

Thermal Decomposition of 3-Bromocyclohexene.—Pure 3-bromocyclohexene (10.0 g., 0.062 mole) was mixed with carbon tetrachloride (75 ml.) and refluxed for 2 days. During this period a very slow stream of nitrogen swept out any gaseous products into a Dry Ice trap and then into an aqueous 5% silver nitrate solution. The silver nitrate solution developed only a very faint cloudiness. The carbon tetrachloride solution was diluted to 100 ml. and two 5-ml. aliquots were analyzed for double bonds^{49a}; found: 0.0682, 0.0685 total equivalent of double bonds. This represents about a 10% increase in the number of double bonds over that present in the starting material. The remainder of the mixture was worked up as in the control run and gave 3-bromocyclohexene (7.4 g., b.p. 59–60° (15 mm.), n_D^{20} 1.5304) and a dark residue (0.9 g.). The small amount of material in the Dry Ice trap apparently was largely hydrogen bromide; it fumed strongly in air and with gaseous ammonia, the fumes being acid to litmus, and gave instantaneously a light yellow precipitate with aqueous silver nitrate. Pure 3-bromocyclohexene does not fume in air or with gaseous ammonia and its reaction with aqueous silver nitrate, although rapid, is not instantaneous.

Effect of Modifiers on Reaction Time.—At least two runs (0.0067-mole size) were made with each substance studied, with an average of a little more than three runs per substance. In these runs the time for complete reaction was taken as the value midpoint of the range usually given; the difference between the upper and lower limits of this range was 6 min. for the long runs (>90 min.) and decreases to 2 min. for short runs (<15 min.). All of the modifiers were tried on cyclohexene 0.022 *M* in peroxide, prepared by diluting cyclohexene freshly distilled from sodium with aged cyclohexene containing less than 0.150 *M* peroxide. About one-third of the modifiers were also tried with cyclohexene freshly distilled from sodium (essentially peroxide-free cyclohexene) and with cyclohexene 0.088 *M* in peroxide. In the runs using cyclohexene containing 0.022 or 0.088 *M* peroxide, the resultant concentrations of cyclohexenyl hydroperoxide in the reactant solutions were, respectively, 0.0037 or 0.0148 *M*; on the same basis, limiting reaction times in Fig. 1 were found to occur at peroxide concentrations of about 0.006 *M*. The results of these runs are summarized in Table II as relative reactivities, *i.e.*, the ratio of the time of reaction for an unmodified run to the time of reaction for a modified run, both runs being made with the same reagents. This means of comparing

results was necessary since it was observed that different batches gave somewhat different reaction times even though purified in an apparently identical manner; expressed in this manner the relative reactivities were fairly reproducible and independent of the batch of NBS used. Relative reactivities were difficult to reproduce when hydroquinone or tetrabromohydroquinone were used, probably due to their marked insolubility in carbon tetrachloride, and when water was added as modifier; a small amount of water very finely dispersed in the carbon tetrachloride usually gave a strong catalytic effect while an equal quantity of water present as two or three relatively large droplets showed essentially no effect. The actual times for runs summarized in Table II varied from 14 min. to greater than 688 min. for 0.00 *M* peroxide runs, from 8 min. to greater than 240 min. for 0.022 *M* peroxide runs, and from 5 min. to greater than 71 min. for 0.088 *M* peroxide runs.

Several check runs were made using modifiers with a nitrogen atmosphere but no differences in reaction times were observed. However, some evidence has been obtained which indicates that dissolved oxygen may act as an inhibitor. Cyclohexene, artificially aged by bubbling oxygen through it at room temperature for several minutes and then allowing it to stand in a stoppered bottle for 2–3 days, was 0.0353 *M* in peroxide and gave a reaction time of 80–85 min. After deoxygenation by bubbling oxygen-free nitrogen through it for 1 hr., the cyclohexene then was 0.0303 *M* in peroxide and showed a reaction time of 70–75 min. Providing that the presence of dissolved oxygen does not interfere with the accuracy of the determination of peroxide concentrations, as found by another analytical method,^{23d} the shorter reaction time given by the deoxygenated cyclohexene possibly indicates an inhibitory effect of oxygen.

Effect of Modifiers on Yields of Products.—These 0.10-mole runs were made with cyclohexene 0.022 *M* in peroxide, except for the use of peroxide-free cyclohexene in the triethylamine run; the amounts of modifiers used, in mole per cent., were: 1% azo-bis-isobutyronitrile, 1% benzoyl peroxide, *ca.* 2–3% hydrogen bromide, 2% piperidine, 2% pyridine, 2% triethylamine and *ca.* 1–3% water. The runs were conducted in the same way as for the control run and again only distillation fractions 1 and 3 were used for comparing yields with the control run. The results are summarized in Table III.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY RUTGERS, THE STATE UNIVERSITY]

The Effect of Structure on the Course of Phosphoryl Chloride–Pyridine Dehydration of Tertiary Alcohols

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The scope of phosphoryl chloride–pyridine dehydration of tertiary alcohols has been broadened by a study of several types of model compounds. Steric effects play a large role in controlling the direction of elimination.

Recent interest in the direction of elimination of various groups from tertiary centers¹ as well as the desire to extend the scope of phosphoryl chloride–pyridine dehydration of alcohols prompted a study of the dehydration of several model tertiary alcohols. Examples were taken from the following categories: aliphatic, alicyclic and bicyclic.

Results and Discussion

Aliphatic.—Dehydration of 2-methyl-2-butanol with phosphoryl chloride in the presence of a large excess of pyridine gave a mixture of 2-methyl-2-butene (73%) and 2-methyl-1-butene (27%).

(1) (a) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *THIS JOURNAL*, **79**, 4729 (1957); (b) H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, *ibid.*, **80**, 4588 (1958); (c) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956); (d) R. A. Benkeser and J. Hazdra, *ibid.*, **81**, 228 (1959).

Since it was shown that the ratio of products was not affected by the reaction conditions, the fact that the yields are sometimes low is probably of little significance.

The product composition found is not surprising in view of the experiments of Brown and Moritani^{1c} who demonstrated the importance of the steric requirements of the leaving group in elimination reactions. A close analogy to the present work involved the dehydration of 2-methyl-2-butanol with *p*-toluenesulfonyl chloride and pyridine.² The mixture of olefins obtained (63:37) agrees qualitatively with the present results.

Alicyclic.—1-Methylcyclopentanol, 1-methylcyclohexanol and 1-methylcycloheptanol were pre-

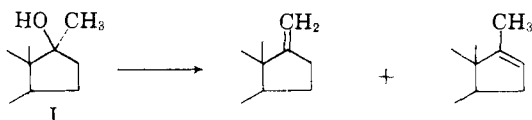
(2) Although the exact nature of the leaving group has not been determined in either case, it seems reasonable to assume that ester formation^{1c} (R–OSO₂C₂H₅ and R–OP(O)Cl₂) precedes elimination.

pared and subjected to phosphoryl chloride-pyridine dehydration. In all cases the endocyclic olefin predominated as seen from Table I. This is interpreted as evidence that the transition state for this reaction involves considerable double bond character.³

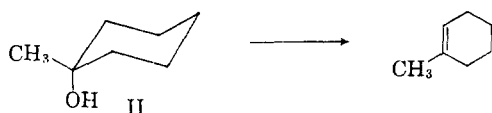
TABLE I
POCl₃-PYRIDINE DEHYDRATION OF ALCOHOLS

Alcohol	<i>endo</i> -Olefin, %	<i>exo</i> -Olefin, %
1-Methylcyclopentyl	91	9
1-Methylcyclohexyl	99	1
1-Methylcycloheptyl	75	25

It is of considerable interest to compare these results with those obtained from similar systems in more rigid ring structures. Julia and Heusser⁴ found that the steroidal alcohol I gave exocyclic endocyclic olefins in the ratio of 1:1.6, a rather striking result in view of the ratio obtained (1:10) in the unsubstituted system. Although interpretation of these results is complicated by the unknown effect of the fused ring on the relative stability of the *exo* versus the *endo* isomer, it is clear that considerable conformational rigidity is imposed on the fused five-membered ring by the adjacent six-membered ring.



Elimination of water from six-membered rings has been studied more thoroughly.⁵ It has been found that equatorial alcohols give predominantly exocyclic olefins, whereas axial alcohols lead to endocyclic olefins. These results suggest that the preferred mode of elimination involves a *trans* orientation of the leaving groups and that a symmetrically solvated carbonium ion is not an intermediate. Thus, elimination of water from 1-methylcyclohexanol apparently proceeds *via* conformation II with the hydroxyl group in the axial position.



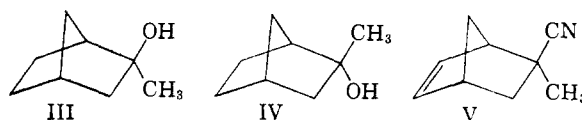
Although the 1-methylcycloheptanol system occurs in several natural products and derived compounds, phosphoryl chloride-pyridine dehydration does not appear to have been tried on these compounds.

Bicyclic.—The two examples studied were 2-exohydroxy-2-*endo*methylnorbornane (III) and 2-*endo*hydroxy-2-*exo*methylnorbornane (IV).

(3) R. B. Turner and R. H. Garner, *THIS JOURNAL*, **80**, 1424 (1958), have shown that 1-methylcyclopentene and 1-methylcyclohexene are more stable than their exocyclic isomers. It seems reasonable to assume the same is true for 1-methylcycloheptene.

(4) S. A. Julia and H. Heusser, *Helv. Chim. Acta*, **35**, 2080 (1952).

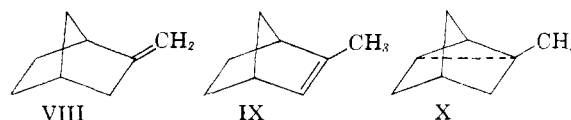
(5) H. Heusser, N. Wahba and F. Winternitz, *ibid.*, **37**, 1052 (1954); D. H. R. Barton, A. daS. Campos-Neves and R. C. Cookson, *J. Chem. Soc.* 3500 (1956).



Alcohol III was prepared in a similar manner to that of Beckmann and Schaber.⁶ Cyclopentadiene and methacrylonitrile condensed to give 5-*exoc*yano-5-*endo*methyl-2-norbornene (V).⁷ Partial hydrolysis of nitrile V gave 5-*endo*methyl-2-norbornene-5-*exoc*arboxamide (VI) which was hydrogenated to give 2-*endo*methylnorbornane-2-*exoc*arboxamide (VII).^{6,7} Oxidation of the amide with hypobromite gave an amine which on diazotization gave the desired alcohol III in 40% yield from VI.

The epimeric alcohol IV was prepared by addition of methylmagnesium iodide to norcamphor.⁶ Although it was not possible to assess the homogeneity of the two alcohols by gas-liquid chromatography on either a silicone or carbowax column, a study of their infrared spectra indicated that the two isomers were substantially free of one another.

Dehydration of alcohols III and IV would be expected to give mainly either 2-methylenenorbornane (VIII) or 2-methyl-2-norbornene (IX).⁸ A third possible product would be methylnortricyclicene (X), since analogous tricyclic products



have been formed under more vigorous conditions in other systems.⁹ Indeed, trace amounts of a third component were observed in the phosphoryl chloride-pyridine dehydration products. Since the percentage of this component increased under more vigorous dehydrating conditions (distillation over *p*-toluenesulfonic acid) it seems likely that X is the third component.

The two major components of the mixture of dehydration products were identified by comparison (gas chromatography and infrared) with synthetic samples prepared by bisdecarboxylation.¹⁰ This important reaction has been extended to the preparation of exocyclic methylene groups. The mixture (XIa and XIb) obtained by Diels-Alder condensation of itaconic acid and cyclopentadiene followed by reduction¹¹ was bisdecarboxylated in 17% yield to give 2-methylenenorbornane.

(6) S. Beckmann, R. Schaber and R. Bamberger, *Ber.*, **87**, 997 (1954).

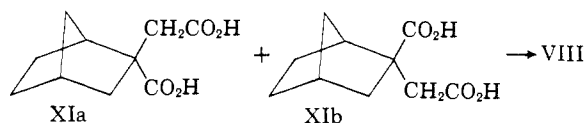
(7) V. G. Yashunskii, A. P. Terent'ev and Ya. G. Nekhlin, *Zhur. Obshchei Khim.*, **26**, 723 (1956), have also carried out this reaction but did not assign any configuration to the product; W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *THIS JOURNAL*, **80**, 5488 (1958), assigned the correct structure on the basis of analogy and the correspondence of the melting point of the amide.

(8) S. Beckmann and R. Schaber, *Ann.*, **585**, 154 (1951).

(9) The usual conditions involve distillation over potassium acid sulfate; for numerous examples, see J. Simonsen and L. N. Owen, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, 1937. See also P. von R. Schleyer, *THIS JOURNAL*, **80**, 1700 (1958), and Abstracts of the 130th A.C.S. Meeting, Atlantic City, N. J., p. 29-0.

(10) W. von E. Doering, M. Farber and A. Sayigh, *ibid.*, **74**, 4370 (1952).

(11) B. E. Tate and A. Bavey, *ibid.*, **79**, 6519 (1957).



The results of the various dehydrations are summarized in Table II.

TABLE II
DEHYDRATIONS OF ALCOHOLS III AND IV

Alcohol	Reagents			
	POCl ₃ -C ₆ H ₅ N % <i>exo</i>	% <i>endo</i>	C ₂ H ₅ SO ₃ H % <i>exo</i>	% <i>endo</i>
III	69	31	71	27
IV	80	20	80	15

The formation of large amounts of the endocyclic isomer IX was unexpected in view of the fact that *trans* elimination between positions 2 and 3 in the norbornane system is known to be energetically unfavorable relative to *cis* elimination.¹² It was expected that *trans* elimination into the methyl group to produce the exocyclic isomer VIII would be virtually the exclusive course of the elimination. The results of acid-catalyzed dehydration preclude the possibility that the endocyclic isomer is much more stable than the exocyclic isomer.⁹ The most likely rationale is that *trans* elimination into the methyl group is hindered by the methylene and ethylene bridges. Since the approach of pyridine to a *trans* hydrogen of the methyl group of III would be expected to be more difficult than the analogous approach in IV, it is not surprising that alcohol III gives less of the exocyclic product.

Acknowledgment.—We wish to thank Mr. S. Schulte for the preparation of several of the compounds used in this study.

Experimental

Dehydration of 2-Methyl-2-butanol with Phosphoryl Chloride-Pyridine.—To an ice-cold solution of 15 g. (0.17 mole) of 2-methyl-2-butanol in 150 ml. of dry pyridine was added 28 ml. (0.3 mole) of phosphoryl chloride over 1 hr. The temperature rose to 52° and then subsided. The reaction mixture was poured cautiously into 1 l. of water and the hydrocarbon layer was separated. After thorough washing with ice-water the olefin mixture (6.3 g., 53%) was dried over sodium sulfate and analyzed on a 5.5' column of silver nitrate-diethylene glycol on Celite.¹³ The major peak (73%) was identified as 2-methyl-2-butene by comparison with a sample prepared by sulfuric acid-catalyzed dehydration.¹⁴ Weak absorption at 11.2 μ confirmed the presence of 2-methyl-1-butene.

Control Experiment.—A solution of 5.3 g. of the above mixed olefins in 100 ml. of pyridine was cooled to 0° and treated successively with 10 ml. of phosphoryl chloride and 1 ml. of water. After 30 min. the recovered olefins (1 g.) had the same composition as the initial mixture.

Dehydration of 1-Methylcyclopentanol.—An ice-cold solution of 8.3 g. (0.083 mole) of 1-methylcyclopentanol in 95 ml. of pyridine was treated with 17 ml. (0.19 mole) of phosphoryl chloride over 30 min. After stirring for 30 min. at 0° and 30 min. at 27°, the reaction mixture was diluted with water and the olefins isolated, yield 3.8 g. (53%). Analysis on the silver nitrate column gave two peaks; the major peak (91%) was identified by comparison with a sample of 1-methylcyclopentene prepared by distillation of 1-methylcyclopentanol over *p*-toluenesulfonic acid.¹⁵ The identity of the minor peak was inferred to be methylenecyclopentane from the presence of weak absorption at 11.3 μ.

(12) S. J. Cristol and E. F. Hoegger, *THIS JOURNAL*, **79**, 3438 (1957).
(13) E. Gil-Av, J. Herling and J. Shabtai, *Chemistry & Industry*, 1483 (1957).

(14) J. F. Norris and J. N. Joubert, *THIS JOURNAL*, **49**, 873 (1927).

Dehydration of 1-Methylcyclohexanol.—Dehydration of 10 g. (0.088 mole) of 1-methylcyclohexanol in 100 ml. of pyridine with 20 ml. (0.22 mole) of phosphoryl chloride (2 hr. at 0°) gave 6.3 g. (75%) of 1-methylcyclohexene. About 1% of methylenecyclohexane could be detected by gas chromatography on the silver nitrate column. Identity of the two peaks was confirmed by comparison with the mixture prepared by dehydration of 1-methylcyclohexanol over *p*-toluenesulfonic acid which was reported by Cope, *et al.*,¹⁶ to give 2-5% methylenecyclohexane; found 3.5%.

1-Methylcycloheptanol.—Reaction of cycloheptanone¹⁵ with methylmagnesium iodide gave 1-methylcycloheptanol, b.p. 123-127° (136-138 mm.) (lit.¹⁶ b.p. 183-185°). A small amount of 1-methylcycloheptene was obtained as a fore-run, b.p. 132-133°, *n*_D²⁰ 1.4567 (lit.⁷ b.p. 136°, *n*_D²⁰ 1.4563).

Dehydration of 1-Methylcycloheptanol.—The alcohol (5.6 g., 0.039 mole) in 100 ml. of pyridine was dehydrated by addition of 11 ml. (0.12 mole) of phosphoryl chloride over 30 min. The temperature rose to 58° during the addition. The temperature gradually fell during the next 40 min. at which time the reaction was quenched with water to give 3.4 g. (79%) of olefins. Gas chromatographic analysis on silver nitrate at 68° indicated the presence of 75% 1-methylcycloheptene. Weak absorption at 11.2 μ coupled with strong absorption at 11.8 μ as well as the order of elution¹⁷ served to identify the two peaks on the chromatogram. The infrared spectrum was very similar to that of the 1-methylcycloheptene isolated from the Grignard reaction.

5-*exo*Cyano-5-*endo*methyl-2-norbornene(V).—A solution of 300 g. (4.54 moles) of cyclopentadiene and 210 g. (3.13 moles) of methacrylonitrile¹⁸ in 480 ml. of dry xylene was heated at reflux for 14.5 hr. The low-boiling materials were removed under vacuum and the residue was distilled to give 160 g. (39%) of 5-*exoc*cyano-5-*endo*methyl-2-norbornene as a waxy solid, b.p. 106° (28 mm.), m.p. 60-61° (lit.⁷ b.p. 67-69° (6 mm.), m.p. 55°).

5-*endo*Methyl-2-norbornene-5-*exoc*carboxamide (VI).—Hydrolysis of the nitrile was effected by heating for 18 hr. with 344 g. of potassium hydroxide in 650 ml. of ethanol. Crystallization of the product from water gave 99 g. (54%) of the amide VI, m.p. 155-157° (lit.⁷ m.p. 159-160°, 150-151°).

2-*endo*Methylnorbornane-2-*exoc*carboxamide (VII).—Reduction of 99 g. (0.65 mole) of amide VI with hydrogen in ethanol in the presence of palladium-charcoal gave 77 g. (77%) of the saturated amide VII on crystallization from water-ethanol, m.p. 158.5-159° (lit.⁶ m.p. 158-159°).

2-*exo*Hydroxy-2-*endo*methylnorbornane (III).—A solution of sodium methoxide prepared by reaction of 18.4 g. (0.80 g. atom) of sodium with 680 ml. of dry methanol was added to a solution of 61 g. (0.40 mole) of amide VII in 200 ml. of methanol. Bromine (21 ml., 0.4 mole) was added rapidly and was followed by heating on the steam-bath for 10 min. The solution was neutralized with glacial acetic acid and evaporated to near dryness. The solids were dissolved in water and the mixture was extracted with low-boiling petroleum ether. Evaporation of the extracts gave an oil which was dissolved in 500 ml. of methanol and treated with a solution of 250 g. of potassium hydroxide in 175 ml. of water. The resulting solution was heated at reflux for 26 hr. and followed by a steam distillation. The total distillate was acidified with concentrated hydrochloric acid and evaporated to dryness to give 44 g. of the amine hydrochloride.

The salt was dissolved in a solution of 25 ml. of glacial acetic acid in 150 ml. of water and diazotized by rapid addition of a solution of 25 g. of sodium nitrite in 70 ml. of water. After 3.5 hr. at 28° the reaction mixture was steam distilled. The distillate was warmed with dilute potassium hydroxide solution and steam distilled again. The distillate was extracted with ether and the dried extracts were distilled to give 20 g. (40% based on amide VII) of 2-*exohydroxy*-2-*endo*methylnorbornane, m.p. 62-74°, b.p. 75-76° (16-18 mm.) (lit.⁶ m.p. 86°, b.p. 79° (18 mm.)).

2-*exo*Methyl-2-*endo*hydroxynorbornane (IV).—Addition of 27.2 g. (0.247 mole) of norcamphor in 110 ml. of dry ether

(15) Th. J. DeBoer and H. J. Backer, *Org. Syntheses*, **34**, 24 (1954).

(16) O. Wallach, *Ann.*, **345**, 139 (1906).

(17) Since the more highly strained olefins form stronger complexes with Ag⁺ (J. G. Traynham and M. F. Sehnert, *THIS JOURNAL*, **78**, 4024 (1956)) they are eluted with greater difficulty.^{1b,13}

(18) Kindly provided by Eastman Chemical Products, Inc., Kingsport, Tenn.

to the Grignard reagent prepared from 71 g. (0.5 mole) of methyl iodide with 12 g. (0.5 g. atom) of magnesium in 125 ml. of ether was followed by stirring at 28° for 16 hr. and standing for 24 hr. at 28°. The mixture was poured into a mixture of 200 g. of ice and a solution of 30 g. of ammonium chloride in 60 ml. of water. Separation of the layers was followed by ether extraction. The extracts were combined, dried and distilled to give 26 g. (88%) of alcohol IV, b.p. 86–88° (30 mm.), freezing point *ca.* 29°. Beckmann, *et al.*,⁶ report this product as an oil, b.p. 83° (20 mm.).

Dehydration of 2-*exo*Methyl-2-*endo*hydroxynorbornane (IV). a. Phosphoryl Chloride-Pyridine.—Five grams (0.04 mole) of alcohol IV in 50 ml. of pyridine was treated with 16 ml. (0.175 mole) of phosphoryl chloride over 1 hr. The temperature was allowed to rise to 52°. After cooling, the reaction mixture was quenched to give 1.7 g. (40%) of olefins. Analysis of the mixture by gas chromatography on a dimethyl sulfolane-Celite column gave the values 80% VIII and 20% IX. Less than 1% of a more volatile material was present; $\lambda_{\text{max}}^{\text{film}}$ 11.35(s) and 12.4(w) μ .

b. *p*-Toluenesulfonic Acid.—Distillation of 1 g. of alcohol IV over a few crystals of *p*-toluenesulfonic acid gave 0.6 g. of olefin which gave the following analysis: 80% VIII, 15% IX and 5% of the more volatile component.

c. Phthalic Anhydride.—Distillation of 3 g. of IV over 3 g. of phthalic anhydride⁶ gave 61% VIII and 39% IX.

Dehydration of 2-*exo*Hydroxy-2-*endo*methylnorcamphane (III). a. Phosphoryl Chloride-Pyridine.—Ten ml. (0.11

mole) of phosphoryl chloride was added to a solution of 5 g. (0.04 mole) of alcohol III in 50 ml. of pyridine. The solution was allowed to warm to 75° and then was kept at 27° for 2 hr. After heating to reflux the mixture was cooled and poured onto ice-water. The olefin mixture (1.2 g., 28%) contained 69% VIII, 31% IX and less than 1% of a more volatile component; $\lambda_{\text{max}}^{\text{film}}$ 11.35(s) and 12.4(w) μ .

b. *p*-Toluenesulfonic Acid.—Distillation of 1 g. of III over a few crystals of *p*-toluenesulfonic acid gave 0.5 g. of olefins containing 71% VIII, 27% IX and 2% of the more volatile component.

2-Methylenenorcamphane (VIII).—The adduct from itaconic acid and cyclopentadiene¹¹ was crystallized once from benzene and hydrogenated over platinum in ethanol. A mixture of 25 g. of diacids XIa and XIb with 60 g. of powdered Pyrex and 60 g. of lead dioxide (Baker analyzed) was slowly heated to 210°. A mixture of water and methylenenorcamphane gradually distilled. The phases were separated and the organic layer was dried over sodium sulfate and distilled to give 2.35 g. (17%) of VIII, n_D^{25} 1.4710 (lit.⁸ n_D^{25} 1.4719). Gas chromatographic analysis indicated that about 2% of IX was present; $\lambda_{\text{max}}^{\text{film}}$ 11.35 μ (C=C₂).

2-Methyl-2-norbornene (IX) was prepared according to Beckmann, *et al.*,⁸ and had n_D^{25} 1.4616 (lit.¹⁹ n_D^{20} 1.4621); $\lambda_{\text{max}}^{\text{film}}$ 12.4 μ (C=C—H).

(10) K. Alder, R. Hartmann and W. Rath, *Ann.*, **613**, 6 (1958).

NEW BRUNSWICK, N. J.

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

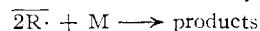
The Decomposition of α, α' -Azoisobutyronitrile in Liquid Bromine

BY ORLIN D. TRAPP AND GEORGE S. HAMMOND¹

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The decomposition of α, α' -azoisobutyronitrile in liquid bromine gives no tetramethylsuccinonitrile. Since the decomposition is no more than a factor of two faster than in other media the spontaneous decomposition is involved. It is concluded that any dinitrile formed in the inefficient decomposition in other solvents must arise from recombination of radicals in the solvent cage and not from non-radical reactions.

It has been suggested that the inefficiency of α, α' -azoisobutyronitrile (ABN), a polymerization and oxidation initiator, is due to primary recombination of the radical pair produced in the first decomposition step.^{2–4} One is hard pressed to devise tests which provide rigorous distinction between radical recombination in the solvent cage and various non-radical side reactions. One possible approach to the problem is the study of the products of decomposition carried out in the presence of high concentrations of very reactive free radical scavengers. Under such conditions one might expect that reactions of the type



will intervene and alter the course of the reaction whereas there should be no interference with non-radical processes.

Such considerations prompted us to study the decomposition of ABN in liquid bromine. At the outset we were most concerned with the determination of the yield of tetramethylsuccinonitrile (RR), the product of symmetrical coupling of cyanopropyl

radicals. Careful examination of reaction mixtures showed that the yield of the dinitrile is vanishingly small. In order to ascertain that the usual, unimolecular decomposition of ABN was actually under observation it was necessary to demonstrate that the decomposition was not greatly accelerated in bromine. Kinetic measurements by the usual techniques are not applicable to the bromine system but an estimate of the decomposition rate was obtained by interrupting reactions, removing the bromine and determining the residual ABN by ultraviolet absorption of a benzene solution of the residue. Results showed that ABN was certainly present although an absorbing by-product was also present which obscured the short wave-length minimum in the ABN spectrum. Figure 1 shows the resolution of the experimental spectrum to obtain an analysis for the azo compound. The rate constants calculated from two such experiments were 4.6 and 5.3 $\times 10^{-4}$ sec.⁻¹ at 80.9°. While the rates are faster by a factor of two or more than rates in other solvents at the same temperature we can be assured that at least a considerable amount of decomposition must have occurred by the usual path of decomposition.

The actual reaction products are unknown except that trace amounts of liquid were obtained which distilled near the boiling point of α -bromoisobutyronitrile. Much more of the ABN decomposed may have reacted to give the bromonitrile since it

(1) Division of Chemistry, California Institute of Technology, Pasadena, Calif.

(2) J. C. Bevington, J. H. Bradbury and G. M. Burnett, *J. Polymer Sci.*, **12**, 469 (1954); J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955); J. C. Bevington, *J. Chem. Soc.*, 3707 (1954).

(3) G. S. Hammond, J. N. Sen and C. E. Boozer, *THIS JOURNAL*, **77**, 3244 (1955).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 74 ff.