extracted with hot benzene. Crystallization from benzene–hexane gave pale yellow crystals, m.p. 146° (0.02 g., 5%).

No apparent reaction occurs in the absence of base, as evidenced by the recovery of a small amount of unchanged dione. Prolonged heating, however, leads to the formation of polymeric material.

Reaction of the Benzylidene Compound with Sodium Hydroxide.—The benzylidene compound (0.0060 g., 6 × 10^{-5} mole) in 0.04 *N* sodium hydroxide in 20% v./v. aqueous ethanol (1 l.) has an ultraviolet absorpton maximum at 265 mμ of intensity corresponding to *ca.* 6 × 10^{-5} *M* dione polymer; 500 ml. of this solution treated with 500 ml. of 1.0 *N* aqueous sulfuric acid has absorption maxima at 246 and 250 mμ, with a shoulder at *ca.* 280 mμ, corresponding to 1–5 × $10^{-5}M$ benzaldehyde and 1–5 × $10^{-5}M$ dione polymer.

The benzylidene compound (0.05 g.) in ethanol (10 ml.) was treated with 0.1 *N* aqueous sodium hydroxide (10 ml.) followed by an excess of a solution of 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid. Dilution with water gave a red precipitate, which was crystallized from aqueous ethanol to yield orange crystals, m.p. 238°, of benzaldehyde 2,4-dinitrophenylhydrazone.

Reaction of the Benzylidene Compound with 2,4-Dinitrophenyl-hydrazine.—The benzylidene compound (0.06 g.) and 2,4-dinitrophenylhydrazine (0.07 g.) in hot ethanol (10 ml.) were allowed to stand at room temperature for 6 hours. Evaporation yielded red material which was dissolved in hot benzene and chromatographed on alumina to give benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 236–237°. A small amount of the benzylidene compound was also recovered.

Reaction of the Benzylidene Compound with Cyclopentadiene.—The benzylidene compound (0.26 g.) and freshly distilled cyclopentadiene (0.225 ml.) were allowed to stand at room temperature in benzene solution (10 ml.) for 24 hours. Evaporation yielded a yellow liquid product from which cyclopentadiene dimer was extracted with pentane. Crystallization (twice) of the residue from benzene yielded white needles, m.p. 180° (0.20 g., 57%), undepressed by admixture with the product obtained (in moderate yield) by the reaction of benzaldehyde with the cyclopentadiene adduct of the dione in aqueous ethanolic sodium hydroxide; principal infrared bands ($CHCl_3$): 1675, 1618, 1397 cm.$^{-1}$.

Reaction of the Dione with Diazotized Aniline.—Aniline hydrochloride (6.5 g., 0.05 mole) was dissolved in hot water (25 ml.) containing concentrated hydrochloric acid (6 ml.), cooled in ice and treated with sodium nitrate (3.65 g.) dissolved in the minimum of water. This solution after standing for 30 minutes was treated with a further 25 ml. of water, mixed with a solution of the dione (3.85 g., 0.04 mole) in water (50 ml.) and treated with excess of a saturated aqueous solution of sodium acetate. A yellow precipitate rapidly formed as soon as the solution became neutral. This was collected, washed well with water and dried at 50° to a yellow powder, m.p. *ca.* 130° (dec.) (7.0 g., 90%). Crystallization from ether gave small yellow needles, m.p. 148° dec., of the 4-phenylhydrazone of cyclopentene-3, 4,5-trione, while sublimation yielded orange and yellow feathery crystals, m.p. 148° dec., with identical infrared spectrum; principal infrared bands (CCl_4) at: 1673, 1532, 1495, 1484, 1283, 1202, 1168, 1151, 1052, 1020 and 852 cm.$^{-1}$; λ_{max} (CCl_4): 378 mμ (4.23); (10% aq. EtOH): 378, 223 mμ (4.55, 4.36); (10%, 0.1 *N* HCl): 380, 224 mμ (4.53, 4.45); (10%, 0.1 *N* NaOH): 358, 272 mμ (4.47, 4.33).

Anal. Calcd. for $C_{11}H_8O_2N_2$: C, 65.98; H, 4.03; N, 13.99. Found: C, 65.94; H, 4.11; N, 14.10.

Cold solutions of the phenylhydrazone in ethanol slowly darken, rapidly in the presence of sodium hydroxide, and evaporation yields a dark brown intractable product. Solutions in carbon tetrachloride gave a similar material after a short period under reflux.

Reaction of the Dione with Diazotized *p*-Nitroaniline.—The dione (2.0 g., 0.02 mole) was treated as described above with *p*-nitroaniline (2.7 g., 0.02 mole) diazotized in aqueous sulfuric acid to yield a yellow product (4.9 g., 96%). Crystallization from acetone gave long, golden-yellow needles, m.p. 230° dec., of the 4-*p*-nitrophenylhydrazone of cyclopentene-3,4,5-trione; principal infrared bands ($CHCl_3$) at: 1681, 1610, 1603, 1550, 1515, 1342, 1143, 1109, and 1020 cm.$^{-1}$; λ_{max} (CCl_4): 381 mμ (4.20); (95% aq. EtOH): 376, 240 mμ (4.32, 3.98); (95% + aq. NaOH): 262 mμ (4.18), with very strong absorption at 400–420 mμ.

Anal. Calcd. for $C_{11}H_7O_4N_3$: C, 53.87; H, 2.88; N, 17.13. Found: C, 53.89; H, 2.98; N, 17.15.

The *p*-nitrophenylhydrazone behaves like the phenylhydrazone above in aqueous ethanolic and sodium hydroxide solutions, but seems to be stable indefinitely in carbon tetrachloride solution.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

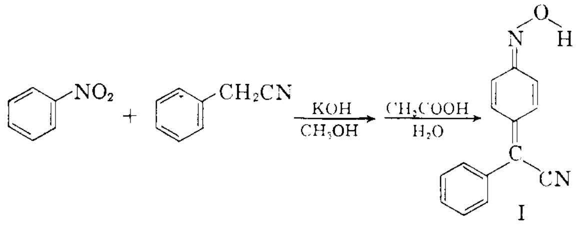
The Condensation of Aromatic Nitro Compounds with Arylacetonitriles.[1] I. Nitrobenzene

BY R. B. DAVIS, L. C. PIZZINI AND J. D. BENIGNI

RECEIVED NOVEMBER 18, 1959

Nitrobenzene condenses with arylacetonitriles to produce a new series of compounds, substituted methylenequinone oximes. Proof of structures is offered. A mechanism for the condensation is proposed.

When benzyl cyanide and nitrobenzene are added to a warm solution of methanolic potassium hydroxide, the reaction mixture turns deep-red and a deep-red solid soon precipitates. The solid is soluble in water, and, on acidification of the solution with acetic acid, a yellow-orange solid precipitates in 77% yield. The product has been shown to be 4-(phenylcyanomethylene)-cyclohexa-2,5-diene-1-one oxime (I).



I

No evidence was obtained for the tautomeric structure II, phenyl-*p*-nitrosophenylacetonitrile. Likewise, attempts to isolate phenyl-*p*-hydroxylaminophenylacetonitrile (III) and phenyl-*p*-nitrophenylacetonitrile (IV) were unsuccessful. Neresheimer and Ruppel[2,3] have reported that the reaction of benzyl cyanide and nitrobenzene in pyridine containing finely divided potassium hydroxide gives a mixture of III and IV.

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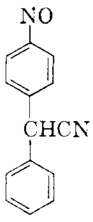
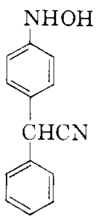
[1] Research project supported in part by National Science Foundation grant, NSF-G10030.

[2] H. Neresheimer and W. Ruppel, German Patent 603,622 (1934).

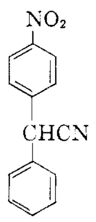
[3] H. Neresheimer and W. Ruppel, U. S. Patent 2,080,057 (1937).



II



III



IV

Nitrobenzene also reacts with substituted benzyl cyanides such as the *p*-chloro and the *p*-methoxy compounds as well as with α-naphthylacetonitrile to produce analogous quinone oximes in good yields.

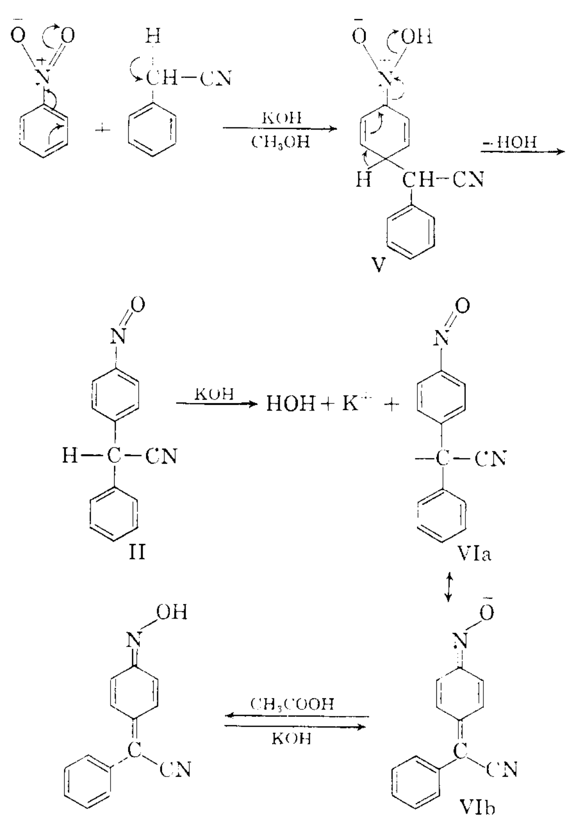
The molecular weight of the product from benzyl cyanide and nitrobenzene was consistent with either the quinone oxime or nitroso structure in the monomeric form.

That attack occurs *para* to the nitro group in nitrobenzene was shown by oxidation of the products to known *p*-nitrobenzophenones. Attempts to oxidize the product from nitrobenzene and α-naphthylacetonitrile to the corresponding diaryl ketone were unsuccessful.

The infrared spectra of the condensation products furnished good evidence for the quinone oxime structures. All the condensation products showed single, sharp absorption bands at 4.53 to 4.54 μ using potassium bromide disks. Kitson and Griffith[4] have shown that unconjugated nitrile groups give absorption bands between 4.42 and 4.46 μ. Nitrile groups conjugated with a double bond show absorption bands between 4.48 and 4.51 μ. Nitrile absorption bands above 4.51 μ suggest that the cyano group is part of a conjugated system more extended than one double bond. The fact that our condensation products showed absorption bands at 4.53 to 4.54 μ supports the quinone oxime structures, and the fact that the absorption bands were single and sharp would exclude appreciable amounts of the tautomeric nitroso compounds and the corresponding hydroxylamino or nitro compounds. The infrared spectrum of the condensation product from nitrobenzene and benzyl cyanide in chloroform solution also showed a single, sharp nitrile absorption band at 4.54 μ. This fact supports the quinone oxime structure I and indicates the absence of appreciable amounts of the tautomeric nitroso compound II in chloroform solution. All our condensation products showed broad absorption bands in the region of 3.15 μ, indicative of associated hydroxyl groups.[5,6] Finally, the absence of significant amounts of the nitroso tautomers in the products was shown by the absence of nitroso absorption bands in the 6.26 to 6.72 μ region.[7]

Nuclear magnetic resonance studies[8] conducted on the product from nitrobenzene and benzyl cyanide confirmed the quinone oxime structure I. The spectra showed peaks typical of oxime hydrogen, of phenyl hydrogen and of quinoid hydrogen. No peak was found corresponding to a hydrogen attached to a tertiary carbon atom, which would be expected for the nitroso structure II. Hence no detectable amount of the nitroso tautomer was present in hexadeuterated acetone solution, the solvent used in the studies.

The subsequent mechanism which follows familiar lines is proposed for the condensation



Nitrobenzene undergoes a nucleophilic attack at the *p*-position by benzyl cyanide anion, followed by the addition of a proton at an oxygen of the nitro group to give intermediate V, which may also exist as a potassium salt. Elimination of a molecule of water from V results in the formation of the nitroso compound II which is rapidly converted to the anion VI of which only two forms are shown. Acidification of the potassium salt of VI yields the quinone oxime I.

Experimental[9,10]

Phenylcyanomethylenequinone Oxime.—To a solution of 60 g. of potassium hydroxide (assay 85%) in 300 ml. of absolute methanol warmed at 50° was added 32.2 g. of benzyl cyanide followed by 30.8 g. of nitrobenzene. The reaction mixture immediately became deep-red in color, and after 5 minutes, copious red solid began to precipitate. The mixture was stirred gently at 50–55° for 4 hours. After cooling, 400 ml. of water was added with stirring. The resulting deep-red solution was then acidified by adding 109 g. of glacial acetic acid in 100 ml. of water with cooling and stirring. The mixture was then filtered, the yellow-orange solid was washed with water–methanol and air-dried. The solid was then boiled with 150 ml. of benzene for 15 minutes, cooled, filtered and dried in a vacuum desiccator. The yield of quinone oxime was 42.9 g. (77%), m.p. 160–

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[4] R. D. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

[5] A. M. Buswell, W. H. Rodebush and M. F. Roy, This Journal, **60**, 2444 (1938).

[6] S. Califano and W. Luttke, *Z. physik. Chem.*, **6**, 83 (1956).

[7] W. Luttke, *Z. Elektrochem.*, **61**, 302 (1957).

[8] The nuclear magnetic resonance studies were conducted by Varian Associates, Palo Alto, Calif., including the interpretation of the data. Appreciation is extended for the above services.

[9] Analyses by the Midwest Microlab, Inc., Indianapolis, Ind.

[10] All melting points are uncorrected.

161° dec. Recrystallization from benzene gave yellow-orange crystals, m.p. 161° dec. Infrared spectra of the product both in potassium bromide disk and in chloroform solution showed a broad band at 3.14 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61; mol. wt., 222.236. Found: C, 75.94; H, 4.62; N, 12.82; mol. wt.,[11] 223.

A sample of the product was also submitted for nuclear magnetic resonance studies[8] made at a frequency of 60 mc. in hexadeuterated acetone solution. An oxime hydrogen peak was found at −274 c.p.s. (relative to benzene in an external annulus). A phenyl hydrogen peak appeared at −23 c.p.s. A family of peaks ranging from about −4 to +33 c.p.s. was attributed to quinoid hydrogen. Under the conditions of the studies, a hydrogen attached to a tertiary carbon atom should have produced a peak in the region of +70 to +100 c.p.s. No peak distinguishable from noise was found in this region.

p-Chlorophenylcyanomethylenequinone Oxime.—Following a similar procedure, 21.20 g. of *p*-chlorobenzyl cyanide and 15.38 g. of nitrobenzene gave 24.8 (77% yield) of the quinone oxime, m.p. 188–189° dec. Recrystallization from benzene gave yellow needles, m.p. 195° dec. The infrared spectrum of the product in a potassium bromide disk showed a broad band at 3.14 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{14}H_9N_2ClO$: C, 65.60; H, 3.53; N, 10.92; Cl, 13.81. Found: C, 65.46; H, 3.58; N, 10.72; Cl, 13.56.

p-Methoxyphenylcyanomethylenequinone Oxime.—In like manner, 10.3 g. of *p*-methoxybenzyl cyanide and 7.86 g. of nitrobenzene gave 12.3 g. (77% yield) of the quinone oxime, m.p. 161° dec. Recrystallization from benzene gave yellow-orange needles, m.p. 161° dec. The infrared spectrum of the oxime in a potassium bromide disk showed a broad band at 3.20 μ and a single, sharp band at 4.54 μ.

Anal. Calcd. for $C_{15}H_{12}N_2O$: C 71.41; H, 4.79; N, 11.11. Found: C, 71.71; H, 5.04; N, 11.12.

α-Naphthylcyanomethylenequinone Oxime.—In the usual manner, 5.85 g. of α-naphthylacetonitrile and 3.93 g. of nitrobenzene produced 5.7 g. (65% yield) of the quinone oxime, m.p. 165° dec. Two recrystallizations from benzene gave yellow crystals, m.p. 169° dec. The infrared spectrum of the quinone oxime in a potassium bromide disk showed a broad band at 3.15 μ and a single, sharp band at 4.53 μ.

Anal. Calcd. for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.67; H, 4.57; N, 10.40.

Oxidation of Phenylcyanomethylenequinone Oxime.—To a solution of 30 g. of potassium hydroxide (assay 85%) in 300 ml. of water was added 11.0 g. of the quinone oxime. The mixture was stirred until all the solid dissolved, producing a deep-red solution. To this solution was added 60 g. of 30% hydrogen peroxide in 140 ml. of water. The reaction mixture was allowed to stand at room temperature for 3 hours during which time a tan solid precipitated. The solid, *p*-nitrobenzophenone, was collected by filtration, washed with water and dried; weight 6.50 g., m.p. 110–120°. After two recrystallizations from ethanol–water: m.p. 137–138° (lit.[12] 138°); phenylhydrazone, m.p. 149–150° (lit.[13] 142°).

Anal. Calcd. for phenylhydrazone $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.59; H, 4.71; N, 13.35.

Oxidation of p-Chlorophenylcyanomethylenequinone Oxime.—In similar manner 12.83 g. of the quinone oxime produced 11.0 g. of crude *p*-nitrophenyl *p*-chlorophenyl ketone, m.p. 90–94°; recrystallized from ethanol, m.p. 100–101° (lit.[14] 98°); phenylhydrazone, m.p. 204–206°.

Anal. Calcd. for $C_{19}H_{14}N_3O_2Cl$: C, 64.87; H, 4.01; N, 11.95. Found: C, 64.76; H, 4.24; N, 11.92.

Oxidation of p-Methoxyphenylcyanomethylenequinone Oxime.—In like manner 15 g. of the quinone oxime produced 9.4 g. of crude *p*-nitrophenyl *p*-methoxyphenyl ketone, m.p. 116–118°; recrystallized from methanol–water, m.p. 121–123° (lit.[15,16] 121°); 2,4-dinitrophenylhydrazone, m.p. 265–266° dec. (lit.[16] 265° dec.).

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[11] Molecular weight determined by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[12] G. Schroeter, *Ber.*, **42**, 3356 (1909).

[13] P. Carre, *Compt. rend.*, **144**, 34 (1907).

[14] J. Boeseken, *Rec. trav. chim.*, **23**, 107 (1904).

[15] K. Auwers, *Ber.*, **36**, 3899 (1903).

[16] H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 529 (1951).

NOTRE DAME, IND.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Mechanism of the Decomposition of 1,1,1,3-Tetranitro-2-phenylpropane to Nitroform and β-Nitrostyrene

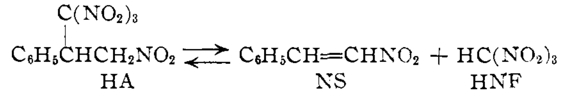
BY JACK HINE AND LLOYD A. KAPLAN

RECEIVED SEPTEMBER 29, 1959

The kinetics of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane to nitroform and β-nitrostyrene in methanol solution have been studied in the presence of hydrogen chloride and of pyridine–pyridine hydrochloride buffers. The reaction was found to be subject to general base catalysis. The reaction mechanism appears to involve the removal of a proton by a base to give the 1,1,1,3-tetranitro-2-phenyl-3-propyl anion which then loses the nitroform (trinitromethyl) anion to give β-nitrostyrene. In strongly acidic solutions the decomposition of the intermediate carbanion is the rate-controlling step of the reaction, while in the pyridine-buffered solutions the carbanion formation is rate controlling. Although the reverse reaction, the addition of nitroform to β-nitrostyrene, can be studied only with considerably less accuracy, its rate was found to be essentially equal to that predicted from the equilibrium constant and the decomposition rate measurements made under non-equilibrium conditions. This observation shows that the undissociated nitroform molecule is probably not important as a proton donor in the rate-controlling step of the addition reaction.

Introduction

While qualitative observations and analogies with more carefully studied reactions may be used to suggest quite plausible mechanisms for the Michael reaction and its reversal, only a few kinetic studies have been reported.[1] It was felt that further kinetic studies would be desirable to learn more about which step of the reaction is rate controlling under various conditions. We have accordingly studied the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (HA) and of the reverse reaction, the addition of nitroform (HNF) to β-nitrostyrene (NS).



$$\underset{\text{HA}}{C_6H_5\overset{\displaystyle C(NO_2)_3}{\overset{|}{C}}HCH_2NO_2} \rightleftharpoons \underset{\text{NS}}{C_6H_5CH{=}CHNO_2} + \underset{\text{HNF}}{HC(NO_2)_3}$$

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[1] *Cf.* W. J. Jones, *J. Chem. Soc.*, **105**, 1547 (1914); M. J. Kamlet and D. J. Glover, THIS JOURNAL, **78**, 4556 (1956); Y. Ogata, M. Okano, Y. Furuya and I. Tabushi, *ibid.*, **78**, 5426 (1956).