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The Preparation of Some Aliphatic Azo Nitriles and their Decomposition in Solution[1,2]

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It has recently been reported by German workers[3] that 2,2'-azo-bis-isobutyronitrile (I, R = CH_3) was used as a blowing agent for the production of polymer foams. Thiele and Heuser[4] had previously prepared 2,2'-azo-bis-isobutyronitrile as well as the tetramethyl succinonitrile, the latter by decomposition of the azo compound by heating a suspension of the solid in water or a solution of the azo compound in phenol or amyl alcohol. This product probably resulted from the coupling of the two tertiary radicals produced in the decomposition of the azo compound. Dox[5] has also reported the preparation of 2,2'-azo-bis-2-ethylbutyronitrile[6] and 2,2'-azo-bis-2-methylbutyronitrile (I, R = C_2H_5). On decomposition of the 2,2'-azo-bis-2-methylbutyronitrile in 75% sulfuric acid, he obtained the tetra-substituted succinic acid resulting from the hydrolysis of the succinonitrile, the anhydride of the succinic acid together with methylethylacetic acid; the latter product was apparently the result of hydrogen abstraction from the solvent by the tertiary radical, followed by hydrolysis of the nitrile group. These facts gave strong support to an initial supposition that radicals were produced in the decomposition.

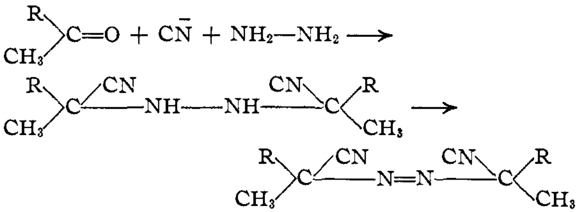
Since the structure of these compounds can be varied within some limitations, we have undertaken the preparation of a series of these azo compounds in order to study steric and polar effects on the rates of their decompositions and, secondly, to investigate the use of these compounds as radical sources for polymerization.

This paper describes the preparation of some azo-bis alkyl nitriles (Table II), the rates of decomposition of these compounds in solution and certain aspects of these results. We have also established that these compounds initiate the polymerization of styrene and of butadiene.

Preparation of Azo Compounds

I. Discussion

The general method of preparation is indicated schematically.



I

The first step[7] in the preparation of these substituted hydrazines may be the addition of hydrazine to the ketone to form an amino alcohol, rather than the addition of cyanide ion to the carbonyl group to give the cyanohydrin. It is not clear in which order the following steps then take place.

Molecular models indicate that only the *trans*-configuration of the azo group is possible. We have not determined whether the hydrazine compounds, their hydrochlorides or the azo compounds, when R is different from methyl, are the *meso*- or *dl*-forms. Since the crude azo compounds generally had a wide melting point range and since extensive recrystallization was always necessary to obtain a sharp melting compound, two forms may have been present. In no instance, however, was more than one crystalline compound isolated in either series. The separation of several of the substituted hydrazines is now being attempted.

The decomposition of the azo-bis nitriles, as shown by Thiele and Heuser[4] in the decomposition of 2,2'-azo-bis-isobutyronitrile, is a convenient synthetic method of obtaining tetrasubstituted succinonitriles.

The substituted hydrazines are described in Table I and the azo compounds are described in Table II.

II. Experimental[8]

Synthesis of Substituted Hydrazines. A. For Water Soluble Ketones and Cyclohexanone.—The method was adapted from that of Thiele and Heuser.[4] From 0.185 mole of hydrazine sulfate, 0.37 mole of sodium cyanide and 0.33 mole of ketone in aqueous solution, there was obtained on shaking at room temperature for two days either a crystalline material, with acetone and cyclohexanone, or an oil, as with methyl ethyl ketone. If the substituted hydrazine was a solid, it was filtered and recrystallized from ether or 95% ethanol. If it was an oil, the

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[1] This work was supported by a contract from the Office of Naval Research.

[2] This paper comprises a portion of a thesis presented by Harold Shalit in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] DeBell, Goggin and Gloor, "German Plastics Practice," The Department of Commerce, DeBell and Richardson, Springfield, Mass., 1946, p. 457.

[4] Thiele and Heuser, *Ann.*, **290**, 1 (1896).

[5] Dox, THIS JOURNAL, **47**, 1471 (1925).

[6] Stefl has also described the preparation of the azo nitriles from methyl ethyl ketone, methyl *n*-propyl ketone and diethyl ketone (Dissertation, Tech. Hochschule, Munchen, 1914, see Beilstein, 1st supplement, Vol. IV, p. 565). We have not been able to find any publication of this dissertation. The hydrazine compound from methyl ethyl ketone was reported to be a solid, m. p. 51-52°, but we have been unable to duplicate this result. Dox, likewise, did not obtain this compound as a solid. Stefl also reported a dihydrochloride of the hydrazine compound, m. p. 110°. We obtained a monohydrochloride, m. p. 107° (dec.) (Table I).

[7] Stewart and Li [THIS JOURNAL, **60**, 2782 (1938)] have presented kinetic evidence that the formation of a simple aminonitrile passes through the intermediate amino alcohol.

[8] All melting points are corrected.

TABLE I

1,2-DISUBSTITUTED HYDRAZINES

R[a] group	Yield, %	M. p.,[e] °C.	Recryst. solvent	Composition, %[f] Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found	Chlorine, % Calcd.	Found
C_2H_5, HCl[b]	80	107 (dec.)		52.06	52.26	8.24	8.19	24.30	23.80	15.40	15.10
iso-C_3H_7, HCl	47	94–96 (dec.)		55.70	56.05	8.90	8.81	21.66	21.26	13.73	13.10
C_3H_5[c]	36	94–95 (uncor.)	Ether	66.06	66.40	8.26	8.36	25.69	25.71		
C_3H_5, HCl		111–113 (dec.)						22.00	22.15		
iso-C_4H_9–	11	95–96 (uncor.)	Ether	67.20	67.52	10.40	10.42	22.40	22.20		
C_6H_{11}[d]	95	139.5–140.5	95% alc.					22.76	22.74[g]		

[a] R = CH_3, yield—80%, m. p. 92–93° (reference 4, m. p. 92–93°). Where R = C_2H_5, n-C_3H_7, iso-C_3H_7 and n-C_4H_9, the 1,2-disubstituted hydrazines were oils. When R = n-C_3H_7, iso-C_3H_7, C_3H_5-, and n-C_4H_9-, dioxane was added to the reaction mixture. [b] The hydrochlorides of R = n-C_3H_7 and n-C_4H_9 were too unstable to be analyzed. [c] Cyclopropyl. [d] Cyclohexanone, the R group and the methyl group are replaced by the cyclohexyl ring. [e] Melting points corrected except when noted. [f] Analyses by Dr. Francis Schwarzkopf. [g] Analyses by Mr. H. S. Clark.

TABLE II

AZO NITRILES

R group	Oxidation in	Yield,[c] %	M. p.,[e] °C.	Recryst. solvent	Composition,[i] % Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found
CH_3–	Water	71	103–104[f]	Ether						
C_2H_5–	Water	79[d]	49–51[g]	Ether	62.51	62.50	8.31	8.31	29.16	29.30
C_3H_5–[a]	Water		77–78	Ether	66.67	66.66	7.41	7.44	25.93	25.62
n-C_3H_7–	Alcohol	90	73–74.5[h]	95% alc.	65.45	65.45	9.09	9.04	25.45	25.23
iso-C_3H_7	Alcohol	71	68.5–70	95% alc.	65.45	65.48	9.09	8.90	25.45	25.74
n-C_4H_9–	Alcohol	78	55.5–57	Ether	67.74	67.48	9.68	9.42	22.58	22.38
iso-C_4H_9	Alcohol	86	74–76	Ether	67.74	67.31	9.68	9.78	22.58	22.30
C_6H_{11}[b]	Water	92	114–115	95% alc.	68.84	68.65[j]	8.20	8.49	22.95	22.85

[a] Cyclopropyl. [b] Cyclohexanone. [c] Crude yield based on substituted hydrazines. [d] Yield based on original methyl ethyl ketone. [e] Melting points corrected except when noted. [f] Reference 4, m. p. 105–106°. [g] Reference 5, m. p. 57°; reference 6, m. p. 54–55°. [h] Reference 6, m. p. 64°. [i] Analyses by Dr. Francine Schwarzkopf. [j] Analyses by Mr. H. S. Clark.

aqueous layer was separated and extracted with two 50-ml. portions of ether which were added to the oil layer. The combined oil and ether extracts were washed with water, dried over anhydrous magnesium sulfate, and the ether was removed, leaving the oily substituted hydrazine. Attempted preparation of benzoates, benzenesulfonates, p-toluenesulfonates and picrates of these hydrazines gave only oily products. The hydrochlorides were prepared by saturation of the ether solution of the base with dry hydrogen chloride, followed by filtration of the solid salt. The salt was washed well with ether to give a white powder with a strong odor of hydrogen cyanide. Although preparation of the hydrochlorides provided a good method of purification, they were not good derivatives due to their ease of hydrolysis in cold water.

B. **For Water Insoluble Ketones.**—The same proportions of reactants were used as for the soluble compounds except that 60 ml. of dioxane was added to increase the mutual solubility of the two phases. The procedure was the same as previously described.

C. **Attempted Purification by Distillation.**—Liberation of the base from the solution of the hydrochloride followed by distillation under reduced pressure resulted, in the four cases tried, in the elimination of two molecules of hydrogen cyanide per molecule of hydrazine. Analyses of the distillates corresponded fairly well with calculated analyses for the corresponding azines. Thus, the distillate of the hydrazine from methyl ethyl ketone was analyzed.

Anal. Calcd. for $C_{10}H_{18}N_4$: C, 61.9; H, 9.28; N, 28.85. Calcd. for $C_8H_{16}N_2$: C, 68.5; H, 11.4; N, 20.0. Found: C, 68.8; H, 11.7; N, 19.4.

Synthesis of Azo Nitriles. A. Oxidation in an Aqueous System.—The procedure of Thiele and Heuser[4] and of Dox[5] was used for all the oxidations carried out in a water system.

B. **Oxidation in an Ethanol System.**—The hydrazine compound (0.04–0.08 mole) was dissolved in a saturated solution of dry hydrogen chloride in absolute alcohol. Occasionally the hydrochloride precipitated, but in any event the mixture was cooled in an ice-bath and a solution containing 4 g. of bromine in 100 ml. of ethanol was dropped in slowly. Usually, the mixture became homogeneous after the addition of sufficient bromine solution. The addition was continued until bromine absorption became very slow. The mixture was then poured into a large volume of ice-water, and the precipitated azo compound was filtered, washed well with water, and dried *in vacuo* at room temperature. The azo compound was recrystallized from ether or ethanol. In general, the oxidation step was unsatisfactory, for although yields of from 70 to 90% of crude product could be obtained, extensive recrystallization was necessary to obtain the pure azo compounds.

C. **Oxidation with Nitrous Acid.**—The method was adapted from that of Thiele and Heuser.[4] From one gram (0.0035 mole) of 1,2-di-2-(2-cyano-4-methyl)-pentylhydrazine hydrochloride dissolved in 10 ml. of ethanol and 10 ml. of 1:1 aqueous hydrochloric acid, and 2 g. of sodium nitrite in 10 ml. of water, there was obtained 0.3 g. (37%) of product. After two recrystallizations this material melted at 74–75°. This method was inferior to the bromine oxidation; see Table II. Attempted oxidation of 1,2-di-2-(2-cyano-4-methyl)-pentylhydrazine with mercuric oxide gave no reaction.

Preparation of Succinonitriles. (1) **sym-Dimethyldiethyl Succinonitrile.**—This was prepared from 2,2′-azo-bis-2-methylbutyronitrile by one of the methods of Thiele and Heuser[4] who suspended the bis-azo compound from acetone in boiling water to effect the decomposition. The yield was 1 g. (59%). Recrystallization from ether gave white crystals, m. p. 96–98°.

Anal. Calcd. for $C_{10}H_{16}N_2$: N, 17.06. Found: N, 17.00.

(2) **1,1-Dicyano-1,1-bicyclohexyl.**—In a 50-ml. beaker was placed 1.92 g. (0.008 mole) of 1,1′-azo-bis-1-cyclohexane nitrile. Nitrogen was passed through the solid

and it was heated to 120° for one hour (caution, explosions may occur if done in larger quantities). The material first melted and then resolidified as nitrogen was evolved. The resultant solid weighed 1.6 g. (98% yield). Recrystallization from acetone gave white crystals, m. p. 224.5–225°.

Anal. Calcd. for $C_{14}H_{20}N_2$: N, 12.96. Found: N, 13.20.

(3) **sym-Dimethyl Di-*n*-propyl Succinonitrile.**—This was prepared in a manner similar to the cyclohexanone derivative. The dinitrile was a white powder, recrystallized from hexane, m. p. 83–83.5°.

Anal. Calcd. for $C_{12}H_{20}N_2$: N, 14.57. Found: N, 14.66.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer in 95% ethanol as a solvent. The cell length used in all experiments was 1 cm. Figure 1 describes the spectra for 2,2′-azo-bis-isobutyronitrile (concn., 0.061 mole/l., 0.0245 mole/l.) and 1,1′-azo-bis-1-cyclohexane nitrile (concn., 0.0272 mole/l.). The spectra of the other azo compounds in Table II were also determined and shown to be similar to those described in Fig. 1. Hantzsch and Lifchitz[9] measured the absorption spectrum of 2,2′-azo-bis-2-methylpropionitrile. They found a very weak absorption band around 3450 Å. Our curves are qualitatively similar.

III. Polymerization Experiments.

Polymerization of Styrene.—A solution of 1 g. of 2,2′-azo-bis-isobutyronitrile, 20 g. of purified styrene and 200 g. of purified benzene were heated at reflux for five and one-half hours. The reaction mixture was then dropped into methanol, and the polymer thus precipitated purified by six reprecipitations by methanol from methyl ethyl ketone; $[\eta]$ = 0.071, mol. wt. (approx.) = 1310 determined by equation of Kemp and Peters.[10]

Anal. Calcd. for $(C_8H_8)_{13}$: N, 1.00. Found: N, 0.78.

Polymerization of Butadiene.—Weighed quantities of butadiene and azo compound initiator were tumbled, in capped Coca Cola bottles, in a constant temperature bath, for times and at temperatures as indicated in Table III. After reaction, the bottles were cooled in Dry Ice and their contents poured into methanol. The precipitated polymers were purified by reprecipitation by methanol, from benzene solution, and dried *in vacuo*. All were clear, viscous oils.

TABLE III

POLYMERIZATION OF BUTADIENE

Catalyst		Temp., °C.	Time, hr.	Polymer yield
R	Mole, %			
CH_3	0.66	50	140	17.5[a]
CH_3	.32	65	113	23.7
C_2H_5	.67	50	140	16.0
C_2H_5	.34	65	113	26.6

[a] *Anal.* Found: N, 1.58.

Kinetic Measurements

I. Procedure for Measuring Rates of Decomposition.—In a typical experiment 45 ml. of solvent was introduced into a 50-ml. two-necked round-bottomed flask, fitted with an inlet tube for bubbling purified nitrogen through the solvent and a capillary tube outlet to a water-jacketed gas buret. A three-way stopcock in the line to the buret vented the nitrogen used in the preliminary flushing. The reaction vessel was immersed in a constant-temperature bath controlled to ±0.1°. The solvent was deoxygenated with a slow stream of nitrogen for a period of thirty minutes, and then allowed a few minutes to attain thermal equilibrium with the bath. A weighed amount, usually between 0.1 and 0.2 g., of solid azo compound was next introduced into the reaction vessel by momentary removal of the ground-glass neck bearing the nitrogen inlet. The flask was then swirled to effect solution and thorough mixing. Timing began with the first introduction of the azo compound. The volume of nitrogen (V) evolved was measured by means of the gas buret at time intervals which varied with the rate of the reaction being followed. Volume readings obtained after twenty-four hours were treated as V_∞ values in most cases. They agreed well with stoichiometric values. For slower decompositions stoichiometric V_∞ values were used. The natural logarithms of the ratios $V_\infty/V_\infty - V_t$ were calculated and plotted as ordinates *vs.* the time abscissa. All these plots revealed apparent induction periods. The slopes or the best straight line through the points so plotted were measured and are the rate constants reported.

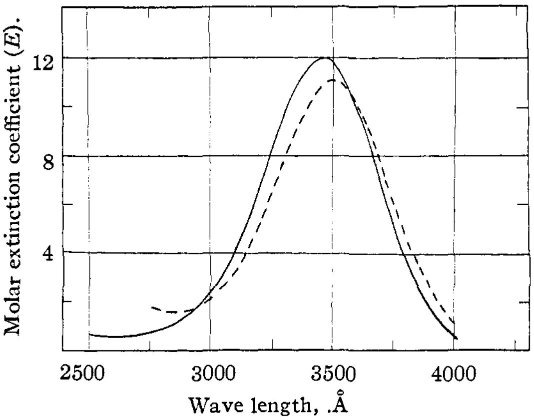

Fig. 1.—Absorption spectrum of 2,2′-azo-bis-butyronitrile—; absorption spectrum of 1,1′-azo-bis-1-cyclohexane nitrile - - - -.

II. Results.—The decomposition, in toluene solution, of the compounds with R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and isobutyl, and that of the azo compound from cyclohexanone

TABLE IV

RATES OF DECOMPOSITION OF AZO NITRILES IN TOLUENE AT 80.2°

R-group	Concn. range. moles/liter	*k* (sec.$^{-1}$ × 10^4) range	No. of runs	Average deviation
CH_3-[a]	0. 137–0.0463	1.72–1.60	3	0.06
C_2H_5-	.0274– .0154	0.94–0.80	4	.06
n-C_3H_7	.0181– .0143	1.74–1.65	2	.05
iso-C_3H_7	.0183– .0135	1.03–1.02	2	.01
n-C_4H_9	.0142	1.58	1	..
iso-C_4H_9	.0193– .0163	7.1	2	.00
C_6H_{11}[b]	.0165	0.083	1	..

[a] Not flushed with nitrogen. [b] Cyclohexanone.

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[9] Hantzsch and Lifchitz, *Ber.*, **45**, 3011 (1912).

[10] Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

has been followed at 80.2° by volumetric measurement of the evolved nitrogen.

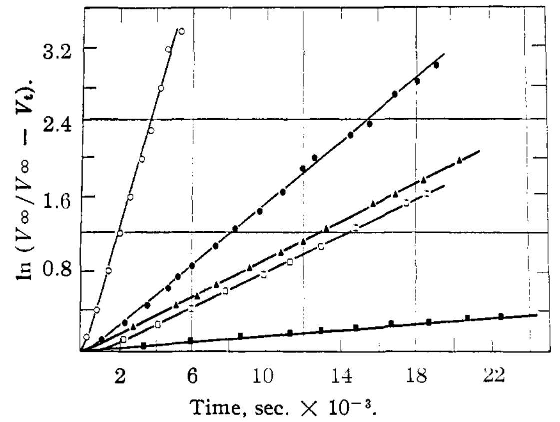

Fig. 2.—Decomposition of azo nitriles in toluene: azo nitriles from methyl iso-butyl ketone, ○; from acetone ●; from methyl isopropyl ketone ▲; from methyl ethyl ketone □; from cyclohexanone, ■.

Table IV contains the values of the rate constants obtained in individual runs of the decomposition in toluene at 80.2°, and average rate constants for each compound. In Fig. 2, plots of ln $V_\infty/V_\infty - V_t$ are reproduced for single runs for five of the compounds. Table V contains the results obtained for the decomposition of 2,2'-azo-bis-isobutyronitrile in isobutyl alcohol, *t*-amyl alcohol and aniline.

TABLE V

EFFECT OF SOLVENTS ON THE RATE OF DECOMPOSITION OF 2,2'-AZO-BIS-ISOBUTYRONITRILE AT 80.2°

Solvent	Concn. (moles/liter)	Dielectric constant at 20°	k (sec.$^{-1}$ × 10^4)
Isobutyl alcohol	0.0278	18.7	1.76
Isobutyl alcohol	.0234	18.7	1.67
Toluene	.0463	2.4	1.60
t-Amyl alcohol	.0501	11.7	1.40
Aniline	.0262	7.2	1.68

Table VI contains the results of experiments at 69.8°, together with approximate values for the energy of activation calculated from these experiments in conjunction with the average rate constants at 80.2°.

TABLE VI

ENERGIES OF ACTIVATION FOR THE DECOMPOSITION OF AZO NITRILES

Run	R group	k (sec.$^{-1}$ × 10^4) at 69.8°	Energy of activation, kcal./mole
37	CH_3–	0.38	34(±3)[a]
38	C_2H_5	.23	31(±3)
33	*n*-C_3H_7	.42	33(±4)
36	iso-C_3H_7	.26	32(±4)
32	iso-C_4H_9	1.98	29(±4)

[a] Limits of error of activation energies calculated on assumption maximum error in individual rate constants is 10%.

The decomposition reactions of these compounds appear to be strictly first order; the rate constant is substantially independent of solvent type within the range studied. This result is to be compared with the work of Grieve and Hey,[11] who showed that nitrosoacetanilide decomposed unimolecularly in a wide variety of solvents with little variation of rate, and with that of Pray,[12] and of Waring and Abrams,[13] who found that dry benzenediazo chloride decomposed unimolecularly in a series of aliphatic alcohols at nearly identical rates.

Kinetic measurements with the compound for which R = cyclopropyl were unsatisfactory and are not reported here; the decomposition of this compound together with more extensive investigation of the behavior of certain of the other compounds of this series from the subject of additional research now in progress.

III. Discussion of Results

The facts that the products of the decomposition of these compounds as solids are tetraalkyl succinonitriles, that the decomposition rate in solution is little affected by change of solvent polarity, and that these compounds initiate vinyl polymerization support the postulate of a primary dissociation into free radicals

$$CH_3R(CN)C{-}N{=}N{-}C(CN)RCH_3 \longrightarrow N_2 + 2CH_3R(CN)C\cdot$$

The final products, in solution, will depend upon the manner and extent of reaction between the primary radicals and the solvent. Whether the initial step involves the breaking of a single C–N bond to form $CH_3R(CN)C\cdot$ plus the highly unstable radical $CH_3R(CN)C{=}N{-}N\cdot$ which then decomposes very quickly or actually involves the breaking of both C–N bonds in a single step, cannot be decided on the basis of the evidence at hand. The first order kinetics and the absence of appreciable solvent effects indicate the absence, in the case of the compounds reported here, of the radical-induced secondary decomposition which has recently been suggested to explain complexities in the decomposition of benzoyl peroxide.[14]

From Table IV, it will be seen that the rate constants are about the same for R = methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl and that when R = isobutyl there is a fivefold augmentation of rate. When the azo compound from cyclohexanone was used there was a twenty-fold diminution of rate as compared with the main group. There does not appear to be any plausible reason for these major differences on the basis

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[11] Grieve and Hey, *J. Chem. Soc.*, 1797 (1934). For a general discussion of the decomposition of azo compounds, see Waters, "The Chemistry of Free Radicals," Oxford University Press, Clarendon, 1946.

[12] Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926).

[13] Waring and Abrams, THIS JOURNAL, **63**, 2757 (1941).

[14] Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947).

of resonance due to hyperconjugation or inductive effects of the alkyl groups. Consideration of Fisher–Hirschfelder molecular models suggests a steric explanation. The following remarks apply equally to the *meso*- and the *dl*-models, of the *trans*-azo compound when R differs from methyl. We have not obtained evidence to indicate which isomer was present. A study of these models revealed considerable interference of pairs of groups, R and methyl, at the two ends of the molecule with each other. This interference was of comparable magnitude for the compounds whose rates of decomposition fall in the main group; it was considerably more serious for the isobutyl compound and very much less so for the cyclohexyl compound as compared with the others.

The extreme crowding of groups in the isobutyl compound is therefore revealed in Fig. 3 as contrasted with the cyclohexyl compound, Fig. 4. In the construction of the isobutyl compound, it was found impossible to arrange the R and methyl groups in a way which avoided contact of alkyl groups across the C—N=N—C linkage. The repulsive forces arising from this crowding of groups may be expected to strain the C–N bond, displacing its potential surface and decreasing its energy of dissociation. The parallelism between rate of decomposition and degree of strain revealed by the models is striking and indicates that the steric factor may indeed control this variation in rates of decomposition.

The activation energies[15] in Table VI are to be considered as provisional values only; the uncertainties arising from the rather low accuracy of the individual rate constants and the small temperature interval are so large that comparisons of the activation energies for the individual compounds do not appear to be justified. In the light of the foregoing discussion, it is interesting, however, that the lowest value reported is that for the iso-butyl compound. The uncertainty in the activation energies gives rise to a greater relative uncertainty in entropies of activation and these are therefore not reported; they appear to be large and positive, of the order of magnitude of 10 to 15 E. U.

Deviations of calculated values of $\ln V_\infty/(V_\infty - V_t)$ from "true" values at accurately constant temperatures arise chiefly from errors in the measurement of V_t and V_∞. While errors in V_t, unless systematic, merely produce a scatter of the points, an error in V_∞ will produce a deviation from linearity increasing rapidly toward longer times. Our curves exhibited both scatter and deviation from linearity, but these were not serious below $\ln V_\infty/V_\infty - V_t = 2.0$. A more serious difficulty was the presence of an apparent "induction period" (see Fig. 2), which was reduced but not eliminated by displacing air from the solvent and the reaction vessel with a stream of nitrogen, before the start of the reaction. This last measure also improved the agreement between the experimental and stoichiometric values of V_∞. A plausible explanation of the induction period is the reaction of oxygen in the solvent and from the gas above it with free radicals formed in the decomposition reaction, thus falsifying the early volume readings. The method used to introduce the sample necessarily admitted some air to the reaction vessel; the persistence of the induction period in the experiments in which nitrogen was used is therefore not inconsistent with this explanation. The induction period introduced additional uncertainty in the drawing of the best straight line through the experimental points by reducing the range of linearity of the $\ln V_\infty/V_\infty - V_t$ curves.

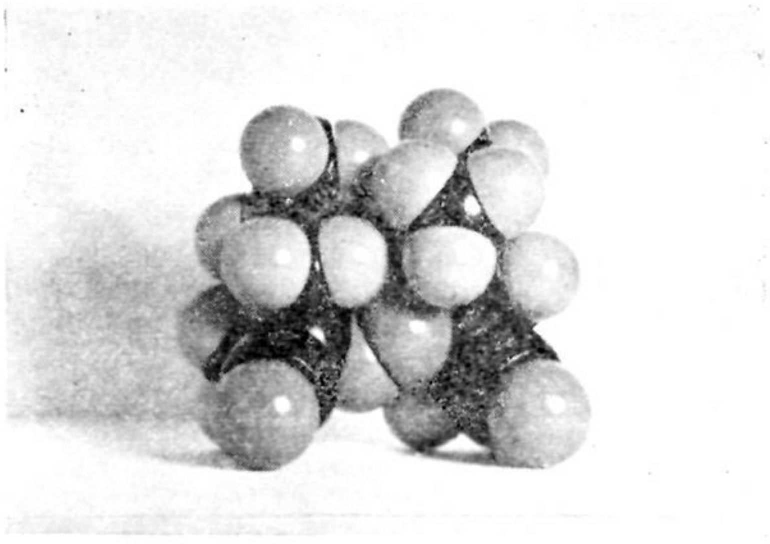

Fig. 3.—2,2′-Azo-bis-2,4-dimethylvaleronitrile (*meso* form).

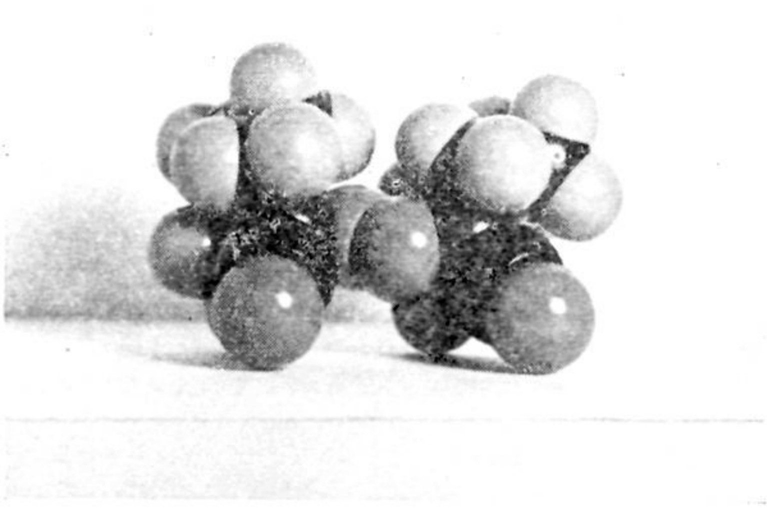

Fig. 4.—1,1′-Azo-1-cyclohexane nitrile.

Summary

1. The preparation and characterization of six new aliphatic azo nitriles is described (R = cyclopropyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and the azo compound derived from cyclohexanone). Three new 1,2-disubstituted hydrazines, intermediates in the preparation of the

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[15] The order of magnitude of these activation energies (30–35 kcal.) is to be compared with 25–31 kcal. for the decomposition of benzene diazochlorides in alcohols and acids,[13] and with 33 kcal. for the spontaneous decomposition of benzoyl peroxide in benzene.[14]

azo compounds have likewise been characterized (R = cyclopropyl, isobutyl and the hydrazine from cyclohexanone). Hydrochlorides of two new 1,2-disubstituted hydrazines (R = isopropyl, R = cyclopropyl) have likewise been characterized.

2. Three new succinonitriles, decomposition products from three of the azo nitriles (R = iso-butyl, *n*-propyl and the azo compound from cyclohexanone) have been prepared and characterized.

3. Rates of decomposition of seven aliphatic azo compounds at 80.2° have been determined in toluene and the reaction shown to be first order.

4. Activation energies have been determined for five of the azo compounds by additional rate measurements at 69.8°.

5. The rate of decomposition of 2,2′-azo-bis-isobutyronitrile has been studied in toluene, isobutyl alcohol, *t*-amyl alcohol and aniline and has been shown to be essentially independent of solvent type.

6. It has been demonstrated that free radicals are produced in the decomposition of the azo compounds. A mechanism for the decomposition reaction is proposed. Major differences in rate constants are ascribed largely to steric factors.

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Polyglycerols. II. Syntheses of Diglycerol[1]

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Diglycerol has long been known to be a constituent of the mixture resulting from the base-catalyzed, thermal condensation of glycerol. The recovery of diglycerol as the tetraallyl ether or as the diisopropylidene derivative from such mixtures has been described by Wittcoff, Roach and Miller.[1a] The isolation of diglycerol as well as higher polyglycerols as the acetates has been reported by Rangier[2] and by Wright and DuPuis,[3] whereas conditions for the direct distillation of polyglycerol mixtures have been published by Istin.[4]

A very interesting reaction which yielded a mixture of glycerol and diglycerol has been carried out by Wright and DuPuis[3] who pyrolyzed the substance resulting from the action of carbon dioxide on calcium glyceroxide. A direct synthesis of diglycerol was accomplished many years ago by Nef[5] who hydrolyzed 2-epoxypropyl ether which he obtained by the interaction of silver oxide and epichlorohydrin.

This paper describes three direct syntheses of diglycerol: (a) by the hydroxylation of allyl ether; (b) by the hydrolysis of the dichlorohydrin resulting from the addition of hypochlorous acid to allyl ether; and (c) by the hydrolysis of 2-epoxypropyl ether prepared from this dichlorohydrin.

Although hydroxylation of allyl ether by action of permanganate proved feasible, considerably better yields of diglycerol were obtained in this work by the use of performic acid[6] as the hydroxylating agent. In both cases, however, it was observed that the product could be distilled from the reaction mixture only with difficulty. Accordingly, the crude reaction mixture was subjected to the action of acidic acetone in order to obtain diisopropylidenediglycerol which could be distilled readily. In addition, some isopropylidenediglycerol was also formed and both of these derivatives were easily hydrolyzed to diglycerol.

The addition of hypochlorous acid to allyl ether occurred readily when the reagent was prepared as described by Kadesch,[7] a procedure which was found superior in this work to the one described in "Organic Syntheses."[8] The dichlorohydrin was hydrolyzed directly to diglycerol by the action of a weak base such as sodium bicarbonate. Sodium hydroxide, on the other hand, converted the dichlorohydrin to 2-epoxypropyl ether, first described by Nef,[5] which likewise was hydrolyzed to diglycerol by the action of dilute aqueous sulfuric acid.

Experimental

Isopropylidene- and Diisopropylidenediglycerol from the Oxidation of Allyl Ether with Performic Acid.—A mixture of allyl ether (57.8 g., 0.59 mole), formic acid (87%, 325 cc.) and hydrogen peroxide (29%, 146.0 g., 1.2 moles) was stirred mechanically, the reaction vessel having been placed behind a safety glass shield. The temperature rose to 40° in fifteen minutes and was maintained there first by external cooling and then by heating for four and one-half hours. When titration of a test sample indicated that practically no peroxide remained, the reaction mixture, having been stirred with sodium bisulfite (7.0 g.) to ensure the absence of peroxides, was concentrated under

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(1) Paper No. 86, Journal Series, Research Laboratories, General Mills, Inc.

(1a) H. Wittcoff, J. R. Roach and S. E. Miller, THIS JOURNAL, **69**, 2655 (1947). See footnote 2 for a discussion of nomenclature.

(2) M. Rangier, *Compt. rend.*, **187**, 345 (1928); *C. A.*, **22**, 4468 (1928).

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(4) M. Istin, *Ann. faculte sci. Marseille*, **13**, 5 (1946); *C. A.*, **41**, 2392 (1947).

(5) J. Nef, *Ann.*, **335**, 238 (1904).

(6) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

(7) R. G. Kadesch, *ibid*, **68**, 41 (1946).

(8) H. Gilman and A. H. Blatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 158.