(0.03%; 1-ml. aliquot of a solution containing 0.050 g. of silver nitrate in 100 ml. of oxygen-free water).

Procedure C: Phenyl vinyl ketone, 2.0 g.; ORR soap, 3.6 g. (2.8% solution, 5%); potassium persulfate, 0.0075 g. (as in procedure A above).

Procedure D: Phenyl vinyl ketone, 2.0 g.; ORR soap, 5.4 g. (2.8% solution, 7.5%); potassium persulfate, 0.004 g. (0.2%; 3-ml. aliquot of a solution containing 0.133 g. of potassium persulfate in 100 ml. of oxygen-free water).

Pertinent infrared bands (chloroform): 3000; 2905; 1677 (ArC=O); 1600, 1585 (aromatic); 1454; 1263; 1225; 1005; 976; 695 cm.$^{-1}$

Anal. Calcd. for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: 81.81, 81.83; H, 6.28, 6.24.

Representative results of these polymerizations are recorded in Table V.

Anionic polymerization of phenyl vinyl ketone. All anionic polymerizations were performed as follows: A mixture of 25 ml. of the solvent and the initiator was placed in a 50-ml. flask and brought to the desired polymerization temperature. To this mixture, 2.0 g. of monomer was added at once and the reaction mixtures allowed to warm to room temperature. In runs using dimethylformamide, solution of the monomer did not occur until the solvent melted as it warmed to room temperature. The polymers were isolated from the indicated solvents by use of the following techniques: (a) Liquid ammonia: ammonia allowed to evaporate and residue dissolved in benzene; (b) Tetrahydrofuran: reaction mixture precipitated by pouring into water; (c) Dimethylformamide: reaction mixture precipitated by pouring into isopropyl alcohol; (d) Dimethylsulfoxide: reaction mixture precipitated by pouring into isopropyl alcohol. Purification was accomplished as previously described. The results of these polymerizations are recorded in Table VI.

Copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime. Polyphenyl vinyl ketone (0.39 g., 0.003 mole) in 50 ml. of dioxane, hydroxylamine hydrochloride (2.09 g., 0.030 mole) in 30 ml. of dioxane to 50 ml. of ethanol, and anhydrous sodium acetate (2.46 g., 0.030 mole) in 20 ml. of dioxane to 50 ml. of ethanol were mixed and allowed to stand at room temperature for 52 days. The inorganic precipitate was removed by filtration and the filtrate added slowly to water to precipitate the polymer. The product was collected on a filter, washed well with water, dried briefly in air, and dissolved in pure tetrahydrofuran. Purification was accomplished by reprecipitating the polymer from tetrahydrofuran into low boiling petroleum ether (repeated 4 times); yield of copolymer: 0.405 g. Significant infrared bands (Nujol): 3500–3260 (—OH); 1665 (ArC=O); 1635 (C=N); 1600, 1580, 1498 (aromatic); 914; 765, 694 cm.$^{-1}$ (monosubstituted phenyl).

Anal. Calcd. for $(C_9H_8O)_{0.298}$—$(C_9H_9NO)_{0.702}$: C, 75.75; H, 6.14; N, 6.89. Found: C, 75.69; H, 6.03; N, 6.89.

On the basis of the analytical results it was concluded that this polymer was 70.2 mole per cent phenyl vinyl ketoxime.

Copolymer of phenyl vinyl ketone and "2,6-diphenylpyridine" (IIb). A solution of 35 g. of hydrogen chloride in 100 ml. of ethanol was gradually added to 10 ml. of pure tetrahydrofuran containing 0.3023 g. of a copolymer of phenyl vinyl ketone and phenyl vinyl ketoxime which consisted of 70.2 mole per cent ketoxime units. After the reaction had been stirred at reflux temperature for 48 hr., the red solution was concentrated to 20 ml. and a sodium carbonate solution was added dropwise until the *p*H reached 8–9. The mixture was diluted with water and extracted with two 50-ml. portions of chloroform. Traces of insoluble material were removed from the chloroform by filtration, the solution was concentrated to 20 ml. and then added slowly to low boiling petroleum ether to precipitate the product. The polymer was purified by reprecipitation from chloroform into low boiling petroleum ether (five times); yield: 0.1089 g.; softening range: 200–235°. Significant infrared bands (chloroform): 3040 (shoulder); 2950; 1673 (ArC=O); 1593, 1577, 1547–1545, 1492 (aromatic C=C and C=N); 1440; 1072; 1016; 693 cm.$^{-1}$ Ultraviolet maxima (dioxane): λ_{max} 236 mμ (ϵ 20,900), λ_{max} 285 mμ (ϵ 11,200).

Anal. Calcd. for $(C_9H_8O)_{0.497}$—$(C_{18}H_{13}N)_{0.503}$: C, 86.39; H, 5.64; N, 3.75. Found: C, 86.09; H, 5.60; N, 4.03.

Thermal stability of copolymers IIa *and* IIb. Previously dried samples of the two polymers were heated in air in aluminum cups and the weight loss was determined at given intervals during the heating period; the results of these tests have been described above.

Acknowledgment. Microanalyses were performed by Mr. Jozsef Nemeth, Miss C. Higham, Mrs. F. Ju, and Mrs. M. Stingl. Infrared spectra were determined by Mr. Paul McMahon, Miss M. DeMott, and Mr. James Brader, and ultraviolet spectra were recorded by Mr. J. Chiu.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY,
SCHOOL OF SCIENCE AND ENGINEERING, WASEDA UNIVERSITY]

Reaction of Hydrazine Hydrate and Phenylhydrazine with Malononitrile

TADASHI SATO

Received December 9, 1958

The condensation products from hydrazine hydrate and phenylhydrazine with malononitrile were examined and are believed to be derivatives of 3-amino-4-cyano-5-(cyanomethyl)pyrazole rather than of 3,5-diaminopyrazole as reported by Rothenberg. Evidence is given for the proposed structures, and the chemical properties are described.

Rothenberg reported that the reaction of malononitrile with hydrazine and phenylhydrazine yielded oily substances which were assumed to be diaminopyrazole derivatives Ia and Ib, on the basis of the elementary analyses of their derivatives.[1]

As a result of repeating his procedure in our laboratory, however, the reaction seemed to proceed not in the way assumed by him and detailed study on the reaction products under various experimental conditions indicated a different process for the reaction. The reaction was studied under

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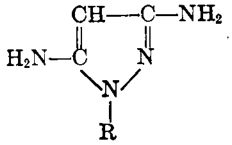
[1] R. v. Rothenberg, *J. prakt. Chem.*, 52, 45 (1895).

three experimental conditions changing the molar ratio of malononitrile to hydrazine. When the molar ratio was 1.0 (the same ratio used in the experiment by Rothenberg), crystals of $C_6H_5N_5$ (named compound A in this report) and an oily substance (named compound B) were obtained with a liberation of ammonia. The chemical composition of compound A indicated that it was produced by a reaction between two moles of malononitrile and one mole of hydrazine with a loss of ammonia. Although the further purification of the oily substance (compound B) was not successful, its hydrochloride and hydrobromide were obtained in crystalline form. These salts had compositions represented by $C_3H_7N_5.2HCl$ and $C_3H_7N_5.2HBr$, respectively, which indicates that the reaction takes place between two moles of hydrazine and one mole of malononitrile.

The decrease of the molar ratio to 0.5 afforded only the oily substance B, and the increase of the ratio to 2.0 gave the crystalline compound A alone, although, in the latter case, the yield was low owing to the formation of large quantities of amorphous by-product.

When phenylhydrazine was used in place of hydrazine hydrate, a compound having the composition of $C_{12}H_9N_5$ was obtained (named compound C). This chemical composition indicates the formation of the phenyl derivative of compound A. A notable fact observed in the experiment with phenylhydrazine was that no substance corresponding to compound B was obtained, even when a large amount of phenylhydrazine was used.

The molecular formulas of the compounds A and C suggest that structures II, III, and IV can be considered for these products. The infrared spectra of A and C showed the bands of NH_2, C=C, and both conjugated and nonconjugated C=N. The spectra of the monoacetyl derivatives showed the N–H band of a secondary amide, which also indicated the existence of primary amino group in A and C. Further evidence against structure II is found in the recent experimental result by Carboni Coffman, and Howard,[2] who obtained compounds having the same melting points and analytical values as those of A and C, by condensing malononitrile dimer V with hydrazine derivatives, although these authors do not reach any conclusions as to whether these compounds have structures III or IV. Although IIIa and IVa are interconvertible with A by a tautomeric shift of hydrogen, such an interconversion is not possible when the hydrogen on the ring was replaced by a phenyl group. That structure IIIb is preferable to structure IVb for C was inferred from comparison of the basicity of A and C. Compound C is a weak base, being soluble in concentrated hydrochloric acid and can be recovered unchanged by diluting this solution with water, whereas A is not basic and is insoluble even in concentrated hydrochloric acid. The nonbasic property of A is considered to result from the formation of the tautomeric structures IVa and VI, in which the C=N group in the ring may give the direct influence on the amino group. The basic property of C can, therefore, be explained more reasonably with structure IIIb, in which such a direct effect on amino group is absent.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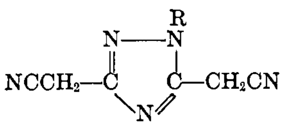
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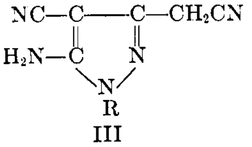
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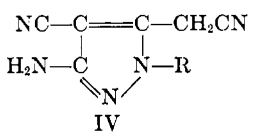
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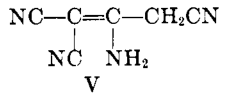
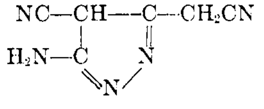

$\mathrm{NC{-}C(CN){=}C(NH_2){-}CH_2CN}$

V

a. R = H
b. R = C_6H_5

Acid hydrolysis of A and C gave yellow crystals of $C_6H_6N_4O_2$ and $C_{12}H_{10}N_4O_2$, respectively. The cyclic imide structures VIIa and VIIb may be assigned to these products, since the infrared spectra showed the presence of NH_2, C=C, and CONH (doublet in the amide carbonyl region).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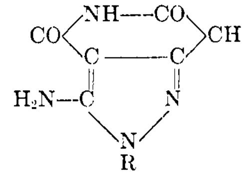
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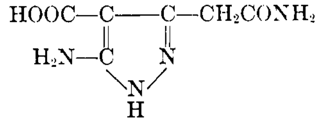
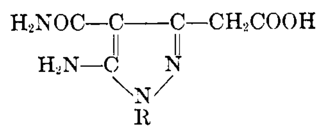

VIII


IX

a. R = H
b. R = C_6H_5

Alkaline hydrolysis of either the compound A or VIIa gave an identical compound, $C_6H_8N_4O_3$. Treatment of the hydrolyzed product with hydrochloric acid afforded VIIa. The infrared spectrum of the alkaline-hydrolyzed product showed the presence of NH_2, C=C, COOH, and CONH, so that the product is apparently either VIII or IXa. In structure VIII, the acidity of the carboxyl group may be

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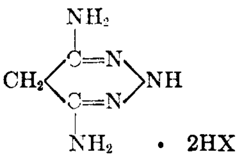
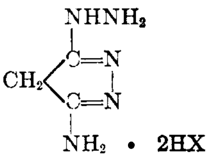
[2] R. A. Carboni, D. D. Coffman, and E. G. Howard, *J. Am. Chem. Soc.*, **80**, 2838 (1958).

reduced owing to the influence of the neighboring amino group, while, in structure IXa, it may be strengthened by the effect of the C=N group in the ring. The pK_a value of the product formed by the alkaline hydrolysis was 3.5, being smaller (stronger in acidity) than that of acetic or benzoic acid. The assignment of structure IXa was also supported by the presence of C=O band of nonconjugated aliphatic carboxyl which was located at 1706 cm.$^{-1}$ for this compound.

Treatment of compound C and VIIb with alkali afforded an acid. The infrared spectra supported structure IXb, but the elemental analysis did not coincide with the calculated value.

The hydrochloride or hydrobromide of the oily substance B showed the infrared absorption bands of NH_2, CH_2, C=C, or C=N. The Schotten-Baumann benzoylation of these salts afforded tribenzoyl derivatives, but acetone did not react even with their free base. From these facts, the dihydrotriazine structure X seems to be most probable for this compound, although the isomeric pyrazole structure XI cannot be excluded at the present stage of investigation.


X


XI

EXPERIMENTAL

3-Amino-4-cyano-5-(cyanomethyl)pyrazole (*compound A*). A solution of 6.6 g. of malononitrile in 20 ml. of ethanol was added to 5 ml. of 80% hydrazine hydrate. After the mixture was kept below 40° for 3 hr., ethanol was removed under reduced pressure. The residual slurry was washed with a little amount of ethanol to remove an oily substance B. Recrystallization from water afforded needles, m.p. 197°.

Anal. Calcd. for $C_6H_5N_5$: C, 48.98; H, 3.40; N, 47.62. Found: C, 48.35; H, 3.61; N, 47.03.

The infrared spectrum showed the presence of NH_2 (3420, 3360, 3230, 1654), nonconjugated C≡N (2245), conjugated C≡N (2200), and C=C (1598 cm.$^{-1}$).

An acetyl derivative was prepared by treating A with acetic anhydride in the presence of a trace of sulfuric acid and recrystallized from acetic acid, m.p. 276°.

Anal. Calcd. for $C_8H_7N_5O$: C, 50.79; H, 3.70; N, 37.03. Found: C, 50.50; H, 3.86, N, 36.77.

The infrared spectrum showed the N—H band of a secondary amide at 3280 cm.$^{-1}$.

4,6-Diamino-2,5-dihydro-1,2,3-triazine dihydrochloride (X). From the ethanol washing obtained in the above procedure, ethanol was removed under reduced pressure. To the residual red oil, concentrated hydrochloric acid was gradually added with cooling. The solid was recrystallized from 18% hydrochloric acid, m.p. 205° (dec.).

Anal. Calcd. for $C_3H_9Cl_2N_5$: C, 19.36, H, 4.84; N, 37.64. Found: C, 19.11; H, 4.78; N, 37.65.

The infrared spectrum showed the presence of NH_2 (3440, 3360, 1640), CH_2 (2920, 1458) and C=C or C=N (1600 cm.$^{-1}$).

A dihydrobromide was obtained by using hydrobromic acid in place of hydrochloric acid in the above procedure, m.p. 205° (dec.).

Anal. Calcd. for $C_3H_9Br_2N_5$: N, 25.43. Found: N, 25.89.

Benzoylation of the hydrochloride in water with benzoyl chloride and sodium hydroxide gave a gummy substance which was chromatographed from benzene on alumina. Elution with ethanol afforded tribenzoyl derivative of X which was recrystallized twice from dilute ethanol, m.p. 239°.

Anal. Calcd. for $C_{24}H_{19}N_5O_3$: C, 67.76; H, 4.47; N, 16.47. Found: C, 66.63; H, 4.51; N, 16.85.

3-Amino-4-cyano-5-(cyanomethyl)-2(or 1)-phenylpyrazole (*compound C*). A mixture of 26 g. of malononitrile and 22 g. of phenylhydrazine in 40 ml. of ethanol was heated at reflux for 3 hr. The solution was concentrated under reduced pressure and water was added. The resulting solid was recrystallized from ethanol, m.p. 169°.

Anal. Calcd. for $C_{12}H_9N_5$: N, 31.39. Found: N, 30.97.

The infrared spectrum showed the presence of NH_2 (3492, 3368, 3200, 1629), nonconjugated C≡N (2233), conjugated C≡N (2195), and C=C (1591 cm.$^{-1}$).

An acetyl derivative was prepared by treating C with acetic anhydride in the presence of a trace of sulfuric acid for 30 min., m.p. 168°.

Anal. Calcd. for $C_{14}H_{11}N_5O$: C, 63.39; H, 4.15; N, 26.41. Found: C, 63.04; H, 4.41; N, 26.36.

The infrared spectrum showed the N—H band of a secondary amide at 3280 cm.$^{-1}$.

A benzal derivative was prepared by heating with benzaldehyde in glacial acetic acid and recrystallizing from ethanol, m.p. 117°.

Anal. Calcd. for $C_{19}H_{13}N_5$: N, 22.51. Found: N, 22.77.

Acid hydrolysis of compound A and its alkaline hydrolysis product (IXa). A suspension of 2 g. of A or IXa (see below) in 25 ml. of concentrated hydrochloric acid was heated at reflux for 3 hr. Most of the starting solid material dissolved within 15 min., but other crystals soon appeared. Recrystallization from 18% hydrochloric acid gave the hydrochloride of VIIa, m.p. >360°.

Anal. Calcd. for $C_6H_7ClN_4O_2$: N, 27.66. Found: N, 28.10.

Treatment of the hydrochloride with water afforded free base which was recrystallized from water, m.p. >360°.

Anal. Calcd. for $C_6H_6N_4O_2$: C, 43.37; H, 3.62; N, 33.74. Found: C, 42.93; H, 3.45; N, 32.25.

The infrared spectrum showed the presence of NH_2 (3430, 3380, 3210, 1640), C=C (1595) and amide C=O (1700, 1682 cm.$^{-1}$).

Acid hydrolysis of compound C. A solution of 2 g. of C in 25 ml. of concentrated hydrochloric acid was heated at reflux for 2 hr., and neutralized with 10% sodium hydroxide. Recrystallization of the resulting solid from dilute acetic acid afforded crystals of VIIa, m.p. 258°.

Anal. Calcd. for $C_{12}H_{10}N_4O_2$: C, 59.51; H, 4.13; N, 23.14. Found: C, 59.41; H, 4.42; N, 23.15.

The infrared spectrum showed the presence of NH_2 (3468, 3380, 3180, 1620), C=C (1595) and amide C=O (1688, 1670 cm.$^{-1}$).

Alkaline hydrolysis of compound A and its acid hydrolysis product (VIIa). A solution of 7 g. of A or VIIa in 35 ml. of 10% sodium hydroxide was heated at reflux for 3 hr. The solution was neutralized with 10% hydrochloric acid and concentrated under reduced pressure to about 10 ml. of volume. Recrystallization of the resulting solid from water afforded the compound IXa, m.p. 208° (dec.).

Anal. Calcd. for $C_6H_8N_4O_3$: C, 39.13; H, 4.35; N, 30.44. Found: C, 39.37; H, 4.64; N, 30.68.

The infrared spectrum showed the presence of NH_2 (3455, 3370, 3200, 1640), C=C (1600), carboxyl C=O (1706), carboxyl OH (2600–2800), and amide C=O (1666 cm.$^{-1}$).

The infrared absorption shown in this report was observed in nujol or in KBr disks with a Koken Infrared Recording Spectrophotometer, Model DS 301.

Acknowledgment. The author is indebted to Prof. M. Ohta of Tokyo Institute of Technology for many helpful suggestions and to A. Kondo for the microanalyses of substances described in this report.

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[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis of Diarylphosphine Oxides by the Friedel-Crafts Method

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The reaction of mesitylene, durene, or pentamethylbenzene with phosphorus trichloride and aluminum chloride catalyst under conditions normally employed for the synthesis of primary phosphonous dichlorides gave instead good yields of secondary phosphine oxides (after hydrolysis). Small amounts of secondary phosphinic acids were obtained as by-products. The three new phosphine oxides were found to be exceptionally stable to oxidation. With a simpler aromatic hydrocarbon, ethylbenzene, the only secondary product obtained was the phosphinic acid.

Very few secondary phosphine oxides[1] (I) have been reported in the literature. Early attempts to prepare them by careful hydrolysis of phosphinous chlorides,[2] esters,[3] or amides[4] showed that they disproportionated readily, even under the mildest conditions, into equal parts of phosphine (II) and phosphinic acid (III).[5] When atmospheric oxygen was not excluded, the phosphine was oxidized and the only product found was the phosphinic acid.

$$\underset{\mathrm{I}}{2R_2P(O)H} \longrightarrow \underset{\mathrm{II}}{R_2PH} + \underset{\mathrm{III}}{R_2P(O)OH}$$

In only two instances were secondary phosphine oxides obtained which were apparently stable to air. They were obtained by hydrolysis of the corresponding phosphinous chlorides (V). The reaction of phosphorus trichloride with dimethylaniline[6] at reflux temperature gave, among other products, a small amount of bis(p-dimethylaminophenyl)phosphine oxide (I, $R = Me_2NC_6H_4$-): and 9,10-dihydro-10-phenophosphazine oxide[7] was isolated from the products of the reaction of phosphorus trichloride and diphenylamine[8] in a sealed tube at 200°.

A synthesis of aliphatic secondary phosphine oxides by treatment of dibutyl phosphite with the appropriate Grignard reagent was described by Williams and Hamilton,[9] but their attempts to extend this reaction to the aromatic series were unsuccessful. The synthesis of aromatic secondary phosphine oxides was recently accomplished by treatment of diethyl phosphite with a Grignard reagent[10] or an aryllithium compound.[11] The three phosphine oxides obtained by these methods (I, $R = C_6H_5$-, o-$MeOC_6H_4$- and p-$MeOC_6H_4$-) were readily oxidizable by hydrogen peroxide.

In the present work a series of diarylphosphine oxides of high oxidative stability were prepared by a method based on the Friedel-Crafts synthesis of aromatic phosphonous dichlorides (IV).[12]

$$RH + PCl_3 \longrightarrow \underset{\mathrm{IV}}{RPCl_2} + \underset{\mathrm{V}}{R_2PCl}$$

When this synthesis was applied without modification to durene, none of the expected product (IV, $R = 2,3,5,6\text{-}Me_4C_6H$-) was found. From the gum which was coprecipitated with the $AlCl_3 \cdot$-$POCl_3$ complex there were isolated two crystalline compounds, one acidic and the other neutral, identified as bis(2,3,5,6-tetramethylphenyl)phosphinic acid (III, $R = 2,3,5,6\text{-}Me_4C_6H$-) and bis(2,3,5,6-tetramethylphenyl)phosphine oxide (I, $R = 2,3,5,6\text{-}Me_4C_6H$-), respectively. The acidic com-

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(1) In the report of the ACS Nomenclature Committee on organophosphorus compounds, *Chem. Eng. News*, **30**, 4515 (1952), these compounds were named phosphine oxides when written $R_2P(O)H$ and phosphinous acids when written R_2POH. In this article they have been named as P^{IV} compounds rather than P^{III}, in keeping with their chemical character.

(2) A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

(3) A. Michaelis and W. LaCoste, *Ber.*, **18**, 2109 (1885).

(4) A. Michaelis, *Ann.*, **315**, 43 (1901).

(5) The hydrolysis of di-n-octylphosphinous bromide and diphenylphosphinous chloride to the corresponding phosphine oxide without disproportionation was recently accomplished by R. C. Miller, private communication.

(6) R. K. Robins and B. E. Christensen, *J. Org. Chem.*, **16**, 324 (1951); see also M. Bourneuf, *Bull. soc. chim. France*, **33**, 1808 (1923); H. Raudnitz, *Ber.*, **60**, 743 (1927); G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

(7) This compound has also been called 10-hydroxy-5(or 9),10-dihydrophenophosphazine.

(8) P. G. Sergeev and D. G. Kudryashov, *J. Gen. Chem. (U.S.S.R.)*, **8**, 266 (1938); see also A. Michaelis and A. Schenk, *Ber.*, **21**, 1497 (1888); *Ann.*, **260**, 1 (1890).

(9) R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952); **77**, 3411 (1955).

(10) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

(11) J. L. Willans, *Chem. & Ind. (London)*, **1957**, 235.

(12) B. Buchner and L. B. Lockhart, Jr., *Org. Syntheses*, **31**, 88 (1951); *J. Am. Chem. Soc.*, **73**, 755 (1951).