble in dilute hydrochloric acid and is converted into an insoluble white hydrochloride by treatment with concentrated hydrochloric acid. In acetone solution it rapidly reduces potassium permanganate.

The 2,4-dinitrophenylhydrazone of (III) was obtained in the form of orange-red needles, m. p. 200.5–201.5° after three crystallizations from ethanol–water mixtures.

Anal. Calcd. for $C_{28}H_{23}O_4N_5$: C, 68.14; H, 4.70; N, 14.19. Found: C, 68.15; H, 4.66; N, 14.19.

A sample of this 2,4-dinitrophenylhydrazone which had been allowed to stand for some time underwent a rise in melting point to 208–209° and appeared, on the basis of a mixed melting point test, to have changed into the 2,4-dinitrophenylhydrazone of 1,2,5-triphenyl-3-pyrrolidone, which is described below.

The N-acetyl derivative (IV) was prepared by heating 3 g. of compound (III) with 45 ml. of acetyl chloride for twenty-five minutes at the reflux temperature. Methanol (60 ml.) was added dropwise to the mixture with stirring and cooling in an ice-bath, and the product was precipitated by dilution of the resulting solution with 200 ml. of water. When the product had separated it was removed by filtration and dried to yield 2.5 g. (72%) of white crystalline material, m. p. 147–148.5°. An analytical sample in the form of colorless prisms of the same melting point was obtained by crystallization from ethanol.

Anal. Calcd. for $C_{24}H_{21}O_2N$: C, 81.10; H, 5.96; N, 3.94. Found: C, 80.81; H, 6.60; N, 4.07.

The acetyl derivative reduced potassium permanganate rapidly in acetone solution.

(B) **1-*p*-Toluidino-1,4-diphenyl-3-butene-2-one (VII).**—To 50 ml. of a 0.5% sodium hydroxide solution was added a solution of 3 g. (0.01 mole) of the bromo ketone (I) in 25 ml. of ethanol and 2 g. (0.019 mole) of *p*-toluidine in 10 ml. of ethanol. The resulting suspension was shaken vigorously for five minutes. The solid brown precipitate was collected by filtration and crystallized from ethanol to give 0.7 g. (21%) of slender orange-yellow needles melting at 154.5–155°. Recrystallization from ethanol gave a sample of m. p. 156.5–157.5°.

Anal. Calcd. for $C_{23}H_{21}ON$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.11; H, 6.32; N, 4.40.

(C) **1-*p*-Chloroanilino-1,4-diphenyl-3-butene-2-one (VIII).**—To 80 ml. of a 5% aqueous sodium bicarbonate solution was added 13.2 g. (0.044 mole) of the bromo ketone (I) in 20 ml. of ethanol and 6.6 g. (0.052 mole) of *p*-chloroaniline in 20 ml. of ethanol. The mixture was shaken vigorously for fifteen minutes. The brown precipitate was removed by filtration and crystallized from absolute ethanol to yield 3.9 g. of bright yellow needles, m. p. 159–160°. By slight concentration and prolonged cooling of the filtrate from the crystallization an additional 0.5 g. of a less pure product was obtained to give a total yield of 4.4 g. (29%). Recrystallization from ethanol yielded a sample melting at 161–161.5°.

Anal. Calcd. for $C_{22}H_{18}ONCl$: C, 75.96; H, 5.22; N, 4.03. Found: C, 75.93; H, 5.27; N, 4.08.

Ring Closure of 1-Arylamino-1,4-diphenyl-3-butene-2-ones to 1-Aryl-2,5-diphenyl-3-pyrrolidones.—The same procedure was successfully applied to the preparation of all three of the pyrrolidones obtained. One-half gram of the arylamino unsaturated ketone was suspended in a mixture prepared from 20 ml. of 20% aqueous sulfuric acid and 15 ml. of ethanol. (The addition of the ethanol was not necessary in the case of the anilino derivative (III) if a heating period of eight to ten hours was used.) The solutions were then heated under reflux until the color of the suspended crystals had changed from yellow to white. This required less than one-half hour in the case of the anilino and *p*-toluidino derivatives, but nearly four hours in the case of the *p*-chloroanilino derivative. The pyrrolidones were purified by crystallization from ethanol, the yields of substantially pure products being 0.3 g. (60%) in the case of 1,2,5-triphenyl-3-pyrrolidone (II) and 1-*p*-chlorophenyl-2,5-diphenyl-3-pyrrolidone (X), but only 0.2 g. (40%) in the case of 1-*p*-tolyl-2,5-diphenyl-3-pyrrolidone (IX). The 3-pyrrolidones were characterized as follows:

(A) **1,2,5-Triphenyl-3-pyrrolidone** (II).—Recrystallization from ethanol gave tiny white prisms, m. p. 186.5–187.5°.

Anal. Calcd. for $C_{22}H_{19}ON$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.25; H, 6.40; N, 4.57.

The compound is insoluble in hydrochloric acid. It fails to reduce potassium permanganate in acetone solution at room temperature.

The 2,4-dinitrophenylhydrazone was obtained after two crystallizations from ethanol–water mixtures in the form of yellow needles, m. p. 207–209°.

Anal. Calcd. for $C_{28}H_{23}O_4N_5$: C, 68.14; H, 4.70; N, 14.19. Found: C, 68.37; H, 4.90; N, 13.98.

The oxime was prepared according to a procedure of Shriner and Fuson,[11] using 0.5 g. of the pyrrolidone, 0.5 g. of hydroxylamine hydrochloride, 3 ml. of pyridine and 3 ml. of ethanol. Following crystallization from an ethanol–water mixture, 0.3 g. (a 57% yield) of the oxime was obtained in the form of round clumps of tiny white crystals, m. p. 212–215°. Two further recrystallizations raised the melting point to 220.5–221.5°.

Anal. Calcd. for $C_{22}H_{20}ON_2$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.41; H, 5.96; N, 8.82.

Treatment of the pyrrolidone with acetyl chloride using conditions described above for acetylation of the anilino ketone (III) failed to yield an acetyl derivative; except for slight contamination with an oily yellow impurity, the starting material was unchanged.

(B) **1-*p*-Tolyl-2,5-diphenyl-3-pyrrolidone (IX).**—The compound was obtained as small white prisms, m. p. 154–154.5° following the recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{21}ON$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.43; H, 6.66; N, 4.48.

(C) **1-*p*-Chloroanilino-2,5-diphenyl-3-pyrrolidone (X).**—Following recrystallization from ethanol, the compound was obtained as white prisms, m. p. 157.5–158°.

Anal. Calcd. for $C_{22}H_{18}ONCl$: C, 75.96; H, 5.22; N, 4.03. Found: C, 76.09; H, 5.48; N, 4.16.

1,2,5-Triphenylpyrrolidine (V).—The Huang-Minlon[12] modification of the Wolff–Kishner method was used for the reduction of 1,2,5-triphenyl-3-pyrrolidone (II). To a mixture containing 23 ml. of diethylene glycol, 2.5 ml. of 85% hydrazine hydrate and 3.15 g. of potassium hydroxide, 1 g. of the pyrrolidone was added and the mixture was heated at the reflux temperature for three and one-half hours. The reaction mixture was then distilled until the boiling point rose from 135 to 195°, and an oil which had separated redissolved. Refluxing was continued at the higher temperature for three hours. The solution was then cooled and diluted with 200 ml. of water. The precipitated product was removed by filtration.

In the first crystallization from absolute ethanol, it was noticed that fine needles first separated from the cooling solution, then stout prisms. By filtering at the appearance of the first prisms, it was possible to obtain two fractions, each of which was purified by repeated recrystallization from ethanol. The less soluble fraction gave fine white needles (Form A), m. p. 204.5–206°; the more soluble fraction yielded colorless stout needles or prisms (Form B), m. p. 138–139.5°.

Anal. Calcd. for $C_{22}H_{21}N$: C, 88.25; H, 7.07. Found for Form A: C, 88.05; H, 6.81. Found for Form B: C, 88.28; H, 7.07.

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[11] Shriner and Fuson, "Systematic Identification of Organic Compounds," Third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

[12] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

Dehydrogenation of 1,2,5-Triphenylpyrrolidine (V) to 1,2,5-Triphenylpyrrole (VI).—A 0.2-g. sample of the pyrrolidine which had not been separated into its diastereoisomeric components (melting range 127–170°) was heated with a mixture of 0.35 g. of chloranil and 5 ml. of *p*-cymene. The mixture darkened as the temperature was raised. When the boiling point was reached an additional 5 ml. of *p*-cymene was added and the mixture was boiled under reflux for one hour.

From the cooled reaction mixture a crystalline precipitate was removed by filtration and was shown by its alkali solubility to be the expected tetrachlorohydroquinone. No further product was precipitated from the filtrate by addition of petroleum ether. The solution was diluted with ether and extracted with an aqueous potassium hydroxide solution containing sodium hydrosulfite to reduce unchanged chloranil. The organic layer was separated, dried over potassium carbonate, and concentrated under reduced pressure to a small volume. The solid which separated was crystallized from butyl cellosolve to give white needles, m. p. 228–229°. The melting point of a mixture of this product with a sample of 1,2,5-triphenylpyrrole (m. p. 230–231°) prepared by the method of Kapf and Paal[13] was not depressed.

Ultraviolet Absorption Spectra.—The curves were plotted from data obtained with a Beckman quartz spectrophotometer, model D.U.

Summary

Reactions of 1,4-diphenyl-1-bromo-3-butene-2-one (I) with primary aromatic amines have been investigated. The initial products obtained with aniline, *p*-toluidine and *p*-chloroaniline are unsaturated arylamino ketones formed by simple replacement of the bromine atom. Treatment of these products with dilute sulfuric acid, however, converts them into 1-aryl-2,5-diphenyl-3-pyrrolidones, and provides a new synthesis of derivatives of 3-pyrrolidone.

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[13] Kapf and Paal. *Ber.*, **21**, 3053 (1888). For one of the intermediates in this synthesis, 1,2,5-triphenyl-3-carbethoxypyrrole, we observed two melting points. The value 149.5–151.5° was always obtained as the initial melting point, but samples which had resolidified in the hot melting-point bath melted at 168–170°. The previous investigators reported only the m. p. 169–170°. The following analytical results were obtained from our preparation in the low-melting form: *Anal.* Calcd. for $C_{25}H_{21}O_2N$: C, 81.72; H, 5.76. Found: C, 81.57; H, 5.68.

PITTSBURGH, PENNA. RECEIVED FEBRUARY 16, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, AND THE INORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

The Oxidation of Di- and Triaminoguanidine with Potassium Iodate[1]

BY GERALD I. KEIM,[2] RONALD A. HENRY AND G. B. L. SMITH

The Jamieson iodate method[3] for the quantitative determination of hydrazine and its salts has also been successfully applied to the estimation of primary hydrazino groups in such compounds as aminoguanidine,[4] benzalaminoguanidine,[4] semicarbazide and semicarbazones,[5] *p*-bromophenylhydrazine,[5] and certain hydrazides.[6] In all these cases the stoichiometric relationship can be expressed in the form

$$N_2H_5^+ + IO_3^- + H_3O^+ + Cl^- \longrightarrow N_2 + ICl + 4H_2O \quad (1)$$

where one mole of iodate is consumed per mole of hydrazino group. However, when carefully purified salts of triaminoguanidine are titrated by the Jamieson method, these results consistently show an equivalence of 2.5 moles of potassium iodate per mole of triaminoguanidine rather than the three demanded by the stoichiometric relationship (Table I). This unexpected behavior warranted a more exhaustive study as to the nature of the products formed in the reaction.

TABLE I

HYDRAZINE NITROGEN ANALYSIS ON SALTS OF TRIAMINOGUANIDINE BY THE JAMIESON METHOD

Salt	% Hydrazine nitrogen found	Theoretical % hydrazine nitrogen[a]	Theoretical % hydrazine nitrogen[b]
Nitrate	41.65 41.77	50.03	41.68
Perchlorate	34.74 34.17	41.08	34.25
Hydrochloride[c]	49.70	59.79	49.82
Picrate[c]	20.61	25.22	21.02

[a] On basis of 3 moles of potassium iodate per mole of triaminoguanidine. [b] On basis of 2.5 moles of potassium iodate per mole of triaminoguanidine. [c] Taken from the results of A. J. Foglia, B. S. Thesis, Polytechnic Institute of Brooklyn, 1943.

According to Equation (1), one mole of nitrogen should be evolved per mole of hydrazino group that is oxidized. Using a gasometric method (see experimental section) this has been found to hold almost exactly for hydrazine and hydrazine derivatives which show an equivalence of one iodate per hydrazino group in the normal Jamieson titration (Table II). As this table shows, however, triaminoguanidonium salts again behave abnormally since four moles of gas are evolved

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[1] The material in this paper pertaining to triaminoguanidine is abstracted from the thesis submitted by Gerald I. Keim to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

[2] Hercules Powder Company, Wilmington, Delaware.

[3] Jamieson, *Am. J. Sci.*, [4] **33**, 352 (1912); "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926. It should be emphasized that the Jamieson method implies that the solutions of hydrazine derivatives are about 6 to 8 *N* with respect to hydrochloric acid prior to titration and about 3 to 5 *N* after the titration is completed. The effect of lower normalities on this titration has been discussed by Kolthoff, THIS JOURNAL, **46**, 2013 (1924), and of higher normalities by Audrieth and Penneman, *Anal. Chem.*, **20**, 1060 (1948).

[4] Fuller, M.S. Thesis, Polytechnic Institute of Brooklyn, 1937; Fuller, Lieber and Smith, THIS JOURNAL, **59**, 1150 (1937); Lieber and Smith, *Chem. Rev.*, **25**, 213 (1939).

[5] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).

[6] Schaeffer and Gardner, *ibid.*, **30**, 333 (1938); Weinberger and Gardner, *ibid.*, **30**, 454 (1938).