shown to us. We also gratefully acknowledge the benefit derived from stimulating conversations with Professor C. K. Ingold, Professor E. D. Hughes, Dr. P. B. D. de la Mare, Mr. C. A. Vernon and other members of the staff of University College, and with Professor P. W. Robertson. In addition, we want to acknowledge the continuous help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo-bis Nitriles. XI.[1] Decomposition of Azo Compounds. Steric Factors

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RECEIVED MAY 28, 1954

The preparation and characterization of six new azo nitriles are described. Their rates of decomposition have been determined in solution. The results substantiate previous suggestions that steric requirements in the alkyl groups are responsible for differences in rates of decomposition.

In previous papers[3] the importance of steric effects on the rates of decomposition of azo nitriles of the type RR'C(CN)N=N(CN)CR'R has been emphasized. In particular, steric interaction between the two halves of a *trans* symmetrical azo compound has been of prime importance,[3a] especially with alkyl groups with branching in the β-position (*R* = isobutyl). This paper reports the preparation and decomposition of azo nitriles which have increased branching in the alkyl groups R = CH_3, R' = $CH_2C(CH_3)_3$; R = CH_3, R' = *n* = C_5H_{11}; R = R' = CH_2—$CH(CH_3)_2$; R = R' = $CH(CH_3)_2$; R = C_2H_5, R' = $CH(CH_3)_2$ and correlates their decomposition rate with previous mechanistic suggestions.

A. Preparation of Azo Compounds

(1) **Discussion.**—The azo compounds from methyl neopentyl, methyl *n*-amyl, diisobutyl, diisopropyl and ethyl isopropyl ketone were prepared according to previously described procedures.[3] Both stereoisomers, the *dl*- and *meso*-forms of the substituted hydrazine and the azo nitrile from methyl neopentyl ketone were isolated and characterized. Ethyl isopropyl ketone was prepared from isobutyronitrile and ethylmagnesium bromide in 65% yield and this method is a useful procedure for its synthesis. The synthesis is of interest because reactions of aliphatic nitriles with aliphatic Grignard reagents usually give poor yields. The branching in the isobutyl group probably prevents the competing reaction of self condensation with the Grignard reagent functioning as the base.

(2) **Experimental.**[4] **2-2'-Azo-bis-2,4,4-trimethylvaleronitrile (2,2'-Azo-bis-2-cyano-4,4-dimethylpentane).**—Methyl neopentyl ketone was prepared by the oxidation of commercial diisobutylene with sodium dichromate and sulfuric acid according to the procedure of Mosher and Cox.[5]

The azine was prepared by refluxing 57.0 g. (0.50 mole) of methyl neopentyl ketone with 8.0 g. (0.25 mole) of anhydrous hydrazine for three days. The aqueous layer was separated, the crude ketazine dried over anhydrous magnesium sulfate and distilled through a short center-tube column to yield 44.2 g. (79%) of a pale yellow oil, b.p. 113–114° (10 mm.), $n^{25}{}_D$ 1.4590, $d^{25}{}_4$ 0.8340, together with 5.5 g. (9.7%) of recovered starting ketone.

Anal.[6] Calcd. for $C_{14}H_{28}N_2$: N, 12.49. Found: N, 12.72.

A solution of 40.4 g. (0.36 mole) of the ketazine in 65 ml. (*ca.* 1.6 moles) of liquid hydrogen cyanide was allowed to stand at room temperature for four days. The reaction mixture was then poured into water and the resulting waxy solid removed by filtration. After trituration with dilute sodium hydroxide solution and several water rinses, the crude product was dissolved in ether; cooling yielded 11.0 g. (22%) of disubstituted hydrazine, m.p. 104–107° dec. Recrystallization from ether raised the melting point to 108.5–110° dec.

Anal. Calcd. for $C_{16}H_{30}N_4$: C, 69.01; H, 10.86; N, 20.12. Found: C, 69.10; H, 10.77; N, 19.96.

The stereoisomeric disubstituted hydrazine was obtained by concentrating the mother liquors after separation of the high melting disubstituted hydrazine and cooling the solution in Dry Ice. The crude product was recrystallized from petroleum ether (b.p. 60–68°) to give 18.9 g. (38%) of material, m.p. 81–83.5° dec. Further recrystallization raised the melting point to 86–87.5° dec.

Anal. Calcd. for $C_{16}H_{30}N_4$: C, 69.01; H, 10.86; N, 20.13. Found: C, 69.12; H, 10.83; N, 20.07.

Both hydrazine compounds were thermally unstable and prolonged refluxing during recrystallization markedly reduced the amount of product obtained.

The azo nitriles were prepared by oxidation of the individual hydrazines.

From 4.8 g. (0.0173 mole) of the hydrazine isomer melting at 108.5–110° and 4 g. (0.025 mole) of bromine in 50–50 ethanol–water solution, 4.1 g. (85%) of azo nitrile melting at 65–67° was obtained. Recrystallization from petroleum ether (b.p. 28–36°) raised the melting point to 66.5–68.5° dec. (65°, a 29% yield of both isomers is reported, no analysis given[7]).

Anal. Calcd. for $C_{16}H_{28}N_4$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.49; H, 10.19; N, 20.20.

The lower melting hydrazine, 7.8 g. (0.0281 mole), and 5 g. (0.031 mole) of bromine in the ethanol–water solution gave 5.7 g. (73%) of azo nitrile, m.p. 88–91°. Recrystallization from chloroform–ether brought the melting point to 94.5–95.5° dec. (102–103°[7]).

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[1] This is the eleventh in a series of articles concerned with the decomposition of azo compounds. For the tenth paper in the series, see C. G. Overberger and Alexander Lebovits, THIS JOURNAL, **76**, 2722 (1954).

[2] This paper contains portions of theses presented by Warren F. Hale in partial fulfillment of the requirements for the degree of Master of Science and by M. B. Berenbaum in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949); (b) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951); (c) **73**, 4883 (1951); (d) C. G. Overberger H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, *ibid.*, **75**, 2078 (1953).

[4] All melting points are corrected.

[5] W. A. Mosher and J. C. Cox, Jr., THIS JOURNAL, **72**, 3701 (1950).

[6] Analyses by Drs. Weiler and Strauss, Oxford, England; Dr. K. Ritter, Basel, Switzerland; Dr. F. Schwarzkopf, New York, N. Y.

[7] J. A. Robertson, U. S. Patent 2,586,995 (Feb. 26, 1952).

Anal. Calcd. for $C_{16}H_{28}N_4$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.61; H, 10.08; N, 20.06.

Azo Nitrile from Methyl *n*-Amyl Ketone (2,2′-Azo-bis-2-cyanoheptane).—The azine was prepared according to the procedure of Szmant and McGinnis.[8] From 95 g. (0.842 mole) of 2-heptanone, 19 g. (0.380 mole) of 64% hydrazine and 4 drops of concentrated sulfuric acid in 700 ml. of absolute alcohol after four days of reflux using the Soxhlet apparatus, there was obtained 77 g. (90.3%) of azine, b.p. 135–137° (10 mm.), n^{25}D 1.4581.

Anal. Calcd. for $C_{14}H_{28}N_2$: N, 12.49. Found: N, 12.70.

To 10 g. (0.44 mole) of 2-heptanone azine was added 21 g. of liquid hydrogen cyanide and one drop of concentrated hydrochloric acid. After standing for 4 days with intermittent shaking, the hydrogen cyanide was allowed to evaporate and the crude hydrazine oxidized directly to the azo nitrile. The crude azo compound was recrystallized from an ether–petroleum ether (b.p. 28–38°) solution at Dry Ice temperatures, 10 g. (82.3%), m.p. 49.5–51°.

Anal. Calcd. for $C_{16}H_{28}N_4$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.48; H, 9.89; N, 20.03.

2,2′-Azo-bis-2-isobutyl-4-methylvaleronitrile (4,4′-Azo-bis-4-cyano-2,6-dimethylheptane).—Diisobutyl ketazine was prepared by the procedure of Alderson and Robertson[9] and Mailhe.[10] From 320 g. (2.25 moles) of diisobutyl ketone, 66.2 g. (1.125 moles hydrazine) of 85% hydrazine hydrate, 10 drops of concentrated sulfuric acid and 1500 ml. of absolute ethanol, there was obtained 128 g. (40.6%) of azine, b.p. 150–155° (15 mm.). The calcium oxide in the Soxhlet thimble was changed periodically until calcium hydroxide was no longer formed. Redistillation through a 12-inch center-tube fractionating column gave pure diisobutyl ketazine, b.p. 111.5° (3 mm.), n^{25}D 1.4568, d^{25}_4 0.8313.

Anal. Calcd. for $C_{18}H_{36}N_2$: C, 77.07; H, 12.94; N, 9.99. Found: C, 77.32; H, 12.70; N, 10.0.

The substituted hydrazine nitrile was prepared by the addition of excess hydrogen cyanide to the ketazine catalyzed by a drop of concentrated hydrochloric acid as described previously.[3b] All attempts to isolate a solid addition product failed and the crude material was oxidized to the azo derivative. Higher yields of azo compound were obtained if the reaction time was increased.

The azo nitrile was prepared as described previously.[3] From 17 g. (0.0638 mole) of hydrazine nitrile in a solution of 45 g. of ethanol, 26.5 g. of water and 50.0 g. of concentrated hydrochloric acid, there was obtained 4.11 g. (19.4%) of product. A white solid separated during the oxidation with bromine at 0°. This was removed by filtration and the filtrate poured into a large volume of ice-water. The oil was dissolved in dry ether and the solid was added to the ether solution. Crystallization was effected at Dry Ice temperatures. Successive recrystallizations from ether gave 2.02 g., m.p. 83–83.5° dec. (90°, 20.3% yield based on ketazine, no analysis reported[11]).

Anal. Calcd. for $C_{20}H_{36}N_4$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.44; H, 10.75; N, 16.65.

2,2′-Azo-bis-2-isopropyl-3-methylbutyronitrile (3,3′-Azo-bis-3-cyano-2,4-dimethylpentane).—Diisopropyl ketazine was prepared by the same procedure used for diisobutyl ketazine. From 171 g. (1.5 moles) of diisopropyl ketone and 44.3 g. (0.75 mole hydrazine) of 85% hydrazine hydrate, 94.5 g. of diisopropyl ketazine was obtained in 56.2% yield. On refractionation, pure azine distilled at 105.0° (12 mm.), n^{25}D 1.4537, d^{25}_4 0.8400.

Anal. Calcd. for $C_{14}H_{28}N_2$: C, 74.93; H, 12.58; N, 12.49. Found: C, 75.30; H, 12.41; N, 12.40.

Diisopropyl ketazine, 22.4 g. (0.100 mole), was treated with a large excess (25 ml.) of liquid hydrogen cyanide and a drop of concentrated hydrochloric acid. After six days at room temperature, the product was isolated as described previously. A white crystalline solid was obtained which was washed with ethanol to give 16.2 g. of crude hydrazine nitrile, m.p. 99–102° (58.2%). The crude material was dissolved in acetone, reprecipitated from water and then recrystallized twice from carbon disulfide, m.p. 108–110°.

Anal. Calcd. for $C_{16}H_{30}N_4$: C, 69.01; H, 10.86; N, 20.13. Found: C, 69.07; H, 10.70; N, 20.27.

The same procedure used for the preparation of the diisobutyl azo nitrile was employed. On recrystallization from carbon disulfide, the diisopropyl azo nitrile was obtained in 57.8% yield from the hydrazine or in 33.6% yield from the azine. On further recrystallization from carbon disulfide, pure product was obtained, m.p. 104–105° dec.

Anal. Calcd. for $C_{16}H_{28}N_4$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.78; H, 10.17; N, 19.97.

2,2′-Azo-bis-2-isopropylbutyronitrile (3,3′-Azo-bis-3-cyano-2-methylpentane).—Isobutyramide and isobutyronitrile were prepared according to the directions in reference 12. Ethyl isopropyl ketone was prepared according to the general directions of Hauser and Humphlett[13] who, however, did not prepare this compound. From 69.1 g. (1 mole) of isobutyronitrile and 435 g. (4 moles) of ethyl bromide in a total volume of 2.4 l. of ether, there was obtained 65.2 g. (65%), b.p. 113.7–114.5°, n^{25}D 1.3961 of ketone (114°, n^{25}D 1.3959 prepared from isobutyric anhydride and ethylmagnesium bromide[14]). The product was purified by initial distillation through a 30-cm. Vigreux column followed by distillation through a 6-inch helices-packed column.

Ethyl isopropyl ketazine was prepared by the same procedure used for the diisobutyl ketazine. From 110 g. (1.1 moles) of ethyl isopropyl ketone and 32.6 g. (0.55 mole hydrazine) of 85% hydrazine hydrate, 96.8 g. of ethyl isopropyl azine were obtained in 89.6% yield. On refractionation, pure azine distilled at 92.5° (10 mm.), n^{25}D 1.4538, d^{25}_4 0.8372.

Anal. Calcd. for $C_{12}H_{24}N_2$: C, 73.40; H, 12.32; N, 14.27. Found: C, 73.26; H, 12.27; N, 14.35.

The azo nitrile was prepared by the same procedure used for the diisobutyl azo compound. On recrystallization from ether, the ethyl isopropyl azo nitrile was obtained in 51.0% yield based on the azine. After four recrystallizations from ether, pure azo compound was obtained, m.p. 50.5–52.5°.

Anal. Calcd. for $C_{14}H_{24}N_4$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.42; H, 9.63; N, 22.73.

Tetraisobutyl Succinonitrile.—The toluene solution from the decomposition of the diisobutyl azo nitrile was evaporated at room temperature. From 1.003 g. (0.0031 mole) of azo nitrile, 0.89 g. (0.0029 mole) of crude dinitrile was obtained in 94% yield. Three recrystallizations from ether yielded pure product, m.p. 89–90°.

Anal. Calcd. for $C_{20}H_{36}N_2$: N, 9.20. Found: N, 9.20.

***sym*-Diethyl Diisopropyl Succinonitrile.**—The yellow oil obtained on evaporation of the toluene solution from the ethyl isopropyl azo nitrile decomposition was allowed to stand for several days in a refrigerator. Crystals were obtained and recrystallized from ether, m.p. 116–118°.

Anal. Calcd. for $C_{14}H_{24}N_2$: N, 12.71. Found: N, 12.48.

B. Kinetic Measurements

I. Procedure.—The procedure for measuring rates of decomposition has been described previously.[3]

II. Results.—The rates of decomposition of the compounds, $RR'(CN)C—N = N—C(CN)R'R$ where $R = CH_3$, $R' = CH_2—C(CH_3)_3$; $R = CH_3$, $R' = n\text{-}C_5H_{11}$; $R = R' = CH_2—CH(CH_3)_2$; $R = R' = CH(CH_3)_2$ and $R = C_2H_5$, $R' = CH(CH_3)_2$ as measured by nitrogen evolution are reported in Table I. Rate constants for both stereoisomers of the compound $R = CH_3$, $R' = CH_2—C(CH_3)_3$ are included. Previous work[3a] has shown that the effect of solvent and concentration on the rate of decompositions is negligible. Activation

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[8] H. H. Szmant and C. McGinnis, This Journal, **72**, 2890 (1950).

[9] W. L. Alderson and J. A. Robertson, U. S. Patent 2,469,358, May 10, 1949.

[10] A. Mailhe, *Compt. rend.*, **170**, 1265 (1920); A. Mailhe, *Bull. soc. chim.*, **27**, 541 (1920).

[11] J. E. Castle, U. S. Patent 2,515,628 (July 18, 1950).

[12] *Org. Syntheses*, **25**, 58, 61 (1945).

[13] C. R. Hauser and W. J. Humphlett, *J. Org. Chem.*, **15**, 359 (1950).

[14] M. S. Newman and A. S. Smith, *ibid.*, **13**, 592 (1948).

TABLE I

DECOMPOSITION RATES OF AZO NITRILES IN TOLUENE, RR′(CN)C—N═N—C(CN)R′R

R	R'	M.p., °C.	Concn. range, mole/liter	k (sec.$^{-1}$ × 10^4)	Temp., °C.	No. of runs	k, sec.$^{-1}$ × 10^4 (cor. to 80.0°)
CH_3[a]	CH_2–$C(CH_3)_3$[b]	67.5–69	0.0199–0.0251	1.175 ± 0.010[d]	40.0	2	158 ± 13[e]
			.0230– .0276	4.45 ± .14	50.0	3	
CH_3[a]	$CH_2C(CH_3)_3$[c]	94.5–95.5	.0247– .0264	0.695 ± .009	40.0	2	136 ± 10
			.0193– .0200	2.89 ± .14	50.0	3	
CH_3	n-C_5H_{11}	49.5–51	.0220– .0258	1.63 ± .10	80.0	3	1.63 ± 0.10
i-C_4H_9	i-C_4H_9	83–83.5	.0258– .0303	3.78 ± .18	60.1	2	49.5 ± 2.5
			.0301	52.8	80.5	1	
i-C_3H_7	i-C_3H_7	104–105	.0377– .0392	1.325 ± .035	80.5	3	1.25 ± 0.04
i-C_3H_7	C_2H_5	50.5–52.5	.0353– .0402	1.01 ± .05	80.5	3	0.95 ± 0.05

[a] Stereoisomers. [b] E^a, 27 ± 1.5 kcal./mole; $\Delta S\ddagger$, 7 ± 4 e.u.; [c] E^a, 29 ± 1.5; $\Delta S\ddagger$, 12 ± 4 e.u.; [d] average deviations; estimated deviations for rate constants including systematic errors are from 3 to 4%, and are larger than the average deviations (see Discussion). [e] Range estimated from the maximum estimated error of the rate constants.

energies and entropies of activation are recorded in the footnotes of Table I for the methyl neopentyl compounds.

Several precautions are necessary to minimize systematic errors. There is a tendency for the toluene used as a solvent to supersaturate with nitrogen resulting in a small induction period and somewhat erratic gas evolution. This is virtually eliminated by first sweeping the apparatus and solvent with nitrogen gas coupled with the use of a sealed-in magnet-driven agitator during the decomposition process. Suitable corrections were made for the vapor pressure of the toluene carried by the nitrogen evolved and the vapor pressure of the water used in the gas buret. The magnitude of the latter must be estimated since the rate of gas evolution is too rapid to permit achieving equilibrium. Temperature control and the use of suitably calibrated thermometers are important since the rate constant varies by 1–2% for a 0.1° rise in temperature. Some of the more unstable azo compounds show significant decomposition rates at room temperature. These must be recrystallized and dried immediately before the kinetic study. This factor was minimized by use, when feasible, of the experimental V_∞ to calculate the rate constant. The errors from these sources are difficult to estimate, but the over-all error in determining the rate constant is 3–4%. The higher the rate of nitrogen evolution, the greater[15] the probable error.

Observational errors in weighing, reading of thermometers, gas burets, etc., are all quite small, with an over-all magnitude of less than 1% and are not as important as the observational errors described above.

III. Discussion of Results

In previous papers,[3a,b,c] we have ascribed the enhanced rate of the azo nitrile from methyl isobutyl ketone to steric interaction of the isobutyl groups between the two halves of the *trans* azo compounds. A study of Fisher–Hirshfelder models indicated that branching in the β-position of the alkyl groups was necessary for this interaction. We have now confirmed this suggestion. From Table I, it is seen that the azo nitrile from diisobutyl ketone (k = 49.5 sec.$^{-1}$ × 10^4) decomposes at a rate 32 times faster than the acetone compound (k = 1.60–1.72 sec.$^{-1}$ × 10^4)[3a], and five times faster than the azo nitrile from methyl isobutyl ketone (k = 10 sec.$^{-1}$ × 10^4)[3b] at 80°. As has been pointed out previously, the azo nitrile from the latter ketone decomposes *ca.* 6 times more rapidly than the acetone compound at 80°. When an additional methyl group is added in the β-position as for example in the azo nitrile from methyl neopentyl ketone (k = 158 sec.$^{-1}$ × 10^4), *the rate of decomposition is 93 times faster than the acetone azo compound at 80°.* These striking increases in rate are best explained by the above steric explanation. Previous examination of the models and the determination of the rate of decomposition of the azo nitrile from pinacolone has revealed that branching on the α-position was unimportant and did not increase the rate of decomposition. Thus the rate of decomposition of the pinacolone azo nitrile is essentially equal to the acetone compound.[3b,15] This suggestion as to the lack of dependence of α-branching on the decomposition rate is supported by the decomposition rates listed for the azo nitriles from diisopropyl ketone, ethyl isopropyl ketone and methyl n-amyl ketone (Table I). No enhancement of rate over the acetone compound is found either by branching in the α-position or extension of the straight chain alkyl group.[15]

Both stereoisomeric forms of the azo nitrile from methyl neopentyl ketone decompose at about the same rate confirming previous work on other stereoisomeric pairs.[3b] As previously stated, back strain does not appear to be a factor affecting the rates of decomposition in the compounds studied to date.

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[15] The rate constants for the decomposition of several other aliphatic azo nitriles are included here for convenience and comparison: R = CH_3, R′ = C_2H_5, k = 1.72 sec.$^{-1}$ × 10^4; R = CH_3, R′ = n-C_3H_7, k = 0.94; R = CH_3, R′ = iso-C_3H_7, k = 1.03; R = CH_3, R′ = n-C_4H_9, k = 1.58; R = CH_3, R' = t-C_4H_9, k = 0.77.