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

Azo-bis Nitriles.[1] The Decomposition of Azo Compounds Derived from Cycloalkanones. An Accurate Measure of Differences in Ring Strain

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The preparation and decomposition of azo nitriles derived from cyclobutanone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, cycloheptanone, cycloöctanone and cyclodecanone are described. The differences in rates of decomposition are attributed to differences in ring strain. A point of view is presented to show that these decompositions represent an accurate measure of differences in ring strain. The thermodynamic data are interpreted in terms of the proposed reaction mechanism. This is the first complete set of data for a free radical reaction which measures differences in ring strain.

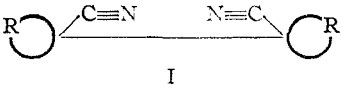
Previous papers have demonstrated the mechanism of the decomposition of aliphatic azo nitriles.[3] In particular, it has been established that the decomposition of azo compounds of the type RR′(CN)C—N=N—C(CN)R′R proceeds by a unimolecular first-order process independent of solvent. Differences in the rate of decomposition of the aliphatic azo nitriles have been explained on the basis of steric and polar factors.

This paper will describe the preparation and decomposition of the azo nitriles derived from cyclobutanone, cyclopentanone, cyclohexanone, 2-methylcyclohexanone, cycloheptanone, cycloöctanone and cyclodecanone and an interpretation of these results. In particular, it will be demonstrated that the rate of decomposition is a measure of differences in ring strain. *This is the first complete set of data for a free radical reaction which measures differences in ring strain.*

A. Preparation of Azo Compounds

I. Discussion.—The azo compound prepared from 2-methylcyclohexanone was prepared as described previously.[3a] The azo compounds from cyclopentanone and cyclohexanone have previously been described.[3a,c] The azo compounds from cyclobutanone, cycloheptanone, cycloöctanone and cyclodecanone were prepared from their azines as described previously.[3b] The azines from cycloheptanone and cycloöctanone were prepared by simple refluxing with hydrazine. In order to prepare the azine from cyclobutanone and cyclodecanone in good yield it was necessary to use special procedures to remove water.

The major products from the decomposition of these azo nitriles were coupled products of the general type I (Table III) and were isolated from the solution in which the decomposition had occurred with the exception of the azo compounds from cyclobutanone and 2-methylcyclohexanone. A further report on the decomposition products from the cyclobutanone compound will be presented in a forthcoming paper. The decomposition product from the 2-methylcyclohexanone azo compound is described separately.



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II. Experimental[4]

1,2-Disubstituted Hydrazine from 2-Methylcyclohexanone.—The procedure was similar to that described previously.[3a] From 21.45 g. (0.165 mole) of hydrazine sulfate, 15.24 g. (0.311 mole) of sodium cyanide and 33.6 g. (0.30 mole) of 2-methylcyclohexanone in 225 ml. of water, there was obtained, after two days of shaking, a viscous oil along with a solid. The solid was removed by decantation of the oil and the solid dissolved in ether. The aqueous layer was extracted with ether and the ether extracts combined and dried. Addition of petroleum ether (b.p. 29–38°) and cooling to Dry Ice temperatures give a solid crystalline compound (15%), m.p. 129–130°. Recrystallization from an ether–petroleum ether (b.p. 29–38°) solution at Dry Ice temperatures gave a m.p. of 129–130°.

Anal. Calcd. for $C_{16}H_{26}N_4$: C, 70.03; H, 9.55; N, 20.42. Found: C, 69.72; H, 9.67; N, 20.66.

1,1′-Azo-bis-1-(2-methylcyclohexane) Nitrile.—The procedure was similar to that described for 1,1′-azo-bis-1-cyclopentane nitrile,[3c] 44%, m.p. 121.4–122.6°.

Anal. Calcd. for $C_{16}H_{24}N_4$: C, 70.55; H, 8.88; N, 20.50. Found: C, 70.59; H, 8.68; N, 20.42.

1,1′-Dicyano-1,1′-bi-2-methylcyclohexyl.—This compound was prepared by the same procedure[3c] as that used to prepare 1,1′-dicyano-1,1′-bicyclopentyl except that the temperature was raised to 120°, m.p. 170–171.5°.

Anal. Calcd. for $C_{16}H_{24}N_2$: N, 11.47. Found: N, 11.85.

1,2-Disubstituted Hydrazines from Cyclobutanone, Cycloheptanone, Cycloöctanone and Cyclodecanone.—Cyclobutanone was prepared according to the directions of Roberts and Sauer,[5] $n^{25}D$ 1.4190 ($n^{25}D$ 1.4189).[5] Cycloheptanone and cycloöctanone were prepared according to the procedure of Kohler, Tishler, Potter and Thompson[6]; cyclodecanone was prepared according to the procedure of Prelog, Frenkiel, Kobelt and Barman.[7]

(A) Preparation of Azines.—The azine from cyclobutanone was prepared by refluxing 3.5 g. (0.049 mole) of the ketone and 1.24 g. (0.0248 mole) of 64% aqueous hydrazine solution in 35 ml. of benzene and 8.5 ml. of ethanol as solvent. After refluxing for 1 hour, the water azeotrope was removed at 62° over a period of 2.5 hours. The reaction mixture was heated at 35° overnight and then allowed to stand at room temperature for 4 hours. The solvents were removed under reduced pressure, the yellow residue taken up in ether and dried over anhydrous magnesium sulfate. The dried ether solution was cooled in a Dry Ice chest and the white crystals which separated were removed by filtration, 1.23 g., m.p. 68.3–69°. A second crop was obtained, 1.58

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[1] This is the eighth in a series of papers concerned with the decomposition of azo compounds. For the seventh paper in this series, see C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **74**, 3293 (1952).

[2] This paper contains portions of theses presented by Jay Lilker and James Herbert in partial fulfillment of the requirements for the degree of Master of Science and by Harry Biletch 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**, 2617 (1951); (c) **73**, 4883 (1951).

[4] All melting points are corrected unless otherwise stated. Analyses by Drs. Weiler and Strauss, Oxford, England; Dr. K. Ritter, Zurich, Switzerland; Dr. F. Schwarzkopf, New York, N. Y.

[5] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[6] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

[7] V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

g., m.p. 68–69°, total yield (84%). An analytical sample was recrystallized from ether, m.p. 68.4–69.1°.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.56; H, 8.89; N, 20.57. Found: C, 70.45; H, 8.80; N, 20.31.

The azine from cycloheptanone was prepared by refluxing 11.2 g. (0.10 mole) of cycloheptanone and 1.6 g. (0.050 mole) of anhydrous hydrazine in a flask protected from moisture. The reaction mixture was heated for 48 hours with a bath temperature of 110°. The lower layer of the cooled reaction mixture was removed with a capillary dropper. The remainder, a dark red-brown liquid, was taken up in ether and dried over anhydrous magnesium sulfate for one hour. The azine, 9.12 g. (83%), boiled at 114° (0.3 mm), $n^{21}\mathrm{D}$ 1.5210.

Anal. Calcd. for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.72. Found: C, 76.07; H, 10.70; N, 12.73.

The azine from cycloöctanone was prepared from 10.5 g. (0.0833 mole) of cycloöctanone and 1.34 g. (0.0417 mole) of anhydrous hydrazine by refluxing for 60 hr. at 100°. The cooled reaction product was taken up in ether and the aqueous portion discarded. After drying the ether solution over anhydrous magnesium sulfate and removing the ether, the residue was distilled to give 6.9 g. (67%), b.p. 147° (1.5 mm.), $n^{25}\mathrm{D}$ 1.5272.

Anal. Calcd. for $C_{16}H_{28}N_2$: C, 77.35; H, 11.36; N, 11.29. Found: C, 77.20; H, 11.22; N, 11.61.

The azine from cyclodecanone was prepared from 4.0 g. (0.026 mole) of cyclodecanone, 0.65 g. (0.013 mole) of 64% hydrazine and 3 drops of concentrated sulfuric acid in 325 ml. of absolute ethanol, according to the procedure of Szmant and McGinnis,[8] using a Soxhlet apparatus with lime to remove water. After refluxing for five days, the reaction mixture was cooled, any colloidal calcium oxide removed by filtration through a filter cell, the alcohol removed at reduced pressure and the residue distilled through a small fractionating column to give, 3.4 g. (86.1%), b.p. 154° (0.25 mm.), m.p. 28–30°.

Anal. Calcd. for $C_{20}H_{36}N_2$: C, 78.94; H, 11.84; N, 9.21. Found: C, 79.21; H, 11.58; N, 8.92.

(B) **1,2-Disubstituted Hydrazines.**—To 0.6 g. (0.0044 mole) of cyclobutanone azine was added 15 g. of liquid hydrogen cyanide and one drop of concentrated hydrochloric acid. After standing for two days with intermittent shaking the hydrogen cyanide was allowed to evaporate. The yellow residue was dissolved in a large excess of ether (*ca.* 600–700 ml.) and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed to a 200-ml. volume and diluted with 200 ml. of petroleum ether (b.p. 28–38°). On cooling, crystals separated, 0.44 g., m.p. 111.5–111.8°. A second crop was obtained, 0.25 g., m.p. 110–111.5°, total yield 82%. An analytical sample was recrystallized from an ether–petroleum ether mixture, m.p. 110–111°.

Anal. Calcd. for $C_{10}H_{14}N_4$: C, 63.11; H, 7.42; N, 29.45. Found: C, 63.35; H, 7.47; N, 29.15.

To 7.23 g. (0.0329 mole) of cycloheptanone azine were added 20 ml. of liquid hydrogen cyanide and one drop of concentrated hydrochloric acid. After standing for three days in a closed system, the hydrogen cyanide was allowed to evaporate in a good hood, 8.0 g. (90%), m.p. 104–105°, recrystallized from ether.

Anal. Calcd. for $C_{16}H_{26}N_4$: C, 70.01; H, 9.54; N, 20.4. Found: C, 69.77; H, 9.27; N, 20.2.

In a similar manner from 10.38 g. (0.042 mole) of cyclooctanone azine and 20 ml. of liquid hydrogen cyanide, there was obtained on recrystallization from ether, 9.5 g. (75%), m.p. 119.5–121°.

Anal. Calcd. for $C_{18}H_{30}N_4$: C, 71.48; H, 10.00; N, 18.55. Found: C, 71.61; H, 9.93; N, 18.11.

In a similar manner from 3.9 g. (0.013 mole) of cyclodecanone azine and 25 ml. of liquid hydrogen cyanide, there was obtained on recrystallization from an ether–petroleum ether (b.p. 28–38°) mixture, 1.7 g. (37%), m.p. 99–100.5° dec.

Anal. Calcd. for $C_{22}H_{38}N_4$: C, 73.67; H, 10.69; N, 15.63. Found: C, 73.70; H, 10.73; N, 15.47.

(C) **Azo Nitriles.**—The procedure was similar to that described previously.[3a] From 2.8 g. (0.015 mole) of the 1,2-disubstituted hydrazine from cyclobutanone, there was obtained, after recrystallization from an ether–petroleum ether (b.p. 28–38°) mixture at Dry Ice temperatures, 1.9 g. (67.9%) of 1,1′-azo-bis-1-cyclobutane nitrile, m.p. 108.5–109° as white needles.

Anal. Calcd. for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43; N, 29.76. Found: C, 64.11; H, 6.47; N, 29.50.

From 2.6 g. (0.0095 mole) of the 1,2-disubstituted hydrazine from cycloheptanone, there was obtained, after recrystallization, from an ether–petroleum ether (b.p. 28–38°) mixture at Dry Ice temperatures 2.3 g. (88.5%) of 1,1′-azo-bis-1-cycloheptane nitrile, m.p. 95–95.5° dec. Successive recrystallization from the mixed solvents did not change the melting point.

Anal. Calcd. for $C_{16}H_{24}N_4$: C, 70.55; H, 8.88; N, 20.6. Found: C, 70.50; H, 8.90; N, 20.5.

From 2.7 g. (0.089 mole) of the 1,2-disubstituted hydrazine from cycloöctanone, there was obtained after recrystallization from the ether–petroleum ether mixture, 2.0 g. (74%) of 1,1′-azo-bis-1-cycloöctane nitrile, m.p. 79.5–80° dec. Recrystallization from the same solvent at Dry Ice temperatures did not change the melting point.

Anal. Calcd. for $C_{18}H_{28}N_4$: C, 71.98; H, 9.35; N, 18.66. Found: C, 72.30; H, 9.06; N, 18.51.

From 1.4 g. (0.0040 mole) of the 1,2-disubstituted hydrazine from cyclodecanone there was obtained after recrystallization from an ether–petroleum ether (b.p. 28–38°) mixture, 0.99 g. (69.9%) of 1,1′-azo-bis-1-cyclodecane nitrile, m.p. 89° dec.

Anal. Calcd. for $C_{22}H_{36}N_4$: C, 74.11; H, 10.19; N, 15.71. Found: C, 74.08; H, 10.20; N, 15.44.

Decomposition Products from Azo Nitriles.—With the exception of the azo compound from 2-methylcyclohexanone, described separately, the decomposition products were isolated from the kinetic experiments (Table III). The solvent was first removed to give a volume of 5 ml., petroleum ether (b.p. 28–38°) was then added, and the solution cooled to give a precipitate.

B. Kinetic Measurements

I. Procedure.—The procedure for measuring rates of decomposition was essentially that described previously.[3a,b]

II. Results.—The rates of decomposition of the compounds, cyclo—R—(CN)C—N=N—C(CN)—R—cyclo, as measured by nitrogen evolution at three different temperatures are reported in Table I. Table I contains values of the rate of decomposition in toluene, xylene and mesitylene at the specified temperature and average rate constants for such compounds. Table II indicates the calculated energies and entropies of activation. In Fig. 1, plots of ln $V_\infty/V_\infty - V_t$ *vs.* time are reproduced for a number of the experimental runs and are examples of the general accuracy of the determination. In Fig. 2, the activation energy plots are represented.

III. Discussion.—In the past several years, a number of investigators have considered the detailed problem of ring strain to explain the differences in reactivity of cycloalkyl halides in reactions of the S_N1 or S_N2 type and reactions of cycloalkanones in carbonyl addition reactions. Likewise, striking differences in strength of cyclic amines have been attributed to differences in ring strain.

The general term "internal strain" was introduced by Brown[9a] and was defined in general terms as that additional strain in a ring which results from

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(8) H. H. Szmant and C. McGinnis, THIS JOURNAL, **72**, 2890 (1950).

(9) (a) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950); (b) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

TABLE I

DECOMPOSITION RATES OF AZO NITRILES FROM CYCLOALKANONES IN TOLUENE, CYCLO-R(CN)C—N=N—C(CN)R-CYCLO

R	Azo nitrile, m.p., °C.	k(sec.$^{-1}$ × 10^4)	Temp., °C.	No. of runs	k(sec.$^{-1}$ × 10^4) cor. to 80.0°
Cyclobutyl	108.5–109	0.205 ± 0.005	120.4[a]	2	0.00173
		0.520 ± .016	130.4[b]	2	
		1.60 ± .03	141.6[b]	2	
Cyclopentyl	84–85 dec.	0.745 ± .039	80.3	2	0.726
		2.43 ± .06	89.2	3	
		5.18 ± .11	95.1	3	
Cyclohexyl	114–115 dec.	0.065 ± .0016	80.3	3	0.063
		0.544 ± .022	95.2	3	
		1.26 ± .010	102.4	3	
Cycloheptyl[3,c]	95–96 dec.	0.269 ± .005	48.9	3	12.22
		0.972 ± .012	58.9	3	
		2.69 ± .12	67.3	3	
Cycloöctyl	79–80 dec.	0.535 ± .008	36.6	3	83.5
		1.45 ± .06	45.4	3	
		2.60 ± .08	49.7	3	
Cyclodecyl	89 dec.	0.540 ± .011	50.8	2	18.42
		1.70 ± .03	60.2	2	
		5.69 ± .02	69.5	2	
2-Methylcyclohexanone	121.4–122.6	0.0743 ± .0018	80.2	3	0.0743

[a] Carried out in xylene as a solvent. [b] Carried out in mesitylene as solvent. [c] Also carried out in acetic acid at 69.5°. k_1 extrapolated from activation energy curve, 3.48 × 10^{-4}/sec.; found, 3.28 × 10^{-4}/sec.

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE DECOMPOSITION OF AZO NITRILES FROM CYCLOALKANONES

R group	ΔE_{act} kcal./mole	$\Delta S^{\ddagger}$, e.u.	$\Delta F^*_{80.0°}$, kcal./mole
Cyclobutyl	32.1 ± 1.0	1.3 ± 2.0	31.6
Cyclopentyl	33.8 ± 0.9	18.9 ± 2.2	27.2
Cyclohexyl	35.4 ± .6	17.8 ± 1.6	29.0
Cycloheptyl	27.5 ± .9	6.1 ± 2.4	25.4
Cycloöctyl	25.9 ± .9	5.9 ± 2.7	23.8
Cyclodecyl	28.0 ± .7	8.5 ± 1.9	25.0

TABLE III

DECOMPOSITION PRODUCTS FROM AZO NITRILES DERIVED FROM CYCLOALKANONES, CYCLO—R—(CN)—(CN)—R—CYCLO

R	Yield, %	M.p., °C.	Recrystallized from	Nitrogen, % Calcd.	Nitrogen, % Found
Cyclopentyl	66.3	95–96	Ether–petroleum Ether (b.p. 28–38°)	14.88	15.11
Cyclohexyl	72.4	224–225	Xylene–petroleum Ether (b.p. 90–100°)	12.96	13.20
Cycloheptyl	74.8	145.5–147	Toluene–petroleum Ether (b.p. 28–38°)	12.06	12.15
Cycloöctyl	51.5	86–87	Ether–petroleum Ether (b.p. 28–38°)	10.42	10.33
Cyclodecyl	62.5	147–148	Toluene–petroleum Ether (b.p. 60–70°)	8.53	8.62

a change in the coördination number and thus the preferred bond angle of a ring atom involved in same reaction, considering the initial state and the transition state. The concept has been discussed adequately elsewhere.[9,12b] A second factor governing the relative reactivities of cycloalkyl derivatives of cyclopentane and higher is the so-called "Pitzer[10]

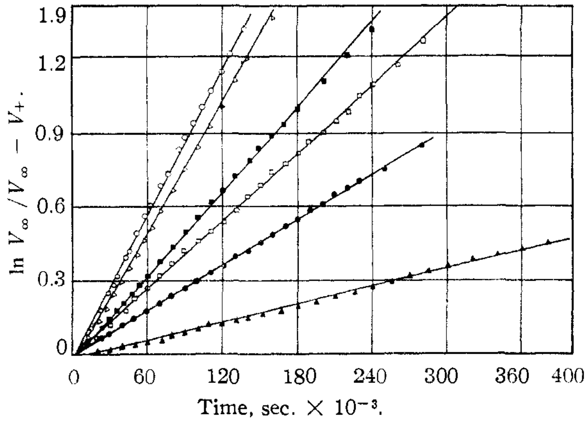

Fig. 1.—Decomposition of azo nitriles: ○, C_{10} at 60.2° in toluene; △, C_8 at 45.5° in toluene; ■, C_7 at 58.9° in toluene; □, C_5 at 80.3° in toluene; ●, C_6 at 95.2° in toluene; ▲, C_4 at 120.4° in xylene.

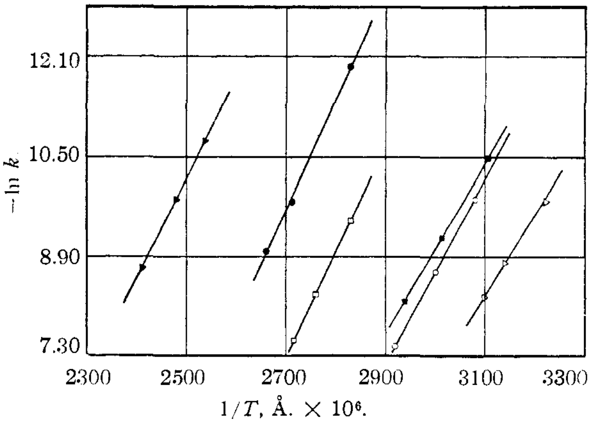

Fig. 2.—Activation energies for the decomposition of azo-bis nitriles derived from cycloalkanones: ▲, C_4; □, C_5; ●, C_6; ■, C_7; △, C_8; ○, C_{10}.

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(10) K. S. Pitzer, *Science*, **101**, 672 (1945); R. Spitzer and H. M. Huffman, *ibid.*, **69**, 211 (1947); C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947). See this latter paper for references to O. Hassel.

or Hassel strain," first discussed by Prelog,[11] which Brown first clearly recognized and has now included under the general term of "internal strain." For a complete discussion see reference 12b.

Although differences in the reactivity of cycloalkyl derivatives have been systematically determined, the results are somewhat dependent on the type of reaction studied. Thus, Roberts and Chambers[12a] have reported on the basis of the solvolysis reactions of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl *p*-toluenesulfonates, that the order of reactivity is cyclopentyl ~ cyclobutyl > cyclohexyl >> cyclopropyl. The hydrolysis rate sequence for the corresponding chlorides in a 50% ethanol–50% water solution was similar except that the cyclobutyl derivative was more reactive than the cyclopentyl derivative. The reactivity sequence of the bromides toward sodium iodide in acetone was found to be cyclopentyl > cyclobutyl > cyclohexyl >> cyclopropyl. Brown and Borkowski[12b] measured the rate of solvolysis of 1-chloro-1-methylcycloalkanes in 80% ethanol–water solutions and found the order to be cyclobutyl < cyclohexyl < cyclodecyl < cycloheptyl ~ cyclopentyl < cyclooctyl.

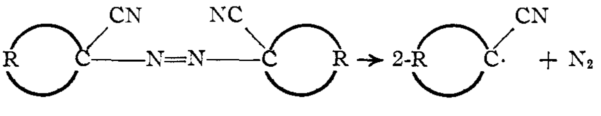
The results of Prelog and Kobelt[13a] in the dissociation of the cyclic cyanohydrins show an order cyclohexyl < cyclopentyl < cycloheptyl < cyclooctyl < cyclononyl < cyclodecyl. Prelog and Hafliger[13b] in the polarographic reduction of the Girard-T derivatives of cyclic ketones report an order cyclohexyl < cyclopentyl < cyclodecyl < cycloheptyl < cyclononyl < cyclooctyl. Although some similarities are present in the solvolysis reactions, it is obvious that many differences are observed, especially when the course of the reaction changes from largely S_N1 to S_N2 even though the I-strain theory would predict similarities. It is obvious that factors other than I-strain (defined now as deformation of angle and Pitzer strain) must be considered. Additional steric factors are to be expected in the S_N2 type with at least cyclohexyl and higher halides due to hindrance by the puckered ring to rearward attack.[12a] The S_N1 type reaction provides a better measure of ring strain; however, since the solvent is always involved to some extent in a rearward attack, a steric factor other than I-strain may influence the rates of solvolysis. Further, Roberts and Mazur[14a] have demonstrated other anomalies in the solvolysis of cyclobutyl chloride due to the unusual nature of the cyclobutylcarbonium ion of the ion pair obtained in the transition state. Interestingly enough, the solvolysis of 1-chloro-1-methylcyclobutane does not proceed with rearrangement.[12b] Differences in the electron-attracting power of the cycloalkyl groups may also affect the order.[14b]

From the work of Doering and Streitwieser[15] on the methanolysis of optically active 2,4-dimethylhexyl hydrogen phthalate, it seems clear that even minor participation of the solvent influences the stereochemistry of the transition state. Although rates may be affected to a minor extent, the entropy of activation will probably be affected by this solvent participation.

In the case of the cyanohydrin dissociation constants reported by Prelog and Kobelt, other steric factors than ring strain, at least with cycloheptanone and higher ketones, must influence the rates. Reactions of cycloalkanes with atoms or radicals which appear to give the general order of reactivity[12b] also may be subject to steric factors other than ring strain since they are radical displacement reactions on hydrogen.

From a consideration of Fisher–Hirschfelder models and previous work,[3] it is unlikely that there is any interference between the two cyclic groups in each half of the molecule in the *trans* azo compounds considered here. This question has been discussed previously[3a] and it need only be pointed out that on the basis of this type of strain, the rate of decomposition of the cyclohexanone compound would be faster than the rate of the cyclopentanone compound. Furthermore, it can be seen from Table I that the decomposition of the azo compound from 2-methylcyclohexanone occurs at the same rate as the cyclohexanone compound, again showing that there is little or no difference in the amount of steric interaction between the two halves of the azo compounds in these cyclic derivatives.

Likewise, it has previously been demonstrated that there are no solvent effects on the rate of decomposition.[3a] From Table I it is noted that the decomposition of the azo compound from cycloheptanone in glacial acetic acid shows no change in rate. Thus, the reaction indicated largely measures the release in strain going from the tetrahedral angle to the planar transition state of 120°. The rate of decomposition therefore clearly represents an accurate measure of differences in ring strain.



The results summarized in Table I indicate that the general order found in the solvolysis of the 1-chloro-1-methylcycloalkanes is present, with minor differences. It would appear that the solvolysis reactions mentioned[12b] provide a good measure of differences in ring strain as determined by an ionic reaction. Thus the decomposition of the azo compound from cycloheptanone is about 17 times faster than the azo compound from cyclopentanone as contrasted with the very similar rates obtained in the solvolysis of 1-chloro-1-methylcyclopentane and the 1-chloro-1-methylcycloheptane. A difference of about 10 times is noted here for decomposition of the cyclopentanone and cyclohexanone azo compounds whereas Brown and Borkowski reported a difference of 130 times at 25° and 95 times at 35° in the solvolysis of the methylcyclopentyl and methylcyclohexyl chlorides. Roberts and Chambers reported a difference of 15 times at 50° in the rates of acetolysis of the cyclo-

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[11] V. Prelog, *J. Chem. Soc.*, 420 (1950).

[12] (a) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951); (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1898 (1952).

[13] (a) V. Prelog and M. Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949); (b) V. Prelog and O. Hafliger, *ibid.*, **32**, 2088 (1949).

[14] (a) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951); (b) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

[15] W. E. Doering and A. Streitwieser, Abst., 119th Meeting Am. Chem. Soc., 1951, 45M.

pentyl and cyclohexyl *p*-toluenesulfonates. Winstein, *et al.*,[16] reported a difference of 21 for the acetolysis of cyclopentyl and cyclohexyl *p*-toluenesulfonates at 50°, a difference of 19 in the rates for the formolysis at 25° and a difference of 38 in the rates for ethanolysis with similar thermodynamic data as that reported by reference 12b. These differences in rate have been attributed to release of Pitzer or Hassel strain in going to the transition state in the cyclopentyl compounds, a factor not present in the chair configuration of the cyclohexyl compound and it is reasonable to assume that a similar reason is responsible for the difference in rates of the cyclopentyl and cyclohexyl azo compounds. A plot of the log of the rate constants for decomposition against ring size is shown in Fig. 3.

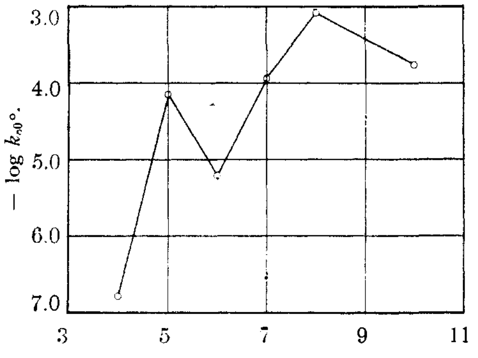

Fig. 3.—Variation of ring size with rate of decomposition.

The order of the activation energies is roughly approximated by the decomposition rates. The entropies of activation are all positive and some interesting differences are noted. The small entropy change for the cyclobutyl compound probably indicates considerable rigidity in its transition state and very little gain in degrees of freedom as the carbon–nitrogen bond is broken. The large change for the cyclopentyl compound indicates a large gain in degrees of freedom in the transition state over that in the ground state. Interestingly, Brown and Borkowski[12b] attribute most of the difference in rate of solvolysis of 1-chloro-1-methylcyclobutane and the cyclopentyl and cyclohexyl compounds to the heat term whereas as noted, a rather large portion of the difference in rates of decomposition of the cyclobutyl and cyclopentyl azo compounds is due to the entropy term. The lower positive values for the cycloheptyl, cyclooctyl and cyclodecyl compounds indicate more degrees of freedom in the ground state and thus less gain in going to the transition state. It seems logical to assume that much of this can be attributed to ring oscillation over and above simple rotational and vibrational degrees of freedom of single bonds.

Unpublished entropies of activation for linear compounds of the type described in reference 3a range from +8 to +15 e.u. so that no simple comparisons can be made at this time.

BROOKLYN, NEW YORK

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[16] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

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

Reactions of Biradicals in Solution.[1] Decomposition Products Obtained from the Oxidation of 3,7-Dicyano-3,7-dimethylhomopiperidazine

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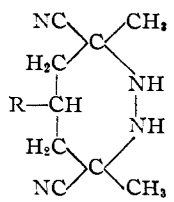
On oxidation of 3,7-dicyano-3,7-dimethylhomopiperidazine, three products (V, VI, VII) resulting from the biradical $CH_3-\dot{C}(CN)-(CH_2)_3(CN)\dot{C}-CH_3$ have been isolated and their structures determined. Two of these products (V and VI) were shown to be *cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclopentanes. The structure of a third product (VII), 2,6-dicyanoheptene-2 was demonstrated. A cyclic radical displacement mechanism to explain the formation of VII is proposed.

A previous paper in this series[4] has described the preparation of 3,7-dicyano-3,7-dimethylhomopiperidazine (I, R = H) and the corresponding 3,5,7-trimethyl compound (I, R = CH_3). Oxidation of I, R = H, gave a quantitative evolution of nitrogen, two solid products and one liquid product. This paper describes the isolation and proof of structure of these products. In particular, we were interested in determining the course of an internal radical displacement reaction (see Discussion).



I, R = H, CH_3

Discussion

Additional experimental confirmation that I is the structure indicated for the reaction product from δ-diketones, cyanide ion and hydrazine has

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[1] This is the ninth in a series of papers concerned with the decomposition of azo compounds. For the eighth, see C. G. Overberger, Harry Biletch, A. B. Finestone, J. Lilker and J. Herbert, THIS JOURNAL, **75**, 2078 (1953).

[2] A portion of a thesis submitted by Pao-tung Huang 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 portion of a thesis submitted by Mr. T. B. Gibb, Jr., in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of the Polytechnic Institute of Brooklyn.

[4] C. G. Overberger, T. B. Gibb, Jr., Sheldon Chibnik, Pao-tung Huang and J. J. Monagle, THIS JOURNAL, **74**, 3290 (1952).