Infrared Data.—Infrared spectra were determined on three of the above compounds on a Perkin-Elmer model 21 infrared spectrophotometer using a potassium bromide wafer. Only the strong absorption bands are listed: compound II, 2210, 1665, 1586, 1512, 1344, 1181, 921 and 847 cm.$^{-1}$; compound IIIa, 3368, 3095, 1734(broad), 1636, 1610(broad), 1550(broad), 1213(broad-shoulder 1228), 1155, 945 and 915 cm.$^{-1}$; compound IIIb, 1655, 1575, 1534, 1338 and 1201 cm.$^{-1}$.

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HOUSTON 4, TEXAS

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

High Pressure–High Temperature Reactions. I. The Trimerization of Aromatic Nitriles

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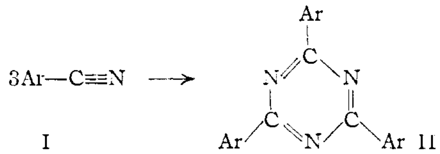
Under the extreme reaction conditions of high pressures (35,000–50,000 atm.) and high temperatures (350–500°), aromatic nitriles are trimerized readily, in the course of a few minutes, to the corresponding 2,4,6-tris-(aryl)-1,3,5-triazines. The conversion may proceed *via* a termolecular reaction or a dipolar intermediate produced by self-ionization under the extreme experimental conditions. Experimental evidence does not indicate a diradical intermediate. It has been shown that the high pressure is necessary, in conjunction with the high temperature, to achieve the trimerization. The quantitative trimerization of *o*-tolunitrile, in the presence of an acidic catalyst, suggests that this is an example of a reaction where extreme reaction conditions can overcome the steric hindrance of an "*ortho* effect."

Aromatic nitriles (I) have been observed to trimerize to the corresponding *s*-triazines (II) in the presence of chemical agents, such as acidic or basic catalysts.[1]



(A)

As in the polymerization of olefins, this trimerization reaction proceeds *via* a transition state of smaller volume than that of the uncombined reactants. This means that ΔV^*, the "volume of activation" in the van't Hoff isothermal equation (B), is negative; the rate of the reaction consequently will increase as the applied pressure is increased.

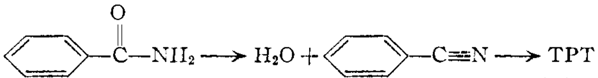
$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \qquad \text{(B)}$$

Thus, Cairns, Larchar and McKusick[1] have shown that benzonitrile in methanolic solution at an initial pressure of 7500 atm. and a temperature of 125° over a period of 18 hours will give an 82% yield of the *s*-triazine. Under the same experimental conditions, but without methanol as a solvent, the yield of *s*-triazine was only 6%.

The present paper deals with the trimerization of aromatic nitriles under more extreme reaction conditions and without a solvent. Benzonitrile is found to give quantitative yields of 2,4,6-triphenyl-1,3,5-triazine (TPT) when it is subjected to pressures of 35,000–50,000 atm. and temperatures in the neighborhood of 400° for periods of 6–18 *minutes*.

The high pressure is necessary, in conjunction with high temperature, to effect the trimerization reaction, for if benzonitrile is heated in a sealed tube at 360° for 14 hours at a maximum autogenous pressure of 225 p.s.i., one obtains only a 2.5% yield of the triazine; the major part of the starting nitrile is recovered unchanged.

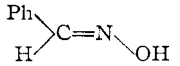
Since other high pressure-high temperature reactions have been observed to occur with a loss of water[2] the suggestion was considered that benzamide and other "hydrates" of benzonitrile could be dehydrated *in situ*, and that the nitrile would then trimerize (eq. C).



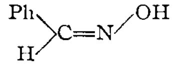
(C)

This reaction has been realized. Thus, at 50,000 atm. and a temperature of 465° for seven minutes, benzamide yielded 30% of TPT, 40% of unreacted amide and 30% of a charred residue; the odor of ammonia also was apparent and indicated partial decomposition of the starting material. The low yield of TPT possibly is connected with the fact that the starting material is a solid. It has been empirically observed in this work that low-melting materials, *i.e.*, liquids at room temperature (benzonitrile, m.p. −13°), give a better yield and a purer reaction product than do starting materials which are solids at room temperature (benzamide, m.p. 130°).

The results were quite different in a further attempt at dehydration, *in situ*, which involved the oxime of benzaldehyde, another "hydrate" of benzonitrile. Benzaldoxime, which is a structural isomer of benzamide, exists in two stereoisomeric forms, *syn*-(III) and *anti*-(IV).



III



IV

The latter, because of the *trans* elimination of the elements of water, is dehydrated readily to benzonitrile by chemical reagents; the *syn* isomer, however, is much more resistant to dehydration. This

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(1) T. L. Cairns, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **74**, 5633 (1952), cite the major references to this reaction.

(2) I. S. Bengelsdorf, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956, Abstracts p. 74-O.

unreactivity was challenging and led to an attempt to dehydrate the more stable *syn* isomer at 38,400 atm. and a temperature range of 150–200°. The only reaction observed was an explosive decomposition of the oxime to ammonia and a carbonaceous material. An X-ray diffraction pattern of the latter material revealed a degree of order intermediate between that of an amorphous carbon and that of graphite.

The realization of the trimerization reaction with benzamide as the starting material promoted the attempt to remove two molecules of water from ammonium benzoate (m.p. 198° dec.).

$$\mathrm{PhCOO^-NH_4^+} \longrightarrow \mathrm{Ph{-}C{\equiv}N} + 2\mathrm{H_2O} \qquad \text{(D)}$$

The only reaction observed was that of extensive decomposition to a black solid.

Steric hindrance has been observed in the trimerization reaction of aromatic nitriles effected by chlorosulfonic acid at atmospheric pressure; the yield of the 2,4,6-tris-(*o*-tolyl)-1,3,5-triazine from *o*-tolunitrile was poor.[3] In a similar manner, under the non-catalytic experimental conditions employed in this work, two of the homologs of benzonitrile, *m*- and *p*-tolunitrile, readily yielded their respective trimers, while the *o*-isomer gave poor yields of the expected *s*-triazine. The steric hindrance, therefore, persists even under these extreme reaction conditions. In the presence of 8 mole per cent. of 85% phosphoric acid, however, *o*-tolunitrile at 37,500 atm. and 350° for a period of 16 minutes gives a quantitative yield of the trimer. The fact that the trimerization of *o*-tolunitrile in the presence of an acidic catalyst is a poor reaction at atmospheric pressure, while it proceeds quantitatively under the above-described conditions, suggests that this synthesis is an example of a reaction where extreme experimental conditions can overcome the steric hindrance of an "*ortho* effect."[4]

An accurate material balance was obtained in the trimerization reaction of *p*-chlorobenzonitrile. As a solid, m.p. 96°, one could avoid the experimental losses encountered with liquid nitriles in the manipulative steps of filling and opening the reaction vessel and in weighing. In experiments conducted at 39,000 atm. and temperatures of 350–390°, one obtained only 30% conversions to the 2,4,6-tris-(*p*-chlorophenyl)-1,3,5-triazine. The remaining 70% of isolated material was unreacted nitrile. The addition of catalytic quantities of 85% phosphoric acid to the nitrile only increased the yield of trimer to 49%.

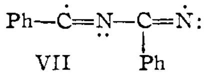
An exception to the trimerization reaction of aromatic nitriles was exhibited by phthalonitrile. In the presence of water at 325° for 20 hours it has been reported to yield the trimer 2,4,6-tris-(*o*-cyanophenyl)-1,3,5-triazine.[5] At the more extreme conditions of 50,000 atm. and 410° for 8 minutes, and in the absence of water, however, phthalonitrile yielded the extremely stable dihydrotetrameric product, phthalocyanine.

Discussion

The acid-catalyzed trimerization of nitriles can be understood readily as proceeding by way of the protonated derivative V. The thermally induced trimerization possibly involves a termolecular reaction between three neutral nitrile molecules, or an intermediate such as VI, produced by a self-ionization process at the high pressures.

$$\underset{\text{V}}{\mathrm{Ph{-}C{\equiv}\overset{+}{N}H}} \qquad\qquad \underset{\text{VI}}{\mathrm{Ph{-}\underset{\cdot\cdot}{\overset{-}{C}}{=}\overset{+}{N}{:}}}$$

Another possible reaction intermediate could be the diradical VII. It could not close to a cyclic dimer of the nitrile as the strain energy in the resultant diazacyclobutadiene would be prohibitive. Reaction of VII with another nitrile, however, would yield the aromatized *s*-triazine ring system. No experimental evidence for a trimerization process which involved diradicals was obtained, however, since the irradiation of benzonitrile with ultraviolet light gave no TPT. Most of the nitrile was recovered unchanged; the odor of phenyl isocyanide was apparent, although the infrared spectrum revealed no isonitrile absorption bands.



VII

$$\mathrm{Ph{-}\dot{C}{=}\underset{\cdot\cdot}{N}{-}\underset{\displaystyle |\atop \displaystyle Ph}{C}{=}\dot{N}{:}}$$

The experimental evidence strongly suggests, therefore, that the extreme reaction conditions of high pressure and high temperature are conducive to either a termolecular reaction of the aromatic nitrile molecules, or their self-ionization and subsequent cyclization to *s*-triazines. Table I summarizes the experimental data concerned with the aromatic nitrile–*s*-triazine reaction.

In addition to these described trimerizations of aromatic nitriles, preliminary experiments have been conducted with the subjection of aliphatic nitriles to extreme pressure–temperature conditions. These experiments, while inconclusive at present, do indicate that aliphatic nitriles are polymerized, but not to *s*-triazines. Further experiments in this direction are in progress.

Experimental

Apparatus.—The high pressure-high temperature equipment used in this investigation is similar to that employed by Hall[6] to study the melting point of germanium as a function of pressure. The reaction vessels are small metallic cylinders (0.200 in. diameter and 0.450 in. long) with a capacity of about 0.2 ml. of liquid and 0.13 g. of solid. Both lead and nickel cylinders were used in this work.

Reactions.—The details of the trimerization reactions are summarized in the table. Further incidental reactions are presented below.

(a) **Benzamide.**—A lead capsule filled with freshly sublimed benzamide was heated to 465° for seven minutes at 50,000 atm. Part of the material was charred and the odor of ammonia was evident. Fractional sublimation of the product gave unreacted benzamide (subl. temp. 135° (0.5 mm.), m.p. 129°, *ca.* 40% yield), 2,4,6-triphenyl-1,3,5-

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[3] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

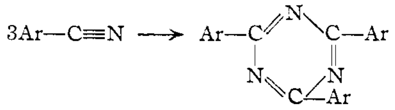
[4] This is not the first report of the effect of high pressure on such steric factors. K. E. Weale, *J. Chem. Soc.*, 2959 (1954), had originally reported that the acceleration of the Menschutkin reaction at 5000 atm. between N,N-dimethyl-*o*-toluidine and methyl iodide in methanol solution, was due to an attenuation of the unfavorable steric conditions. Subsequent work in acetone solution, however, recently has led him (K. E. Weale, Disc. Faraday Soc., Sept., 1956, University of Glasgow, Paper 15) to reconsider the acceleration in rate as due to an ionic solvation effect (see J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953)) and not to a reduction of the steric "*ortho* effect."

[5] S. D. Ross and M. Fineman, THIS JOURNAL, **72**, 3302 (1950).

[6] H. T. Hall, *J. Phys. Chem.*, **59**, 1144 (1955).

TABLE I

THE TRIMERIZATION OF AROMATIC NITRILES



Ar–	Pressure, "kats."[a]	Temp., °C.	Time, min.	Reaction vessel	s-Triazine m.p. (uucor.), °C.	Comments
C_6H_5–	50	430	6	Pb	234–235[b]	Near-quant. yield of white solid, subl. at 220° (0.5 mm.); infrared spect. is identical with that of authentic sample
C_6H_5–	35	400	18	Pb	233–234	Near-quant. yield of gray solid recrystd. from acetic acid-toluene mixt.
C_6H_5–	(225 p.s.i., autogenous)	360	(14 hr.)	Glass-lined steel bomb	234–235[b]	96.5% of nitrile recovd. unchanged; 2.5% yield of TPT recrystd. from acetic acid and sublimed; infrared spect. (Nujol) is identical with that reported.[c] Hydrolysis gave benzamide, m.p. 127–128°
C_6H_5–	0.001	50–60	(50 hr.)	Mercury resonance lamp[d]	......	U.v. irrad. in a nitrogen atm.; odor of phenyl isocyanide although infrared spect. did not detect isonitrile group; recovd. the nitrile unchanged
C_6H_5–	.001	100	(12 hr.)	Mercury resoonance lamp[d]	......	U.v. irrad. in a nitrogen atm. in presence of 10 mole % H_3PO_4; 95% of nitrile recovd. unchanged; 5% yield of benzamide, m.p. 128–129°
o-$CH_3C_6H_4$–	50	480	6	Ni	100–106	About 50% yield of brown solid, subl. 150° (0.5 mm.) to give impure prod.
o-$CH_3C_6H_4$–	37.5	350	16	Pb	110–111[e]	Reaction run with 8 mole % of H_3PO_4; near quant. yield of tan solid; recrystd. from HAc, followed by subl. at 160–180° (0.5 mm.). *Anal.* Calcd. for $C_{24}H_{21}N_3$: C, 82.0; H, 6.0 Found: C, 82.0; H, 5.7
m-$CH_3C_6H_4$–	50	545	7	Ni	151–152[f]	Near-quant. yield of gray solid; recrystd. from gl. HAc
p-$CH_3C_6H_4$–	50	400	5	Pb	......	Nitrile recovd. unchanged, $n^{20}D$ 1.5291; starting material $n^{20}D$ 1.5292
p-$CH_3C_6H_4$–	50	500	6	Pb	283–285[g]	Near quant. yield of tan solid, subl. at 200° (0.5 mm.)
p-ClC_6H_4–	38.5	350	16	Pb	334–335[h]	70% of nitrile recovd. and 30% of triazine obtained by subl. with a free flame (0.5 mm.)
p-ClC_6H_4	39.2	380	18	Pb	......	Same result as above. In the presence of 8 mole % of 85% H_3PO_4 the yield of s-triazine was raised to 49%
o-C_6H_4<	50	410	8	Ni	......	Near quant. yield of a deep green-black solid; dissolved in concd. H_2SO_4 at room temp.; poured onto ice, the greenish-yell. soln. regenerated blue-green phthalocyanine

[a] The abbreviation "kats." for kilo atmospheres = (atm. × 10^3) is suggested by H. T. Hall and F. P. Bundy. [b] T. L. Cairns, A. W. Larcher and B. C. McKusick, ref. 1, report a m.p. 231–232°. [c] S. D. Ross and M. Fineman, ref. 5. [d] For an illustration of a mercury resonance lamp apparatus, see p. 275 of Vol. II, 2nd ed. of "Technique of Organic Chemistry," edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1956. [e] The 2,4,6-tris-(o-tolyl)-1,3,5-triazine has only been prepared once previously by A. H. Cook and D. G. Jones, ref. 3, who record a m.p. 110°. [f] M. A. Kunz, K. Koberle and E. Berthold, German Patent, 549,969 (1929), observe m.p. 152–153°. [g] F. E. Francis and O. C. M. Davis, *J. Chem. Soc.*, **85**, 263 (1904), indicate a m.p. 278°. [h] O. C. M. Davis, *ibid.*, **87**, 1831 (1905), report m.p. 334°, while A. H. Cook and D. G. Jones, ref. 3, observe m.p. 335°.

triazine (subl. temp. 220° (0.5 mm.), m.p. 234–235°, *ca.* 30% yield), and a dark, unsublimable residue.

(b) *syn*-**Benzaldoxime**.—Treatment of the oxime at 200° for 6 minutes and 38,400 atm. in a lead capsule resulted in an explosive decomposition reaction. The odor of escaping ammonia was evident; the residue was a lustrous black solid reminiscent in appearance to anthracite coal. An X-ray diffraction pattern of the solid indicated that although it was not graphite, its structure exhibited a greater degree of order than that associated with an amorphous carbon.

The same reaction conducted in the presence of 5 mole per cent. of 85% H_3PO_4 resulted in a violent explosive decomposition after being heated to 150° for two minutes. The reaction products were similar to those described above.

(c) **Ammonium Benzoate**.—The reaction was conducted at 50,000 atm. and 490° for five minutes in a lead capsule and gave an unsublimable carbonized residue.

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