Azo-Bis Nitriles. V.[1] Mechanism of the Decomposition of Azo Nitriles. Decomposition Products

BY C. G. OVERBERGER AND M. B. BERENBAUM

Evidence is presented which shows that the free radicals produced from azo-bis nitriles are relatively free in solution. Diastereomeric azo compounds have given identical mixtures of racemic and *meso*-dinitriles and the decomposition of the mixtures of azo-bis-nitriles has yielded both symmetrical and mixed dinitriles.

Previous papers[2] have established that the decomposition of azo compounds of the type $RR'(CN)C$—N=N—$C(CN)R'R$ proceeds by a unimolecular first-order process independent of solvent or monomer. Although one might suspect from the above kinetic facts that the radical $[RR'(CN)C\cdot]$ becomes relatively free in solution, we decided to carry out some decomposition experiments the results of which would indicate how free the radical $[RR'(CN)C\cdot]$ becomes before recombination.

This paper reports the products resulting from the coupling of radicals formed in the decomposition of both stereoisomeric forms of 2,2'-azo-bis-2,4-dimethylvaleronitrile and the products obtained from the decomposition of a mixed solution of 2,2'-azo-bis-isobutyronitrile and 1,1'-azo-bis-1-cyclopentanenitrile.

Discussion

The *dl*- and *meso*-forms of 2,2'-azo-bis-2,4-dimethylvaleronitrile were available from other work.[3] Decomposition of both forms in benzene gave essentially the same mixture of two coupled products $[(CH_3)_2CH$—$CH_2(CH_3)(CN)$—$C]_2$. These are undoubtedly the two possible stereoisomers of the *sym*-dimethyldiisobutylsuccinonitrile. The possibility that one of these products might be $(CH_3)_2CH$—$CH_2(CH_3)(CN)C$—$CH[CH(CH_3)_2]$—$CH(CH_3)(CN)$ (I) or $(CH_3)_2$—CH—$CH_2(CH_3)(CN)C$—CH_2—$CH(CN)[CH_2$—$CH(CH_3)_2]$ (II) the product resulting from the addition of the tertiary radical to the disproportionated products $(CH_3)_2CH$—CH=$C(CH_3)(CN)$ or $(CH_3)_2CH$—CH_2—$C($=$CH_2)(CN)$ followed by abstraction of a hydrogen atom by the adduct was rendered unlikely since both products gave no reaction with bromine and phosphorus tribromide.[4] This reaction was carried out with isobutyronitrile and trimethylacetonitrile as controls. A good recovery of the two decomposition products and trimethylacetonitrile was effected under the same reaction conditions that gave a 71% yield of α-bromoisobutyronitrile. This indicates that no tertiary hydrogen is present alpha to the nitrile group as would be required in structures I and II. To further substantiate this point, C-methyl determinations[5]

were carried out for both isomers, as well as isobutyronitrile, trimethylacetonitrile, isovaleronitrile and tetramethylsuccinonitrile. The results are summarized in Table I. If the assumptions are made described in footnotes *c*, *d* and *e*, it would appear that structure I is eliminated. The elimination of structure II is not as definite but the latter is a less likely structure since disproportionation prior to addition of the tertiary radical occurred by loss of a primary hydrogen instead of a secondary hydrogen. Unfortunately, errors are quite large on C-methyl determinations. Thus, such evidence as presented here is only complementary and is based on the assumptions as indicated. The fact that both isomers (A,B) gave nearly identical C-methyl determinations when run at the same time is a strong indication that A and B are only stereoisomers and not position isomers (see footnotes *f* and *g*).

TABLE I

C-METHYL DETERMINATIONS[a]

Compound	Calcd., %	Found, %
Isobutyronitrile	21.8[b]	8.05
Trimethylacetonitrile	18.1[b]	4.15
Isovaleronitrile	18.1[b]	8.8
Tetramethylsuccinonitrile	....	None
Isomer A	6.64[c]	6.6[f]
(94.8–95.2)	8.18[d]	6.6[f]
	10.7[e]	
Isomer B	6.64[c]	
(58.5–59.0)	8.18[d]	6.6[g]
	10.7[e]	

[a] C-Methyl determinations by Drs. Weiler and Strauss, Oxford, England, % by weight. [b] Calcd. on basis of one available methyl group. [c] $(CH_3)_2CH$—CH_2—$C(CN)(CH_3)$—$C(CH_3)(CN)C$—CH_2—$CH(CH_3)_2$, calculated as two isovaleronitrile structures and one tetramethylsuccinonitrile. [d] $(CH_3)_2$—CH—CH_2—$(CH_3)(CN)C$—CH_2—$CH(CN)[CH_2$—CH—$(CH_3)_2]$ (II), calculated as two isovaleronitriles and one trimethylacetonitrile. [e] $(CH_3)_2$—CH—$CH_2(CH_3)(CN)C$—CH—$[CH_3(CH_3)_2]CH(CH_3)(CN)$ (I), calculated as two isovaleronitriles, one trimethylacetonitrile and one isobutyronitrile. [f] Average of two determinations on different samples (5.9, 7.2). [g] Average of two determinations on different samples (5.6, 7.7).

This is an indication that the intermediate radical $(CH_3)_2$—CH—CH_2—$\dot{C}(CN)(CH_3)$ *is obtained relatively free and assumes a planar configuration regardless of the configuration of the initial azo compound before decomposition.* The assumption that the radical becomes planar seems reasonable since no optically active free radicals have been shown to retain their asymmetry and since from both stereoisomers the same mixture of isomers is obtained indicating a common intermediate.

Decomposition of a solution of 2,2'-azo-bis-isobutyronitrile and 1,1'-azo-bis-1-cyclopentanenitrile

(1) This work was supported by a grant from the Research Corporation. For the fourth paper in this series, see C. G. Overberger and Harry Biletch, THIS JOURNAL, **73**, 4880 (1951).

(2) (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949); (b) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949); (c) C. G. Overberger, P. Fram and T. Alfrey, Jr., *J. Polymer Sci.*, **6**, 539 (1951).

(3) C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 2618 (1951).

(4) (a) C. L. Stevens, *ibid.*, **70**, 165 (1948); (b) C. L. Stevens and T. H. Coffield, *ibid.*, **73**, 103 (1951).

(5) R. Kuhn and H. Roth, *Ber.*, **66**, 1274 (1933).

in toluene gave three coupled products. These two azo compounds were used since they decomposed at approximately the same rate and since they would give rise to products of considerably different molecular weights which would be easier to separate by ordinary methods. Considerable amounts of tetramethylsuccinonitrile, 1,1'-dicyano-1,1'-bicyclopentyl[6] and the mixed coupled product (III) were isolated. Reaction with bromine and phosphorus tribromide again gave no reaction, further confirming structure III.

III
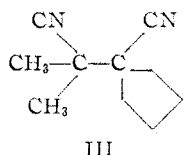
In addition, the amide of isobutyric acid and cyclopentenecarboxylic acid and its amide were isolated on hydrolysis of low boiling material and characterized. The absorption spectrum of the cyclopentenecarboxylic acid indicated an α,β-unsaturated acid. The isobutyronitrile is probably formed by the abstraction by the radical $(CH_3)_2\text{-}\dot{C}CN$ of a hydrogen from the solvent or products. The cyclopentene products are derived from cyclopentenenitrile which is probably formed by disproportionation of the radical initially formed on decomposition of 1,1'-azo-bis-1-cyclopentanenitrile. *The isolation of a mixed coupled product (III) is indicative of a decomposition mechanism by which relatively free radicals are produced.*

Experimental[7]

1,2-Disubstituted Hydrazine from Cyclopentanone.[8]—The procedure was similar to that described in reference 2a. From 6.0 g. (0.046 mole) of hydrazine sulfate, 4.5 g. (0.092 mole) of sodium cyanide, and 6.94 g. (0.0826 mole) of cyclopentanone, there was obtained on shaking for 12 hours, 8.0 g. (89%) of crude product. The white solid which separated on shaking was removed by filtration, washed with an additional 100 ml. of water, dried and powdered (6.6 g., 73%). Additional material was isolated from the filtrate after additional agitation for 12 hours. Agitation beyond a total of 24 hours led to a yellow coloration of the product. Recrystallization of the hydrazine from ether–petroleum ether (b.p. 29–38°) at Dry Ice temperatures gave a white crystalline product, m.p. 86–87°.

Anal. Calcd.[9] for $C_{12}H_{18}N_4$: C, 66.02; H, 8.31; N, 25.67. Found: C, 66.06; H, 8.38; N, 25.43.

1,1'-Azo-bis-1-cyclopentanenitrile.—The procedure was similar to that described in reference 2a. From 4.5 g. (0.021 mole) of the substituted hydrazine, there was obtained 2.1 g. (47%) of crude product. As the bromine solution of ethanol and water was added, the solution became homogeneous. The reaction mixture was then poured onto chipped ice. The crude product was removed by filtration, washed with water and dried. Recrystallization from ether at Dry Ice temperatures gave white crystals, m.p. 83–84°.

Anal. Calcd. for $C_{12}H_{16}N_4$: C, 66.64; H, 7.46; N, 25.90. Found: C, 67.05; H, 7.37; N, 25.68.

1,1'-Dicyano-1,1'-bicyclopentyl.—In a 50-ml. beaker there was placed 0.433 g. (0.0020 mole) of 1,1'-azo-bis-1-

cyclopentanenitrile and this was heated at 100° under nitrogen for 12 hours. The azo nitrile melted with some darkening of the color. On cooling, the reaction product solidified, 0.342 g. Recrystallization from ether gave a product, m.p. 94.2–96.2°. Sublimation and recrystallization from petroleum ether (b.p. 28–36°) raised the m.p. to 98.5–99.0°.

Anal. Calcd. for $C_{12}H_{16}N_2$: N, 14.88. Found: N, 15.11.

***sym*-Dimethyldiisobutylsuccinonitrile.**—Decomposition of each of the isomers of 2,2'-azo-bis-2,4-dimethylvaleronitrile in benzene produced the same mixture of two isomeric dinitriles. From 5.00 g. of one azo isomer, m.p. 56–57°, was obtained on fractional crystallization, 1.68 g., m.p. 85–93° of an isomer A and 1.44 g., m.p. 48–55° of isomer B, total yield 70.5%. Recrystallization of isomer A from petroleum ether (b.p. 60–70°) gave a m.p. of 94.8–95.2°.

Anal. Calcd. for $C_{14}H_{24}N_2$: N, 12.73. Found: N, 12.73.

Recrystallization of isomer B from petroleum ether (b.p. 28–36°) gave a product, m.p. 58.5–59.0°.

Anal. Calcd. for $C_{14}H_{24}N_2$: N, 12.73. Found: N, 12.78.

From 4.60 g. of the second azo isomer, m.p. 75–76°, was obtained 1.62 g. of isomer A and 1.35 g. of isomer B; total yield 72.8%. The products were recrystallized from petroleum ether (as above); isomer A, m.p. 94–95°, mixed m.p. 94–95°; isomer B, m.p. 58–59°, mixed m.p. 58–59°.

Reactions of Coupled Products with Bromine and Phosphorus Tribromide.—The reactions were carried out on 1.5- to 2.5-g. samples of nitrile according to the procedure of reference 4. Isobutyronitrile and trimethylacetonitrile were used in control experiments.

In the case of isomer A from the decomposition of 2,2'-azo-bis-2,4-dimethylvaleronitrile, 80% of the starting material was recovered, m.p. 95–95.5°, mixed m.p. 95–95.5°; isomer B recovery was 77%, m.p. 53–55°, mixed m.p. 53–55° (starting material of 53–55° m.p. was used because of difficulty in obtaining quantities of this isomer in a pure form). Treatment of the mixed coupled product III resulted in an 88% recovery of starting material, m.p. 69–70°, mixed m.p. 69–70°. Trimethylacetonitrile did not react, 73% of material $n^{25}\text{D}$ 1.3748–1.3762 ($n^{25}\text{D}$ 1.3751)[10] being recovered by distillation of the washed reaction product through a Craig[11] still; while isobutyronitrile yielded 71% of α-bromoisobutyronitrile, $n^{25}\text{D}$ 1.4448 ($n^{25}\text{D}$ 1.4447, 76%).[4a]

Decomposition of Azo Nitrile Mixture.—In 1400 ml. of benzene was dissolved 80.0 g. of 2,2'-azo-bis-isobutyronitrile ($k = 1.60 \text{ sec.}^{-1} \times 10^{-4}$ at 80.2°) and 53.5 g. of 1,1'-azo-bis-1-cyclopentanenitrile ($k = 0.76 \text{ sec.}^{-1} \times 10^{-4}$ at 80.2°) and the reaction mixture was refluxed for 65 hours. The bulk of the solvent was carefully removed by fractional distillation and the remaining solution was set in the ice-box. From this solution, 38.9 g. of crude tetramethylsuccinonitrile, m.p. 163–168°, was obtained. Recrystallization from toluene raised the m.p. to 170–171° (m.p. 169°).[12]

Careful distillation of the residual solution gave benzene and a higher boiling fraction, b.p. 83–84°, which still contained some benzene. Treatment of 1.05 g. of this fraction which had a sharp nitrile odor with 10 cc. of 10% hydrogen peroxide, 2 cc. of 10% sodium hydroxide and 20 cc. of acetone according to the procedure of Mooradian and Cloke[13] gave 0.13 g. of crude amide, m.p. 119–123°. Recrystallization from petroleum ether (b.p. 60–70°) gave a m.p. of 127–128° (m.p. of isobutyramide prepared by hydrolysis of isobutyronitrile, 126.8°).[14]

The residual material was submitted to vacuum distillation to give the following fractions: (a) 11.3 g., b.p. 90–100° (36 mm.); (b) 14.0 g., b.p. 70–82° (1.5 mm.); (c) 14.6 g., b.p. 80–90° (1.5 mm.); (d) 9.1 g., b.p. 90–98° (1.5 mm.); (e) 12.2 g., b.p. 100–165° (1.5 mm.). A tarry residue of five grams was discarded. Fractions b to e were waxy solids and considerable difficulty was encountered during distillation.

Fraction a was redistilled to give 9.9 g. of a colorless mobile liquid, b.p. 84° (36 mm.), which was not further purified. Hydrolysis of 1.00 g. of this liquid with 2.0 g. of potassium

(6) The decomposition rate of 1,1'-azo-bis-1-cyclopentanenitrile will be described in a forthcoming publication.

(7) All melting points are corrected.

(8) This compound and the succeeding two were prepared by Mr. James Herbert.

(9) Analyses by Mr. H. S. Clark, Urbana, Illinois; Mr. Harry Biletch, Polytechnic Institute of Brooklyn; Drs. Weiler and Strauss, Oxford, England.

(10) M. T. Rogers, THIS JOURNAL, **69**, 457 (1947).

(11) L. C. Craig, *Ind. Eng. Chem., Anal. Ed.,* **9**, 441 (1937).

(12) J. Thiele and K. Heuser, *Ann.,* **290**, 1 (1896).

(13) A. Mooradian and J. B. Cloke, THIS JOURNAL, **68**, 785 (1946).

(14) C. de Hoffman and E. Barbier, *Bull. soc. chim. Belges,* **45**, 565 (1936).

hydroxide in 7 cc. of diethylene glycol gave 0.87 g. (78%) of crude acidic material. Vacuum sublimation and recrystallization from aqueous alcohol gave white needles, m.p. 120.5–121.5° (121°)[15] indicating that the compound was cyclopentenecarboxylic acid. The ultraviolet absorption spectrum of the acid in 95% ethanol indicated[16] that the double bond was in the α,β-position, λ_{max}. 2210 Å., ϵ, 9200.

Treatment of 1.00 g. of the nitrile with 15 cc. of 10% hydrogen peroxide, 2 cc. of 10% sodium hydroxide and 20 cc. of acetone gave 0.98 g. (82%) of crude cyclopentene amide, m.p. 161–182°. Vacuum sublimation and recrystallization from methanol raised the m.p. to 206–208°.

Anal. Calcd. for C_6H_9ON: C, 64.84; H, 8.16. Found: C, 64.94; H, 7.94.

Fractions b to e were distilled through a Claisen flask

(15) E. Urion, Compt. rend., 190, 1512 (1930).

(16) For a comparison of absorption spectra of α,β-unsaturated acids, see C. G. Overberger and C. W. Roberts, This Journal, 71, 3618 (1949). See also H. E. Ungnade and I. Ortega, ibid., 73, 1564 (1951).

equipped with a wide bore sausage-shaped receiver. Four arbitrary fractions were taken. The first three fractions were then purified by fractional crystallization from petroleum ether (b.p. 60–70°) to give 6.5 g. of tetramethylsuccinonitrile, m.p. 168–170° (combined yield with previously separated material, 44.5 g. (40.7%)), 15.1 g. (13.6%) of 1,1'-dicyano-1,1'-bicyclopentyl, m.p. 94–96° and 19.0 g. (17.2%) of the mixed nitrile (III), m.p. 69.5–70.5.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.06; H, 8.68; N, 17.21. Found: C, 73.96; H, 8.78; N, 17.16.

The fourth fraction, a heavy oil, b.p. 135–145° (0.5 mm.), amounted to 6.8 g. This apparently contains an addition product containing two molecules of cyclopentanenitrile plus one of isobutyronitrile since hydrolysis of 1.00 g. of this oil with 2.0 g. of potassium hydroxide in 10 cc. of diethylene glycol gave 0.83 g. (68%) of crude acid, m.p. 182–192°. Vacuum sublimation and recrystallization from toluene gave a m.p. of 199.5–201.5°.

Anal. Calcd. for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.52; H, 7.72.

Alkylation with Long Chain p-Toluenesulfonates. II. Reaction of n-Octadecyl p-Toluenesulfonate with Mercaptans and Thiophenols[1]

By David A. Shirley and William H. Reedy

n-Octadecyl p-toluenesulfonate has been examined as an alkylating agent for a variety of mercaptans and thiophenols. The n-octadecyl aryl and alkyl thioethers were produced in yields ranging from 40 to 85%.

We have underway in this Laboratory a program of systematic evaluation of long chain aliphatic p-toluenesulfonates as alkylating agents for a variety of organic types. In the first paper, we reported the alkylation of phenols with n-octadecyl p-toluenesulfonate.[2] The n-octadecyl aryl ethers were formed in 50–75% yields.

It was next undertaken to alkylate mercaptans and thiophenols with n-octadecyl p-toluenesulfonate, and it was found that corresponding thioethers could be obtained in yields in the range of 40 to 85% all but one being obtained in above 60% yield. The compounds alkylated were thiophenol, p-nitrothiophenol, o- and p-thiocresol, n-butyl, decyl, dodecyl and octadecyl mercaptans, and 1,2-ethanedithiol. The results of these experiments are summarized in Table I.

$$RSH + NaOH \longrightarrow RSNa + H_2O$$

$$RSNa + SO_3(CH_2)_{17}CH_3 \longrightarrow RS(CH_2)_{17}CH_3 + SO_3Na$$
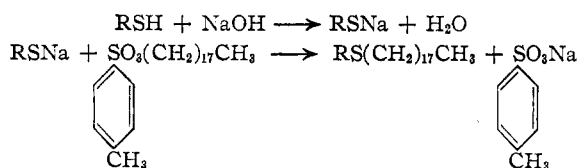
Several of the thioethers were oxidized to sulfones by conventional methods.

Experimental

The n-octadecyl p-toluenesulfonate used in this work was prepared as described earlier.[2]

p-Nitrophenyl n-Octadecyl Sulfide.—p-Nitrothiophenol[3] (16.0 g. or 0.103 mole) was added to a solution of 4.1 g.

(2) D. A. Shirley and W. H. Reedy, This Journal, 73, 458 (1951).

(3) C. C. Price and G. W. Stacy, ibid., 68, 499 (1946).

(0.102 mole) of sodium hydroxide in 150 ml. of water. n-Octadecyl p-toluenesulfonate (42.4 g. or 0.100 mole) was then added and the resulting mixture stirred and heated to reflux for 20 hours. The hot mixture was placed in a separatory funnel and the aqueous layer separated. The oily layer was washed two times with hot 3 N aqueous sodium hydroxide solution, two times with hot 3 N hydrochloric acid, and finally several times with hot water. The remaining organic material was recrystallized once from methanol and once from petroleum ether (b.p. 70–90°) to give 26.3 g. (65% yield) of p-nitrophenyl n-octadecyl sulfide melting at 68–69°.

Anal. Calcd. for $C_{24}H_{41}NO_2S$: S, 7.87. Found: S, 7.89.

The mercaptans and thiophenols listed in Table I were alkylated with n-octadecyl p-toluenesulfonate in general accordance with the procedure given above.

p-Aminophenyl n-Octadecyl Sulfide.—A solution of 10 g. of stannous chloride dihydrate in 100 ml. of glacial acetic acid was added to a solution of 5.0 g. (0.012 mole) of p-nitrophenyl n-octadecyl sulfide in 100 ml. of glacial acetic acid. The resulting mixture was heated to boiling for 30 minutes and then poured into 100 ml. of 6 N hydrochloric acid. The white solid which precipitated on cooling was collected by filtration and suspended in water. The mixture was made alkaline with excess 6 N sodium hydroxide and benzene added to dissolve the organic material. The benzene layer was separated and washed two times with water. Most of the benzene was removed by distillation, and ethanol was added to the hot solution. Cooling precipitated 3.2 g. (70% yield) of amine melting at 70–71°.

Anal. Calcd. for $C_{24}H_{43}NS$: S, 8.48. Found: S, 8.44.

p-Nitrophenyl n-Octadecyl Sulfone.—A mixture of 5.0 g. (0.012 mole) of p-nitrophenyl n-octadecyl sulfide, 4.0 g. (0.025 mole) of potassium permanganate, and 200 ml. of glacial acetic acid was heated to reflux temperature for three hours. Sodium bisulfite solution and hydrochloric acid were added to destroy excess potassium permanganate and manganese dioxide. The mixture was added to excess ice-water and the precipitated solid collected by filtration. The product was recrystallized from ethanol and the yield of sulfone, melting at 82–83°, was 4.0 g. (74%).

Anal. Calcd. for $C_{24}H_{41}NO_4S$: S, 7.29. Found: S, 7.36.

Phenyl n-Octadecyl Sulfone.—Phenyl n-octadecyl sulfide (5.0 g. or 0.0138 mole) was oxidized to the sulfone as de-