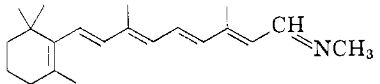
error at every pH between 1 and 3 since, in the measurement of pK_1, if some species other than Ia and Ib were present in varying concentration, the straight-line plot of unit slope in Fig. 1 would not have been obtained.


IV

Semi-quantitative hydrolysis and spectral data for solutions of retinylidenemethylamine (IV) in the pH region 1.0–8.6 indicate that the hydrolysis of this Schiff base has a maximum rate at around pH 5.7.[16] The stability of IV in acid solution is considerably greater than that of any diaryl Schiff base reported. At pH 2.0, it appears to be more stable than I by at least five orders of magnitude. Our rate law and the suggested mechanism do not accommodate a maximum in the log k_f–pH profile. The interpretation of the data on the stability of IV is complicated by the fact that the solutions contained a dispersing agent, Tween 80, which could have stabilized the Schiff base by mixed micelle formation. It has been shown here that some surfactants can stabilize ionic Schiff bases markedly in mildly acid solution at concentrations greater than the critical micelle concentration. It has also been demonstrated that surfactants decrease the rates of hydrolysis of certain indoaniline dyes by several orders of magnitude,[17] presumably by incorporation into micelles. It may be that the uncharged IV and charged conjugate acid have different distribution coefficients between micelle and bulk solvent or different stabilities in their respective micelles. Nevertheless, the observations suggest that an investigation of a solubilized dialkyl anil, having a larger pK than the diaryl Schiff bases, might yield additional information regarding the mechanism of the acid-catalyzed hydrolysis of the —C=N— bond.

Acknowledgment.—We wish to acknowledge aid from W. R. Ruby in the polarographic work and helpful discussions of the kinetics with L. K. J. Tong.

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[16] R. A. Morton and G. A. J. Pitt, *Biochem. J.*, **59**, 128 (1955).

[17] R. L. Reeves and L. K. J. Tong, *J. Am. Chem. Soc.*, **84**, 2050 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

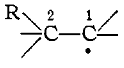
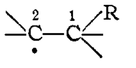
Reactions of the 2-Bornyl Radical. II. A Free Radical Wagner–Meerwein Rearrangement[1]

BY JEROME A. BERSON, CARL J. OLSEN[2] AND JASJIT SINGH WALIA

RECEIVED MARCH 2, 1962

The thermal decomposition of 2-azobornane in the solvents diphenyl ether and *n*-hexadecane at temperatures above 250° gives a mixture of hydrocarbons, among which is 2,3,3-trimethylnorbornane (isocamphane), resulting from formal Wagner–Meerwein rearrangement. The latter hydrocarbon arises by a cleavage–recyclization mechanism, an interpretation supported by the formation of isocamphane as well as bornane, 1-*p*-menthene, tricyclene and bornene in the decomposition of either 2-azocamphane or 1-azo-bis-2-(2,2,3-trimethyl-3-cyclopentenyl)-ethane. Further support for classical rather than mesomeric product-forming intermediates is provided from the normal rates of decomposition of the azo compounds, from the dependence of the product distribution on the source of radicals, and from the stereochemistry of the hydrogen-abstraction by the 2,3,3-trimethyl-2-norbornyl radical, which gives both isomers of isocamphane.

The system I, embodying the formal prerequisites for a vicinal (*i.e.*, 1,2) intramolecular free radical



I R = alkyl II

alkyl group rearrangement to II, has been generated in many reactions,[3] but the rearrangement has consistently failed to occur. Until such a migration has been observed, however, it is impossible to know the rigor of the interdiction against it. A major difficulty in previous studies has been that the methods by which system I has been generated unavoidably have permitted the radical to suffer some fate other than rearrangement: Diversion to a stable product by hydrogen abstraction, dimerization, and disproportionation are usually fast processes, and the alkyl radical rearrangement has not been able to compete with them under the conditions examined. In many cases, aryl groups have been attached to C.2, and these have migrated in preference to the alkyl group. Further, most of the reactions have been carried out at relatively low temperatures, so that processes of high activation energy could not have occurred. In these respects, the alkyl group rearrangement may be said not to have received a fair chance. In the present paper,[1c] we report the first clearly intramolecular example of a free radical alkyl group rearrangement of the type I → II.

Results

The 2-bornyl radical affords a suitable system for study because rearrangements of the related cation are well known and provide a sinigficant comparison

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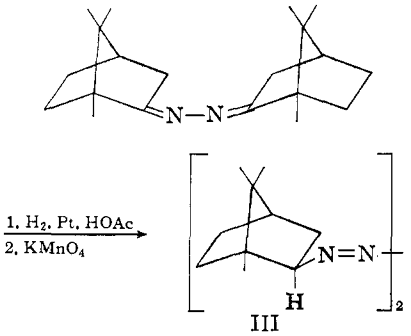
[1] Taken from portions of the dissertations presented by (a) Carl John Olsen and (b) Jasjit Singh Walia in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) For a preliminary report, see J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960). (d) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)-1544. Reproduction in whole or in part is permitted for any purpose of the United States Government. Also supported in part by the Office of Ordnance Research under Contract No. DA-04-495-ORD-532. We are indebted to these agencies, to the Alfred P. Sloan Foundation, and to the Richfield Oil Corporation for support.

[2] Richfield Oil Fellow, 1956–1957.

[3] For a summary of references, see ref. 1c.

with the radical rearrangement. Since the 2-bornyl radical does not rearrange[4] when generated by decarbonylation of 2-formylbornane at 138°, a study of its behavior at higher temperature using 2-azobornane (III) as a convenient source of radicals,[5] is indicated. The azo compound III is prepared from racemic camphor azine by catalytic hydrogenation to 2-hydrazobornane (not isolated) and oxidation of the latter. Although the azo compound thus prepared has a sharp melting point, it is uncertain that it is a single stereoisomer. If it is permissible to draw an analogy between the catalytic hydrogenation of camphor azine and that of camphor, the azo compound probably has predominantly the *exo* configuration at C.2, since catalytic hydrogenation of camphor gives[6] mainly isoborneol (*exo*-hydroxyl). We assume that the stereochemistry of the azo link is *trans*.[7]



III

2-Azobornane suffers ready thermal decomposition at temperature above 250° in the solvents *n*-hexadecane and diphenyl ether. The volatile portion of the product is removed in a vacuum line and the fraction passing through a trap at 0° is analyzed by vapor chromatography. This "volatile fraction" contains 97% of the hydrocarbon product up to and including C_{10} fragments, as is shown by control experiments.

From decompositions in both solvents there is obtained a complex mixture of hydrocarbons. In *n*-hexadecane, fragments derived from the solvent accompany those derived from the azo compound, and all the normal alkanes from C_1 to C_{10} are identifiable in the product mixture. The products from both the diphenyl ether and *n*-hexadecane runs contain olefinic materials, which are readily removed by percolation of a pentane solution of the "volatile fraction" through silica gel.[8]

The identity of the products derived from the azo compound is established: (i) by comparison of the order of emergence and retention times with those of known mixtures on four different vapor chromatographic columns; (ii) by cochromatography of samples of the "volatile fraction" with authentic samples of components suspected to be present; (iii) by the chemical nature (saturated or unsaturated) of each component, as evidenced by persistence or disappearance of the corresponding vapor chromatographic peak after silica gel treatment; and (iv) by preparative vapor chromatography and infrared spectroscopic examination of the resulting fractions. Among the compounds identified by all four criteria are bornane (IV), 1-*p*-menthene (V) and 2,3,3-trimethylnorbornane (isocamphane) (VI), *the latter arising by formal Wagner–Meerwein rearrangement.* In addition, tricyclene (VII) and bornene (VIII) are identified by criteria i, ii and iii, although the application of iv is attended by difficulties (see Experimental). Camphene (VI with $=CH_2$ replacing the lone methyl) cannot be detected by our procedures when present in small amounts and is not observed.

The occurrence of the monocyclic olefin 1-*p*-menthene (V) among the products provides a clue to the mechanism of the rearrangement observed in the formation of VI (see Chart I). *p*-Menthene apparently results from β-elimination in the initially formed bornyl radical IVa; cleavage at C.1–C.7 would lead to the monocyclic radical Va and thence by hydrogen abstraction to V. Of the three remaining formally possible β-eliminations of IVa, the one involving the C.10–C.1 bond is prohibited by Bredt's rule. The one involving the C.3–C.4 bond is not thus prohibited, and although we have not yet found the olefin that would result, it probably is present among the several still unidentified reaction products. Cleavage at C.1–C.6 would lead to monocyclic radical IXa, which could give olefin IX by hydrogen abstraction, radical IVa by re-cyclization at C.1, or radical VIa, the precursor of rearrangement product VI, by cyclization at C.2.

There are strong indications that olefin IX is present in small quantities in the mixture of products from the decomposition of 2-azobornane. An authentic sample of 1,5,5-trimethyl-4-ethyl-1-cyclopentene (IX), prepared as described below, emerges from our analytical gas chromatography columns in a position between those of tricyclene (VII) and bornane (IV). The retention time is very close to that of tricyclene, and consequently IX is not readily discernible by direct gas chromatography unless present in substantial amount. Nevertheless, the infrared spectrum of a vapor chromatographically separated fraction shows absorptions corresponding to those characteristic of authentic IX, and the relative area of the vapor chromatographic peak corresponding to tricyclene is decreased in a sample of the reaction product after passage through silica gel, indicating the presence of olefin.

Support for the hypothesis that monocyclic radical IXa is an intermediate in the formation from azobornane of the rearranged product 2,3,3-trimethylnorbornane (VI) is provided by the behavior of radical IXa generated in an independent manner: The azo compound X is prepared from the aldehyde XI (campholenaldehyde; (2,3,3-trimethyl-Δ^3-cyclopentenyl)-acetaldehyde), which is readily avail-

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(4) J. A. Berson and C. J. Olsen, *J. Am. Chem. Soc.*, **84**, 3178 (1962).

(5) For a discussion of the generation and reactions of free radicals from azo compounds, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 511 ff., and references therein cited.

(6) G. Vavon and P. Peignier, *Bull. soc. chim. France*, [4] **35**, 925 (1924).

(7) For a discussion of the stereochemistry of some aliphatic azo compounds, see C. G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.*, **73**, 2618 (1951).

(8) F. D. Rossini, B. J. Mair and A. J. Streiff, "Hydrocarbons from Petroleum," A.C.S. Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1953, pp. 159–160.

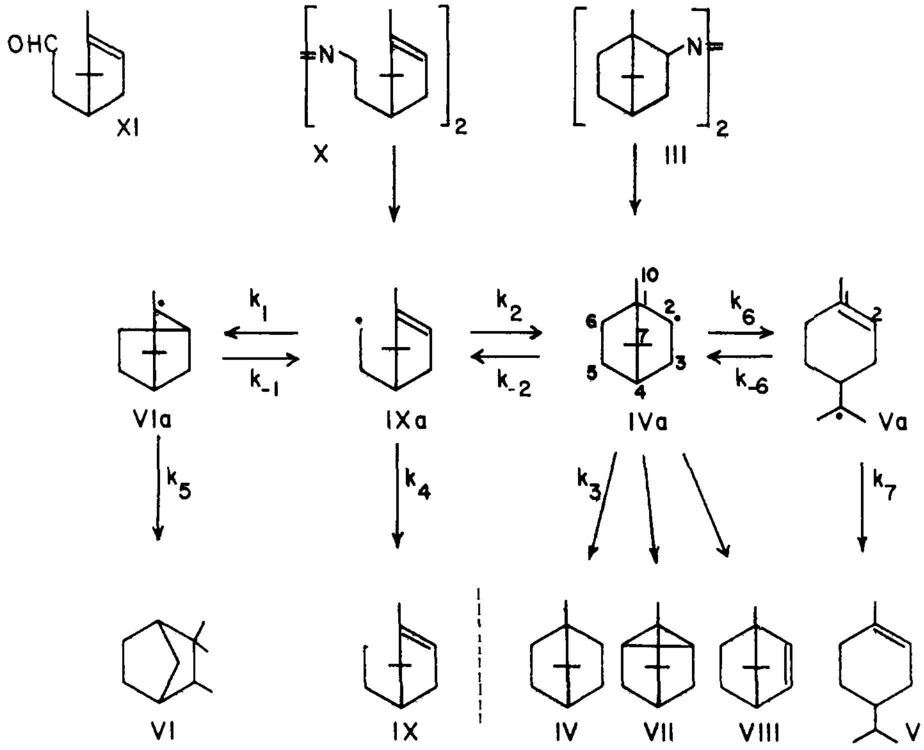

CHART I.

able by zinc bromide-induced rearrangement of α-pinene oxide.[9] Wolff–Kishner reduction of XI gives the pure hydrocarbon IX. Conversion of XI to the azine, lithium aluminum hydride reduction to the hydrazo compound (not characterized) and mercuric oxide oxidation of the latter give the azo compound X as a yellow liquid, $\lambda\lambda_{max}$ 207, 360 mμ, ϵ 7600, 29.5. Under the conditions used in the decomposition of azobornane, X decomposes to give a complex mixture of products, in which the hydrocarbon VI is present. A necessary condition for IXa to be an intermediate in the III → VI rearrangement is thus satisfied (see Chart I).

Radical IXa also cyclizes in the alternative sense to give the 2-bornyl radical IVa, as is shown by the presence of bornane IV and the secondary product 1-*p*-menthene (V) in the reaction mixture. Tricyclene (VII) and a trace of bornene (VIII) are also present.

Isocamphane (VI) is formed from either azo compound as a mixture of stereoisomers in the ratio of about 3:1. The major isomer is the same as that which predominates in the mixture obtained from the catalytic hydrogenation of camphene; in fact, the product ratio in the latter reaction is also about 3:1. Application of the *exo* addition rule[10] suggests that hydrogenation occurs mainly from the *exo* side and consequently that in the major isomer, the lone methyl is *endo*.

The distribution of products from the two azo compounds III and X varies with the reaction conditions. A summary of the results is given in Table I.

The Distribution of Products.—Attack of the radicals on the solvent is apparent in the decompositions in *n*-hexadecane. As judged from the distribution of *n*-alkanes in the product, the attack on the methylene groups in the interior of the solvent chain is relatively indiscriminate, as might be expected; the amounts of butane, pentane, hexane and heptane are all about the same.

There are strong indications that the azo compounds themselves also serve as sources of hydrogen for the radicals. This is reasonable, since the α-hydrogens of aliphatic azo compounds are far more susceptible to abstraction by radicals than are those of the methylene groups of alkanes. The reactivity to CCl_3 radicals per C–H bond relative to 1-hexadecene, which is a much more reactive hydrogen donor than *n*-hexadecane, is 32 for 4,4′-azoheptane and 160 for *sym*-α-phenylazoethane.[11] Thus, although in a 0.17 *M* solution of azo compound in *n*-hexadecane the statistical ratio of aliphatic C–H bonds to α-azo C–H bonds is about 320 for X and 160 for III, the far greater reactivity of the azo C–H bonds still allows the azo compound to compete with the solvent in hydrogen-donating capacity.

The involvement of the azo compounds in hydrogen donation is most pronounced when the initial concentration of these substances is high. At 0.172 *M* initial concentration, the yield of nitrogen is always less than quantitative, suggesting that

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(9) B. Arbusov, *Ber.*, **68**, 1434 (1935).

(10) (a) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); **515**, 185 (1935). (b) An example of this rule that is particularly pertinent to the present case is the one recently reported by S. Beckmann and H. Geiger, who showed that *exo* addition of methyl Grignard reagent is strongly preferred by both isomers of 3-methyl-2-norbornanone [*Chem. Ber.*, **94**, 1905 (1961)].

(11) E. C. Kooyman, *Rec. trav. chim.*, **74**, 117 (1955); *Trans. Faraday Soc.*, **10**, 163 (1951). The relative reactivity ratios would be somewhat lower when based on the presumably more reactive and less selective alkyl radicals encountered in our work.

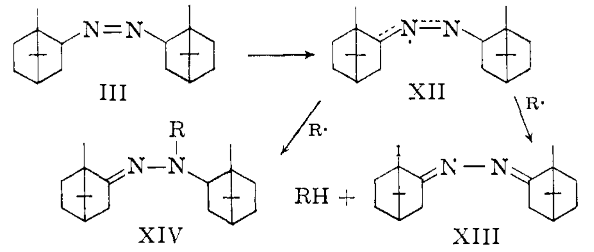
Table I

Products from the Decomposition of Azo Compounds III and X

Expt. no.		4	5	6	7	8	9	10	11
Solvent and azo cpd.		III[a]	III[b]	III[b]	III[b]	III[b]	III[b]	X[b]	X[b]
Temp., °C.		255	255	255	285	285	285	285	285
Init. concn., mole/l.		0.172	0.172	0.0056	0.172	0.0191	0.0056	0.172	0.0196
Apparent % N_2		52	42	95	52	94	145	74	102
G. of "volatiles"/g. of azo cpd.		0.20	0.21	0.67	0.19	0.60	0.96	0.28	0.42
V.P.C. no.[c]	Component	V.P.C. area, relative units							
1-9	[d]	0.005[e]	0.005	0.330	0.244[g]	0.709	2.20	0.466[h]	2.02[h]
10	Octane + olefin[f]	.015	.004	.116	.094	.396	0.630		
11	Olefin[f]	.015	...	.014	.070	.116	.014		
12	Nonane + olefin[f]	.019	.033	.129	.020	.370	.548		
13	Bornene VIII	.141	...	.020	.007	.038	.002	Trace	Trace
14	Tricyclene VII	.063	...	.029	.020	.060	.009	0.292	0.284
15	Olefin IX	.022	...	.028	.010	.030	...	2.08	3.21
16	Bornane IV	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
17	Isocamphane VI	0.130	0.024	0.059	.035	0.080	0.090	0.506	0.333
18	Decane	...	.011	.100	.041	.090	.100	...	...
19	Olefin[f]	.152	...	.007	.002	.065	.029	.808	.740
20	1-*p*-Menthene V	.043	.103	.269	.171	.178	.228	.341	.284

[a] Diphenyl ether. [b] *n*-Hexadecane. [c] In order of emergence. [d] 1 = butane, 2 = pentane, 4 = hexane, 8 = heptane, 3, 9 and 5–7 not identified. [e] Component 7 only. [f] Not identified. [g] Component 6 = 0.006, 1–5 and 7–9 all about 0.02–0.04. [h] Components 1–12.

the radical (*e.g.*, XII) resulting from hydrogen abstraction from the azo compound suffers some other fate. Two such possibilities, giving rise to camphor azine (XIII) and an N-alkyl camphorbornylhydrazone (XIV), are shown. The presence of XIII in a sample of the residue from a decomposition of azo compound III is confirmed by the infrared spectrum, although it is possible that at least some of the XIII may arise by another route (see below).



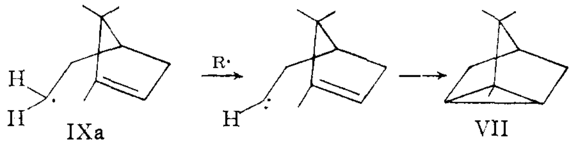
At lower initial concentrations of the azo compound (0.0056 to 0.0196 *M*, runs 6, 8, 9, 11), the yield of nitrogen is much higher. At 0.0056 *M* concentration and 285° (run 9), the yield of gas exceeds the theoretical, methane, ethane and propane being present in the gaseous fraction. These materials are also identified in the gas from runs 5–8.

An increased importance of the solvent as a hydrogen source is also manifested in the higher yields of *n*-alkane products from the runs in *n*-hexadecane at low initial concentration of azo compound. The yields of these products also increase with increasing temperature at a given initial concentration of azo compound (compare runs 6 and 9). This is to be expected if the *n*-alkanes arise by processes such as the sequence 1 and 2; the fragmentation step 1 requires activation energies much higher[12] than those of radical disproportionation or hydrogen-abstraction reactions; consequently it should be more sensitive to a change of temperature and should increase in relative importance with increase of temperature.

$$\mathrm{R'{-}CH_2{-}\underset{\cdot}{C}H{-}R \longrightarrow RCH{=}CH_2 + R'\cdot} \qquad (1)$$

$$\mathrm{R'\cdot + R''H \longrightarrow R'{-}H + R''\cdot} \qquad (2)$$

Tricyclene (VII), previously observed[4] as a disproportionation product of the bornyl radical at lower temperature, is formed from either azo compound III or X under all the conditions of Table I. In addition to the two conceivable mechanisms suggested[4] for the formation of VII from the bornyl radical, we must now also consider the possibility that VII can arise from the monocyclic radical (IXa) by an intramolecular carbene–olefin addition[13]



We have no direct evidence to support such a hypothesis, although it may be significant that tricyclene constitutes a substantially higher fraction of the total "volatile portion" from the decomposition of X than from that of III.

In some of the decompositions of azo compound X, *ammonia* is observed as a product. It is apparently formed in smaller amounts from III, from which it is detectable only in large-scale decompositions. Although it is possible to suggest several mechanisms for production of ammonia from X or III, there is no experimental evidence at present to allow a decision among them. It is reasonable to

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(12) See (a) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, 2nd Edition, Vol. 2, Chapter VI; (b) J. G. Calvert and W. C. Sleppy, *J. Am. Chem. Soc.*, **81**, 1544 (1959); (c) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602 (1960).

(13) For *inter*molecular analogs, see W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 2688 (1954); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496, 6577 (1956).

TABLE II

KINETICS OF THERMAL DECOMPOSITION OF AZO COMPOUNDS

Compound	A, sec.$^{-1}$	$\Delta S^{\ddagger}$ at 250°, e.u.	E_a, kcal./mole	$k_{287°}$, sec.$^{-1}$	Rel. rate at 287°	Ref.
Azocamphane III	4.3×10^{14}	7.2	43.9	2.86×10^{-3}	32.6	^{c}
				9.08×10^{-3a}	..	^{c}
				3.24×10^{-4b}	..	^{c}
X	....	..	..	5.81×10^{-4}	6.7	^{c}
$(\text{Et-N}{=})_2$	5.87×10^{14}	12.5	48.5	8.71×10^{-5d}	1.00	^{e}
$(i\text{-Pr-N}{=})_2$	5.6×10^{12}	3.3	40.9	7.05×10^{-4d}	8.1	^{f}
$(t\text{-Bu-N}{=})_2$	2.2×10^{15}	15.2	42.8	5.52×10^{-2d}	634	^{g}
$[\text{Me}_2\text{C}(\text{C}_6\text{H}_5)\underset{\text{CH}_3}{\text{CH}}\text{-N}{=}]_2$	....	..	..	1.55×10^{-3i}	..	^{h}

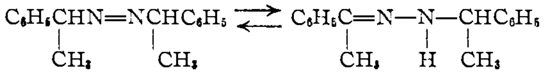
[a] At 269.5°. [b] At 257°. [c] This work; solvent *n*-hexadecane. [d] Gas phase. [e] D. F. Swinehart, as quoted in Levy and Copeland (footnote *g*). [f] H. C. Ramsperger, *J. Am. Chem. Soc.*, 49, 912 (1927). [g] J. B. Levy and B. K. W. Copeland, *ibid.*, **82**, 5314 (1960). [h] Ref. 17. [i] Solvent, diphenyl ether, 255°.

assume that the ammonia-producing process is initiated by radical attack on the azo compound, since ammonia is not observed when the initial concentration of azo compound is low. Regardless of the details, the formation of ammonia involves complex processes. As far as we are aware, there is only one other report of its presence in the products from decomposition of an azo compound, Bickel and Waters[14] having detected it in the reaction mixture from thermal decomposition of ω,ω′-azotoluene.

The most significant aspect of the distribution of products derived from the hydrocarbon moiety of the azo compounds is the dependence on the starting material. In both cases, the major product (IV from III, and IX from X) is derived without alteration of the carbon skeleton.

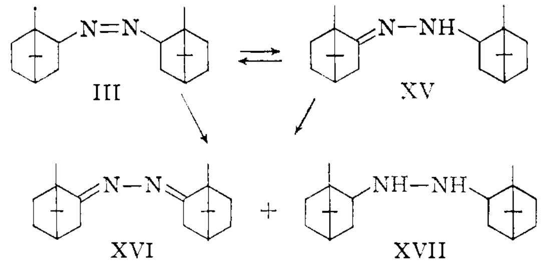
Kinetics.—The rates of decomposition of the two azo compounds, as measured by the liberation of gas, are given in Table II. At low initial concentration of azo compound (0.0196 M), X shows clean first-order kinetic behavior and evolves the theoretical quantity of gas. At higher initial concentration (0.172 M), the apparent first-order rate "constant" drifts downward during a run, and the yield of gas is less than the stoichiometric, implying the consumption of X in side reactions of the type discussed above. With azo compound III, the rate again corresponds to a first-order law at low initial concentration, although the infinity values sometimes differ from the stoichiometric. In these cases, V_∞ is chosen to give the best linear first-order plot by procedures described in the Experimental section. At higher initial concentration, the data cannot be made to conform to first-order plots. The activation parameters given in Table II are calculated from data at 257°, 269.5° and 286.6°.

The decomposition of III apparently is affected by traces of impurities, presumably in the solvent, since a given batch of azo compound sometimes gives little or no nitrogen in one batch of solvent and good yields of nitrogen in another. Peterson and Ross[15] report a similar observation in the decomposition of 1-azo-bis-1-phenylethane. They attribute this behavior to the presence of an acidic impurity which catalyzes the isomerization of their azo compound to the hydrazone



$$\underset{\text{CH}_3}{\text{C}_6\text{H}_5\text{CH}}\text{N}{=}\text{N}\underset{\text{CH}_3}{\text{CH}}\text{C}_6\text{H}_5 \rightleftarrows \text{C}_6\text{H}_5\underset{\text{CH}_3}{\text{C}}{=}\text{N}{-}\underset{\text{H}}{\text{N}}{-}\underset{\text{CH}_3}{\text{CH}}\text{C}_6\text{H}_5$$

Applied to our system, such an isomerization can account for a retardation of the rate of nitrogen evolution but (unless it is essentially irreversible) not for the virtual cessation we observe. As an alternative explanation, we suggest that there is an impurity-catalyzed disproportionation of III (or the isomeric hydrazone XV) to the azine XVI and the hydrazo compound XVII. Some evidence for this scheme is available from an examination of the non-volatile residue from a decomposition of III



after cessation of nitrogen evolution. The ultraviolet spectrum of the residue reveals the presence of 19% of the original azo compound, a quantity sufficient to give a measurable rate of nitrogen evolution if the azo compound were present in the pyrolysis medium. This suggests that the pyrolysis mixture does not actually contain any azo compound, but that the latter is formed from some precursor during the work-up of the reaction mixture. A plausible precursor is the very readily oxidized hydrazo compound XVII. Although the hydrazone XV may be a component of the non-volatile residue, its presence is not established with certainty, since it has no strong absorption distinguishing it from the azine XVI, the presence of which in substantial quantity is indicated by the infrared spectrum.

Although rates of thermal decomposition of azo compounds in solution are probably not strictly comparable to those in the gas phase (as has been pointed out[16,17]) the rate constants and activation parameters observed for III and X in *n*-hexadecane solution are sufficiently close to those reported (Table II) for simple azoalkanes that there is little

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(14) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

(15) R. C. Peterson and S. D. Ross, *Tetrahedron Letters*, No. 23, 18 (1960).

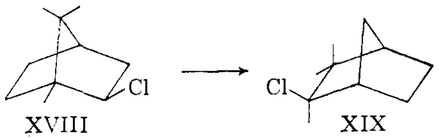
(16) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457 (1955).

(17) C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

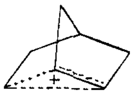
doubt that the reactivities of III and X are normal. Azocamphane III is about four times as reactive as azoisopropane, a model secondary azoalkane at 287° while X is about six or seven times as reactive as azoethane. If it is assumed[16,17] that the decompositions in solution are slightly faster than they would be in the gas phase, a closer correspondence could hardly be expected. The activation parameters for III are also very close to those of the model substances, and the enhancement in reactivity associated with a change from primary (X) to secondary (III) structure amounts to a factor of 4.9, which is roughly commensurate with the factor of 8.1 for the series azoisopropane > azoethane. The rate of decomposition *in solution* of 2-azo-3-methyl-3-phenylbutane, a model secondary azo compound, differs from that of III by only about a factor of five at 255–257°.

Discussion

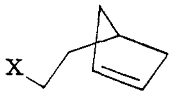
As a guide in interpreting our observations in mechanistic terms, it is helpful to examine the extent to which analogy may be drawn between the azobornane (III) → isocamphane (VI) free radical rearrangement and the structurally similar carbonium ion process, *e.g.*, isobornyl chloride (XVIII) → camphene hydrochloride (XIX). The latter reaction has been studied extensively,[18] and the salient features of the mechanism apply in general to the reactions of other 2-bicyclo[2.2.1]heptyl cations.[18i,19] The points pertinent to the present discussion are: (1) The cationic intermediates are mesomeric (*e.g.*, XX).



XVIII XIX



XX



XXI

(2) As a consequence, the transition state leading to the intermediate benefits energetically from the onset of the mesomerism when, as is the case with *exo* derivatives, solvolytic departure of the leaving group can occur in concert with the movement of the bridging carbon atom. The solvolytic reaction rate is therefore exceptionally fast.[19a]

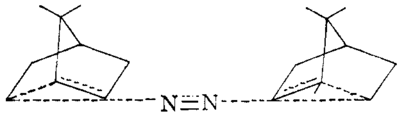
(3) The same mesomeric cation may also be generated by solvolysis of 2-(Δ^3-cyclopentenyl)-ethyl derivatives (*e.g.*, XXI → XX), the rate again being exceptionally fast.[20]

(4) The partial covalences in the intermediate protect the *endo* side of the bridge from attack by external nucleophiles, with the result that *exo* products are formed exclusively.[18i]

(5) Nucleophiles preferentially attack an unsymmetrically substituted ion at that one of the two cationic sites that bears the greater number of alkyl substituents.[18d,g-i,21,22]

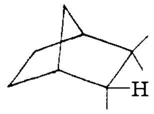
In none of these respects is there any analogy whatsoever between the carbonium ion and radical rearrangements:

Whereas the rate-enhancements observed with anchimerically assisted solvolyses of *exo*-2-bicyclo-[2.2.1]heptyl or 2-(Δ^3-cyclopentenyl)-ethyl derivatives are typically factors of hundreds or thousands, the decompositions of the azo compounds III and X occur at rates that hardly differ from those of simple model substances in which anchimeric assistance is absent. It is unlikely, therefore, that bond delocalization in the alkyl group of the azo compounds (*e.g.*, XXII) plays a significant role in the transition state leading to release of nitrogen. This conclusion is similar to that reached by Overberger and Gainer[17] in their study of the decomposition of 2-azo-3-methyl-3-phenylbutane, where the alkyl group is α-methylneophyl; the product hydrocarbons result entirely from rearrangement of a phenyl group, but the rate of decomposition is normal.

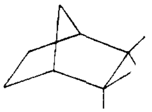


XXII

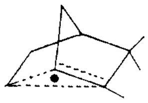
Although the stereochemistry of the hydrogen abstraction step leading to bornane in the decompositions of III and X is not established, that leading to the rearrangement product isocamphane (XXIIIa,b) is non-stereospecific, both isomers being present. While this observation alone does not exclude the possibility that *part* of the product arises from a mesomeric radical XXIV, it is difficult to reconcile with XXIV as the *sole* intermediate.



XXIIIa



XXIIb



XXIV

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(18) *Cf. inter alia* (a) H. Meerwein and K. van Emster, *Ber.*, **53**, 1815 (1920); (b) **55**, 2500 (1922); (c) P. D. Bartlett and I. Pöckel, *J. Am. Chem. Soc.*, **59**, 820 (1937); **60**, 1585 (1938); (d) T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (e) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H Marshall, *J. Am. Chem Soc.*, **74**, 1127 (1952); (f) F. Brown, E. D. Hughes, C K. Ingold and J. F. Smith, *Nature*, **168**, 65 (1951); (g) Y. Pocker, *Proc. Chem. Soc.*, 216 (1960); (h) P. Beltrame, C. A. Bunton and D. Whittaker, *Chemistry & Industry*, 557 (1960). For reviews, see (i) J. A. Berson, in "Molecular Rearrangements," edited by P. de Mayo, Interscience Publishers, Inc., New York, N. Y., in press; (j) P. D. Bartlett, in "Organic Chemistry, an Advanced Treatise," edited by H. Gilman, Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 66; (k) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 482; (l) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(19) *Cf. inter alia* (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952); (b) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (c) S. Winstein, XIVth International Congress of Pure and Applied Chemistry, Experientia Supplementum II. Birkhaüser Verlag, Basel, 1955, p. 137.

(20) (a) P. D. Bartlett and S. Bank, *J. Am. Chem. Soc.*, **83**, 2591 (1961); (b) R. G. Lawton, *ibid.*, **83**, 2399 (1961); for related work in other systems, see (c) G. LeNy, *Compt. rend.*, **251**, 1526 (1960); (d) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

(21) J. A. Berson, *Tetrahedron Letters*, No. **16**, 17 (1960).

(22) For related work in other systems, see J. D. Roberts, Abstracts of Papers, Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959; M. S. Silver, M. C. Caserio, H. E. Rice and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961)

The hydrogen abstraction appears to be sterically rather than stereoelectronically controlled.

That the proximate product of the decomposition of each of the azo compounds, a non-mesomeric radical, is not rapidly converted to a common mesomeric product-forming intermediate XXIV is also attested by the data on the distribution of products.

As is indicated by Table I, the products from azo compound III are formed in proportions drastically different from those from X when the decompositions are carried out under the same conditions of temperature, solvent and initial concentration. At low initial concentration, the azo compound is not a major source of hydrogen. Were a common intermediate formed from either azo compound, its fate would therefore be nearly independent of its antecedent. That this is *not* the case indicates that a common species is not the sole intermediate.

An instructive analysis of the dependence of the product distribution on the starting material can be made on the basis of the scheme of Chart I and the following simplifying assumptions: (i) the radical intermediates may be treated by steady-state methods; (ii) the products once formed are not consumed by reactions with the radicals or by other processes; (iii) the hydrogen source is the solvent, the concentration of which is constant during a run; (iv) radical–radical reactions (dimerization, disproportionation) are of negligible importance in comparison to hydrogen abstractions by radicals. If these assumptions are made, it can be demonstrated that the ratio of any two products on a given side of the dotted line of Chart I is independent of the time and of the source of radicals (X or III), but that the ratio of any two products on opposite sides of the dotted line, while also independent of time, is in the general case not independent of the source of radicals. For example, the ratio IV/V from either azo compound is given by eq. 3, where the primed quantities represent products of the solvent concentration and the rate constant of the corresponding subscript of Chart I.

$$(\mathrm{IV/V})_{\mathrm{X\ or\ III}} = \frac{k_3'(k_{-6} + k_7')}{k_6 k_7'} \qquad (3)$$

The ratio IV/IX, however, depends on the source of radicals, as is indicated by eq. 4 and 5. For the ratio IV/IX to be independent of the starting

$$(\mathrm{IV/IX})_{\mathrm{III}} = \frac{k_3'k_2}{k_4'k_{-2}}\left[1 + \frac{1}{k_2}\left(k_1 + k_4' - \frac{k_{-1}k_1}{k_{-1} + k_5'}\right)\right] \qquad (4)$$

$$(\mathrm{IV/IX})_{\mathrm{X}} = \frac{k_3'k_2}{k_4'k_{-2}}\left[\frac{1}{1 + \frac{1}{k_{-2}}\left(k_6 + k_3' - \frac{k_{-6}k_6}{k_{-6} + k_7'}\right)}\right] \qquad (5)$$

materials it is necessary for k_2 and k_{-2} to be much larger than any other primed or unprimed rate constant in the system, which is kinetically equivalent to a common intermediate or a rapid interconversion of IXa and IVa.

Although the first two of the above assumptions probably are valid at low initial concentration of azo compound, the third and fourth are not, since substantial quantities of disproportionation products are formed. Our earlier conclusion that a common species is not the sole intermediate is not affected by the falseness of these assumptions, but the relationships deduced from Chart I regarding the dependence of the various product ratios on the starting material when each azo compound generates a *discrete* radical (k_2 and k_{-2} not very much larger than any other k) are seriously affected, since eq. 3, 4 and 5 no longer apply. For this reason, it is to be expected that these relationships will be violated, as is observed in Table I.

To complete the destruction of the analogy between the behavior of radicals and cations in the bornyl system, we note that whereas the cation forms stable product predominantly by acquisition of a nucleophile at the tertiary center (to give mainly camphenehydro derivatives), the radical system abstracts hydrogen to give more secondary product (bornane) than tertiary (isocamphane).

There are sound quantum mechanical reasons for expecting free radical alkyl group rearrangements to be energetically less favored than the corresponding carbonium ion processes. The energy levels for the cyclic three-atom pseudo-π-electron system representing a transition state or intermediate for such a rearrangement are distributed in such a way that only two electrons can be placed in bonding orbitals. This accommodates the carbonium ion case, but the extra electron in the radical case must occupy an anti-bonding orbital, with the result that the delocalization energy is less.[23] Depending on the value chosen for the parameter β (the resonance integral), conversion of a simple alkyl radical to the "half-migrated" mesomeric state is π-electronically endothermic by 6–20 kcal./mole, whereas the corresponding change in the cation case is exothermic by about the same amount.[23b] These considerations are in accord with the general experience that free radical rearrangements are rarely encountered, but they do not eliminate the need for a consideration of the structure of the species involved now that the radical rearrangement has been observed.

Even if one disregards the stereochemical evidence, the experimental results make it clear that if one insists upon formulating the reaction with mesomeric species as the sole product-forming intermediates, one is obligated to postulate at least *two* such species, each of which is generated from the corresponding azo compound, gives a characteristic distribution of products and is not in rapid equilibrium with the other. One might imagine the difference between the two mesomeric radicals to be merely a structural one arising from the bond-length difference depicted in Chart II; for example, the radical Xb derived from X might have relatively long bonds from C.6 to C.1 and C.2, while IIIb derived from III might have shorter bonds. To account for the results on such a basis, it is necessary that the rates of isomerization of Xb to IIIb and *vice versa* (characterized by k_i and k_i') be slow compared to the competing reactions (principally hydrogen abstraction). A rough estimate

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[23] (a) J. de Heer, as quoted by S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954); (b) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961); (c) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 380.

of how slow this isomerization rate would have to be is afforded by a comparison with the rate of hydrogen abstraction from *n*-hexane by methyl radicals (eq. 6), which serves as a model for the rates of conversion of Xb and IIIb to products. (Note that the choice of this model is a conservative one, since the actual rates of hydrogen abstraction by IIIb or Xb might reasonably be expected to be even slower.) The rate constant (k_6'') for the model reaction is derived from the experimental[24] ratio k_6''/k_7'' and the absolute value[25] of k_7''; it has the form $\log k_6'' = 6.83 + \log T^{1/2} -$

$$CH_3 + n\text{-}C_6H_{14} \xrightarrow{k_6''} CH_4 + C_6H_{13} \qquad (6)$$

$$2CH_3 \xrightarrow{k_7''} C_2H_6 \qquad (7)$$

8100 cal./mole/2.3RT when k_6'' is expressed in l. mole^{-1} sec.$^{-1}$. In the decomposition of X, with the *n*-hexadecane solvent at about 5 *M* concentration, k_i could not be very much faster than $5k_{px}$ (Chart II) if a set of products different from those arising from III were to be obtained. The value of k_6'' obtained from the above equation is *ca.* 10^5 l. mole^{-1} sec.$^{-1}$ at 287°. Therefore, to the extent that k_6'' is a reasonable approximation of k_{px}, k_i at 287° could not be much greater than *ca.* 5×10^5 sec.$^{-1}$. The change Xb → IIIb is unimolecular and involves merely a minor adjustment of atomic positions. It is hard to imagine that the pre-exponential term for such a process would be very different from "normal" (*i.e.*, *ca.* 10^{13} sec.$^{-1}$). A rate as slow as 5×10^5 sec.$^{-1}$ would therefore imply an activation energy of some 19 kcal./mole! Even with a pre-exponential factor a thousandth as large, the activation energy would still be 11 kcal./mole. Activation energies this large seem entirely unreasonable for a reaction like the hypothetical Xb → IIIb; the conclusion that the scheme of Chart II cannot account for the results seems inescapable.

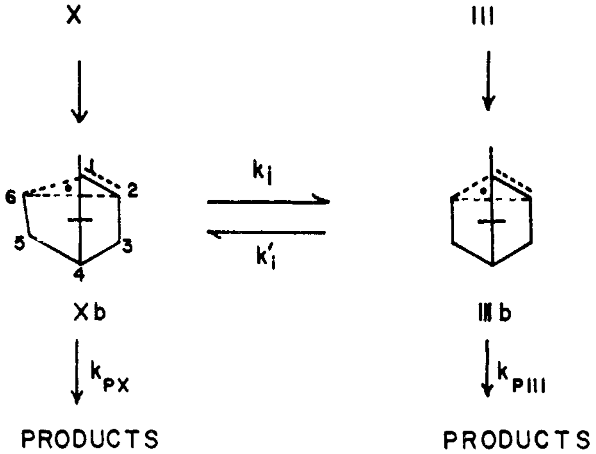

CHART II.

Although we cannot eliminate the possibility that *part* of the 2-azo-camphane–isocamphane rearrangement involves mesomeric intermediates, it is certain that this is not the exclusive path. At least a major fraction of the rearrangement must pass over non-mesomeric intermediates which are most simply designated as classical radicals, as in the scheme of Chart I. The cleavage and re-cyclization steps in the proposed mechanism may pass over *transition states* that are mesomeric, with three atomic centers bonded by three electrons, although no experimental evidence on this point is available. The cleavage–recyclization mechanism, with classical radicals as the product-forming *intermediates*, already shown to be compatible with the nonstereospecificity of hydrogen capture by the isocamphyl radical VIa, with the absence of rate enhancement in the azo compound decompositions and with the dependence of the product composition on the source of the radicals, also explains the absence of rearrangement or ring-opening observed[4] when the bornyl radical is generated at lower temperature: The cleavage step, by analogy to the behavior[12] of simple alkyl radicals, would be expected to have a high activation energy and would be observed only at high temperature. It is likely that cleavage of the bornyl radical is facilitated by the release of strain in the bridged bicyclic ring system.[26] Conversely, the rates of the cyclization steps (IXa → VIa, IXa → IVa) are presumably retarded to some extent relative to the rates for a hypothetical unstrained analog. The effect of the strain in reducing the rate of cyclization is apparently not prohibitive for the formation of a bicyclo-[2.2.1]heptyl ring system. The strain introduced by formation of a bicyclo[3.1.1]heptyl system, however, as in the pinyl radical that would result from cyclization of Va at C.2, may be enough to preclude the reaction. We are unable to find pinane or α-pinene in the product mixture, although the presence of small quantities would have escaped detection.

Although free radical 1,2-rearrangements of alkyl groups appear to be involved in the reaction of 2,2,4-trimethylpentane with oxygen at 450° (from which 2,5-dimethyl-1-hexene and 2-methyl-2-butene are observed among the products),[28] it is not clear that these are true intramolecular processes. As is recognized,[28] these products can also be accounted for by a fragmentation–re-addition mechanism. The objection[28] that the latter mechanism is unlikely because the fragmented radicals would react much faster with oxygen than with the olefins is reasonable but not entirely conclusive. The rearranged products constitute a very small fraction of the reaction mixture, and at the completion of the reaction, the ratio of olefinic products to unconsumed oxygen is 4:1; it is therefore conceivable that the addition of radicals to olefins could compete with the radical–oxygen combination to

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[24] A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

[25] (a) G. B. Kistiakowsky and E. K. Roberts, *ibid.*, **21**, 1637 (1953). (b) *Cf.* S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 303.

[26] Some support for this is available from a study[27] of the *cis*-2-decalyl radical, generated from 2-azo-*cis*-decalin in diphenyl ether at *ca.* 250°. This species gives pure *cis*-decalin, the products of cleavage (4-cyclohexyl-1-butene) and cleavage-recyclization (*trans*-decalin) being absent. Apparently, cleavage of the unstrained *cis*-2-decalyl radical does not occur under conditions that produce cleavage of the bornyl radical.

[27] J. A. Berson and J. W. Wilson, unpublished observations; J. W. Wilson, M.S. Thesis, University of Southern California, 1962.

[28] F. F. Rust and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954).

an extent sufficient to produce the small quantities of rearranged materials observed.

The rearrangement of the bornyl radical observed in the present work is intramolecular perforce, despite the cleavage–recyclization mechanism, because the group that is eliminated (the C.5–C.6 chain of IVa) is firmly tied by its far end to the species from which it is detached and remains so throughout.

Experimental[29]

Camphor Azine (XIII, XVI).—A mixture of 398 g. of racemic camphor, 500 ml. of benzene, 65 g. of 99% hydrazine hydrate and 0.1 g. of *p*-toluenesulfonic acid was heated under reflux in an apparatus equipped with a Dean–Stark trap. The water liberated in the reaction together with some hydrazine that co-distilled was collected, and aliquots were titrated each day to determine the amount of hydrazine lost from the reaction mixture. The calculated amount of hydrazine was added to replenish the loss, and after a total of 4 days of reaction time, the benzene solution was washed with three 50-ml. portions of 5% sodium bicarbonate and three 50-ml. portions of water and dried over calcium sulfate. The benzene and unreacted camphor were removed under vacuum, leaving 556 g. (72%) of crude azine. Three recrystallizations from 95% ethanol gave material of m.p. 186–187.5°, reported[30] for optically active camphor azine, m.p. 185–186°.

Anal. Calcd. for $C_{20}H_{32}N_2$: C, 79.94; H, 10.74; N, 9.32. Found: C, 79.66; H, 11.07; N, 9.27.

2-Azobornane (III).—Camphor azine was recovered unchanged from refluxing solutions of lithium aluminum hydride in ether or tetrahydrofuran under conditions that effected smooth reduction of the azine of the aldehyde described below. Catalytic hydrogenation proceeded without difficulty, however. A mixture of 30 g. of camphor azine, 0.3 g. of platinum oxide and 100 ml. of glacial acetic acid absorbed two molar equivalents of hydrogen in 12 hours, whereupon hydrogenation ceased. The filtered solution was poured into an ice-cold solution of 75 g. of sodium hydroxide in 1500 ml. of water, the precipitated solid was collected at the pump, washed well with water, and dissolved in 150 ml. of pentane. After having been washed with 5% bicarbonate solution and water, the solution was dried over calcium sulfate, and the solvent was removed under vacuum. The residue, 2-hydrazobornane (29.4 g.), was dissolved in 400 ml. of acetone, treated with 20 g. of anhydrous magnesium sulfate, stirred, and treated with portions of a solution of potassium permanganate in acetone until a faint permanganate color persisted. The filtered solution was concentrated under vacuum to a volume of about 150 ml., and the 2-azobornane was allowed to crystallize, giving 23.0 g. (76%) of material of m.p. 161.5–164° (nitrogen-filled capillary). Recrystallization from 95% ethanol gave material with m.p. 164–165° (nitrogen-filled capillary), λ_{max} 368 mμ, ϵ 17.0; reported[30] for optically active 2-azobornane, m.p. 185–186° dec.

Anal. Calcd. for $C_{20}H_{34}N_2$: C, 79.40; H, 11.33; N, 9.26. Found: C, 79.63; H, 11.29; N, 9.22.

Camphor Acetylhydrazone.—To a solution of 60 g. of camphor in 100 ml. of acetic acid was added in portions with stirring 20 g. of 99% hydrazine hydrate. Acetic anhydride (50 ml.) was added and the mixture was heated on the steam-bath for 2 hr. The solution was concentrated to a volume of 50 ml., 50 ml. of 95% ethanol was added, the mixture was heated on the steam-bath for 30 min., and then concentrated to dryness. Two recrystallizations of the residue from 95% ethanol gave 30 g. (37%) of camphor acetylhydrazone, m.p. 189–190.5°; reported[30] for the optically active form, m.p. 210°.

Anal. Calcd. for $C_{12}H_{20}N_2O$: C, 69.19; H, 9.69; N, 13.45. Found: C, 69.04; H, 9.73; N, 13.69.

2-Bornylhydrazine Hydrochloride.—A mixture of 10.5 g. of camphor acetylhydrazone and 0.5 g. of platinum oxide in 100 ml. of acetic acid absorbed one molar equivalent of hydrogen in 3 hr., whereupon the solution was filtered and concentrated to dryness. The residue was treated with 10 ml. of concentrated hydrochloric acid and 50 ml. of methanol, and the whole was again evaporated to dryness under vacuum. The residue was dissolved in 75 ml. of 95% ethanol and the solution was saturated with dry hydrogen chloride. After 2 days at room temperature, 9.5 g. (92%) of colorless, shiny platelets was obtained which, after recrystallization from 95% ethanol, had m.p. 251–252° dec.; reported[30] for the optically active form, m.p. 225°.

Anal. Calcd. for $C_{10}H_{21}N_2Cl$: C, 58.66; H, 10.34; N, 13.69. Found: C, 58.52; H, 10.29; N, 13.88.

The stereochemistry of the hydrazino group is unknown but probably is *exo*.

Camphor 2-Bornylhydrazone (XV).—A solution of 1.8 g. of 2-bornylhydrazine hydrochloride and 2.6 g. of sodium acetate in 15 ml. of water was added to a solution of 3.0 g. of camphor in 30 ml. of 95% ethanol. After having been heated at reflux for 12 hr. in a nitrogen atmosphere and then stored at 0° for 12 hr., the mixture deposited 2.1 g. (79%) of material, which after recrystallization from 95% ethanol, had m.p. 180–180.5° (nitrogen-filled capillary), λ_{max} 232 mμ, ϵ 8400.

Anal. Calcd. for $C_{20}H_{34}N_2$: C, 79.40; H, 11.33; N, 9.26. Found: C, 79.33; H, 11.26; N, 9.09.

Hydrogenation of camphor 2-bornylhydrazone in acetic acid over platinum oxide resulted in consumption of one molar equivalent of gas in 1 hr. The product was oxidized directly with potassium permanganate in acetone to give 2-azobornane, m.p. 163–164° (nitrogen-filled capillary), λ_{max} 368 mμ, ϵ 17.0.

α-Pinene oxide was prepared from racemic α-pinene (see below) according to Arbusov[9] with the modification that monoperphthalic acid was used as the epoxidizing agent instead of peracetic acid. The oxide had b.p. 32–34° (1.5 mm.), n^{20}D 1.4699; reported[9] b.p. 61–62° (10 mm.), n^{20}D 1.4702. This material was also purchased from Food Machinery and Chemical Corporation. The fraction boiling at 65–67° (10.5 mm.) had an infrared spectrum identical with that of the synthetic sample.

Campholenic aldehyde (XI) was prepared according to Arbusov[9] with some modifications of his procedure. The reaction between freshly distilled α-pinene oxide and freshly fused anhydrous zinc bromide was extremely violent when the reagents were mixed at room temperature. The optimum conditions involved addition of the zinc bromide to a cold (0–5°) solution of the oxide in dry benzene and storage of the solution at that temperature for 1 hr., after which time the mixture was allowed to come to room temperature and to stand for 2–3 hr. Most of the solvent was removed at aspirator pressure, and the aldehyde was distilled. It had b.p. 78.5–79° (11 mm.), n^{20}D 1.4652; reported[9] b.p. 83° (12 mm.), $n^{17.5}$D 1.4668.

1,5,5-Trimethyl-4-ethyl-1-cyclopentene (IX) was prepared from XI by the Huang-Minlon modification of the Wolff–Kishner reduction. A mixture of 2.50 g. of campholenic aldehyde, 2.16 g. of potassium hydroxide, 30 ml. of freshly distilled triethylene glycol and 1.6 ml. of 85% hydrazine hydrate was heated at reflux for 1 hr. in an oil-bath kept at 120–130°. The aqueous liquor was removed by simple distillation until the temperature inside the flask rose to 170–180°, whereupon heating at reflux was continued for an additional 4 hr. The reaction mixture and the aqueous distillate were combined, diluted with 20 ml. of water, and extracted with ether. The ethereal extract was washed with water, dried over sodium sulfate, evaporated, and the residue distilled from sodium to give 2.0 g. (88%) of IX, b.p. 68–68.5° (43 mm). An analytical sample, redistilled from sodium, had n^{25}D 1.4429, infrared spectrum free of carbonyl impurity, vapor chromatographically homogeneous.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.85; H, 13.14. Found: C, 86.68; H, 13.21.

An alternative preparation was achieved, albeit in lower yield (49%) by the Cook–Linstead[31] modification of the Wolff–Kishner reaction, in which campholenic aldehyde semicarbazone, m.p. 135–136°, reported[9] m.p. 137–138°, was fused with potassium hydroxide at 145°. The hydrocarbon thus obtained had b.p. 70.5–71° (45 mm.), n^{25}D

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[29] Melting points are corrected; boiling points are uncorrected. The elemental analyses were by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, California, and by Dr. Joseph Alicino, Metuchen, N. J.

[30] K. A. Taipale, *Ber.*, **63**, 243 (1930).

[31] A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).

1.4428, infrared spectrum identical with that of the above sample.

Addition of nitrosyl chloride to a chloroform solution of the olefin at −5° gave two products: the first, extremely soluble in cold pentane, had m.p. 95–96°; the second was obtained as dense volatile crystals, m.p. 122.5–123° after recrystallization from ether–pentane.

Anal. Calcd. for $C_{10}H_8NOCl$: C, 58.95; H, 8.91; N, 6.88. Found (for 123° form): C, 58.85; H, 8.85; N, 6.96.

Campholenic Aldehyde Hydrazone.—A mixture of 45.6 g. of campholenic aldehyde XI, 23.0 g. of 99–100% hydrazine hydrate and 50 ml. of absolute ethanol was heated at reflux for 11 hr. The mixture was cooled, diluted with water and extracted with ether. After having been washed with water and dried over sodium sulfate, the ether solution was evaporated and the residue distilled under reduced pressure to give two fractions: (a) 35 g. (70%) of campholenic aldehyde hydrazone, a colorless liquid, b.p. 95–96° (1.5 mm.); (b) 7.0 g. (8%) of campholenic aldehyde azine (see below), b.p. 164–166° (1.5 mm.), a pale yellow oil.

The hydrazone was unstable and readily disproportionated to a mixture containing the azine and hydrazine. An analytical sample was thrice distilled *in vacuo*, stored under nitrogen, and analyzed within 2 hr. after distillation.

Anal. Calcd. for $C_{10}H_{18}N_2$: C, 72.23; H, 10.91; N, 16.86. Found: C, 72.16; H, 11.00; N, 16.74.

Campholenic Aldehyde Azine.—A mixture of 45.6 g. of aldehyde XI, 7.5 g. of 99–100% hydrazine hydrate and 50 ml. of absolute ethanol was allowed to stand at room temperature for 12 hr., poured into ice-water, and extracted with ether. Isolation of the product was accomplished as in the case of the hydrazone; the azine was a light yellow oil, b.p. 164–166° (1.5 mm.), $n^{25}D$ 1.5028, λ_{max} 206 mμ, log ϵ 4.37 (95% ethanol).

Anal. Calcd. for $C_{20}H_{32}N_2$: C, 79.91; H, 10.74; N, 9.32. Found: C, 79.69; H, 10.75; N, 9.21.

1-Azo-bis-2-(2,2,3-trimethyl-3-cyclopentenyl)-ethane (X).—To a stirred solution of 7.0 g. of lithium aluminum hydride in 50 ml. of anhydrous ether was added dropwise a solution of 24.4 g. of campholenic aldehyde azine in 50 ml. of ether during 30 min. The reaction mixture was stirred for 12 hr. at room temperature and then was cooled in ice and treated slowly and cautiously with 50 ml. of ice-cold 28% potassium hydroxide. The ether layer was decanted off and the inorganic residue was washed with several fresh portions of ether. The combined ether solutions were washed with water, dried with sodium sulfate, and the ether was removed in a current of nitrogen. Distillation of the residue gave 21 g. (89%) of the hydrazo compound as a colorless oil, b.p. 165–170° at 1 mm. This material was not further characterized but was oxidized directly by adding a solution of it in 25 ml. of anhydrous ether to a stirred suspension of 34 g. of yellow mercuric oxide and 10 g. of anhydrous sodium sulfate in 100 ml. of anhydrous ether. In a few minutes, the orange-yellow color of the mixture had turned to brownish-black. Stirring was continued for about 5 hr., and the solids were removed by filtration through diatomaceous earth. The filtrate was evaporated under nitrogen and the residue was distilled to give 13.3 g. (65%) of the azo compound, b.p. 149–154° (1.5 mm.). A small fore-run and an after run which consisted of mixtures of X with unidentified impurities, were not further investigated. The main fraction was re-distilled to give material of b.p. 150–152° (1.5 mm.), $n^{25}D$ 1.4858; λ_{max} 207, 360 mμ, log ϵ 3.88, 1.47.

Anal. Calcd. for $C_{20}H_{34}N_2$: C, 79.41; H, 11.33; N, 9.25. Found: C, 79.37; H, 11.39; N, 9.20.

Omission of the sodium sulfate in the oxidation step reduced the yield of azo compound and produced an increased quantity of the above-mentioned by-products. The latter showed absorption in the 3 μ region of the infrared.

Thermal Decompositions of the Azo Compounds III and X. A. Analysis of Products.—The apparatus for the decompositions was similar to that used[4] for decarbonylation of 2-formylbornane with a few exceptions. The reaction tube and Vigreux column were replaced by a flask fitted with a thermometer well and a standard taper joint connected to a vertical tube bearing a small dropping funnel and having a side arm connected to a cold trap. Freshly distilled solvent was placed in the flask, and the apparatus was repeatedly evacuated and filled with oxygen-free nitrogen (purified by passage through Fieser solution[32] and concentrated sulfuric acid). The exit side of the trap led through a three-way stopcock to a water-jacketed gas buret. The stopcock was set to vent the preliminary nitrogen flow used for flushing and then was re-set to collect the permanent gas liberated during the decompositions. A measured volume of solvent was brought to the desired temperature with a heating mantle. The azo compound was dissolved in a measured small volume of solvent, flushed with nitrogen, and run rapidly into the reaction mixture. There was a brief initial decrease in temperature, but the desired temperature was regained in 1–3 min. by adjustment of the voltage supplied to the heating mantle. Temperature control was ±0.5° at reflux temperature of the solvent and ±0.5–2° otherwise. At the completion of the reaction, the volatile products were analyzed by preliminary fractionation in a vacuum line, as described in the accompanying paper,[4] followed by vapor chromatography.

The vapor chromatographic identification of components was achieved by a comparison of retention times (and co-chromatography) with those of authentic samples. The preparations of authentic samples of **bornane**, **bornene** and **tricyclene** have been described already.[4] A sample of **1-p-menthene** was kindly supplied by Dr. A. Hussey of Northwestern University, to whom we are indebted for this favor. **Isocamphane** (2,2,3-trimethylnorbornane) was prepared by catalytic hydrogenation of camphene[33]; the saturated hydrocarbon product showed two partially overlapping peaks in the vapor chromatogram in the ratio of about 3:1. Authentic samples of *n*-alkanes were obtained commercially. Racemic α-**pinene** was prepared by mixing appropriate quantities of (+)- and (−)-α-pinene. The (+)-isomer, obtained from commercial turpentine by preliminary distillation from sodium followed by careful fractionation through a 6-ft. column packed with cylinders of stainless steel screen, had b.p. 156–156.3°, $n^{22.5}D$ 1.4643, $[\alpha]^{28}D$ +34.3° (*c* 10, ethanol), reported[34] b.p. 155–156°, $n^{20}D$ 1.4663. The (−)-isomer, b.p. 153–153.5°, $n^{20}D$ 1.4661, $[\alpha]^{28}D$ −43.9° (*c* 10, ethanol), was prepared by steam distillation of a mixture of Oregon fir balsam (Mefford Chemical Co.) and one-third its weight of 10% sodium carbonate solution, then drying and fractionating from sodium. **Pinane** was prepared by catalytic hydrogenation of α-pinene. **Camphene** was prepared according to Bertram and Walbaum[35] by dehydration of racemic isoborneol with zinc chloride.

The columns and conditions used for vapor chromatographic analysis are listed below. Helium was the carrier gas in all cases; the analyses were performed with the Perkin–Elmer model 154C instrument except for the preparative scale runs, which were carried out with the instrument described below. The analytical columns were: (i) 6-ft. Perkin–Elmer "C" column (silicone oil), 105 ml./min. at 80°; (ii) 9-ft. × 0.25-in., Dow Corning 702 silicone fluid on 40–60 mesh firebrick, 120 ml./min. at 85°; (iii) Trend,[36] a commercial detergent, 5.2 ml./min. at 162°; (iv) the preparative scale column, 12 ft. × $^7/_8$-in., 15 wt. % Dow Corning High Vacuum grease on 40–60 mesh fire brick, 500 ml./min. at 95°. The conditions used for all analyses and separations were those that gave the best resolution of a synthetic mixture of bornene, tricyclene, bornane and isocamphane. The order of emergence of the components from the chromatogram is given in Table I. Camphene had a retention time on these columns intermediate between that of 1,5,5-trimethyl-4-ethyl-1-cyclopentene (IX) and bornane. The latter two components were almost but not quite completely separated, and consequently it was difficult to detect camphene in small quantity. Similarly, it was difficult to detect α-pinene and pinane in small quantities.

Vapor chromatograms of samples of the volatiles were run before and after passage through silica gel and elution with

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(32) L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 2639 (1924).

(33) *Cf.* P. Lipp, *Ann.*, **382**, 265 (1911).

(34) F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1030 (1931).

(35) J. Bertram and H. Walbaum, *J. prakt. Chem.*, [2] **49**, 1 (1894).

(36) Trend is the trade name of Purex Corporation, Ltd., South Gate, California, for a detergent whose active ingredient is sodium dodecylbenzenesulfonate. The sample used in this work had the analysis: sodium dodecylbenzenesulfonate, 35 ± 2%; $Na_5P_3O_{10}$, 15 ± 2%; sodium sulfate, 50 ± 2%. Before use, the material was sieved and dried for 24 hr. at 140° under 2.5 mm. pressure. We are indebted to Dr. Robert Petterson of the Purex Corporation who supplied a generous quantity of this material as well as its analysis.

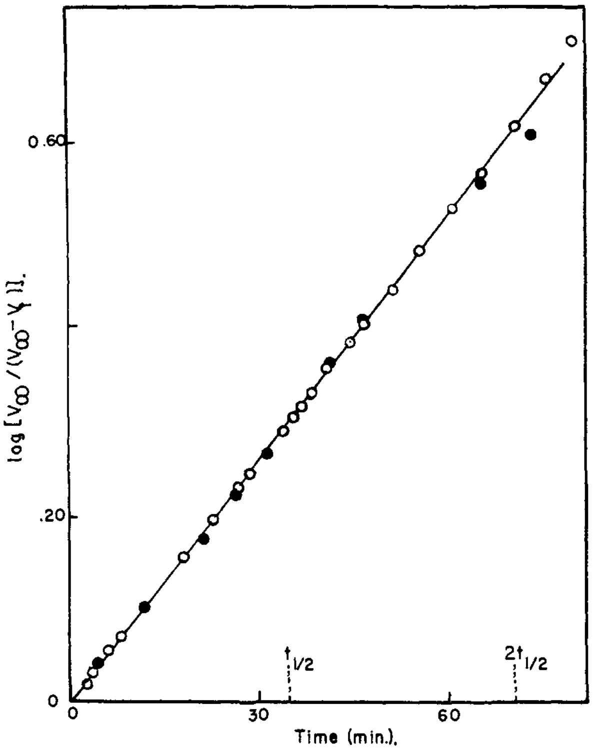

Fig. 1.—Decomposition of 2-azobornane (III) in *n*-hexadecane at 257°; open circles represent data at 5.63 × 10^{-3} *M* initial concentration; filled circles at 1.00 × 10^{-2} *M* initial concentration.

pentane. Olefinic materials were completely removed by this treatment. Control experiments with synthetic mixtures showed that this procedure did not cause fractionation of saturated components, and that vapor chromatographic peak areas were directly proportional to weight fraction. Another control experiment showed that tricyclene could be recovered in 95% yield, vapor chromatographically homogeneous, after having been heated in boiling *n*-hexadecane at reflux for 6 hr.

Preparative Vapor Chromatographic Separations.—The column consisted of eight 18 × 7/8-in. brass tubes filled with packing (iv) described above and connected in series by means of short U-tubes of 3/16-in. copper tubing equipped with flanged fittings. The connections were silver-soldered in place after the individual tubes had been packed. This arrangement permitted the tubes to be mounted in a vertical parallel manner within a cylindrical space 20 × 6 in. The outlet end of the column was connected *via* a short 0.25-in. copper tube to a Gow-Mac model 9285 pretzel geometry gas thermal conductivity cell. The inlet end of the column was attached to a short 0.25 in. copper tube silver-soldered to one end of a 1/8-in. T-shaped chamber drilled in a 2 × 2 × 4-in. brass block which served as a flash vaporizer. The other two ends of the T were connected, respectively, to the inlet helium line and to a threaded cap holding a silicone rubber septum, which served as the sample injection port. The brass block was drilled to hold a 220-watt cartridge heater. The inlet helium line was equipped with a by-pass, mounted inside the heated zone of the apparatus, which led directly to the reference side of the detector.

The whole assembly was mounted in a cylindrical oven, equipped with a 500-watt Nichrome wire heater and a circulating fan, and insulated with a 2-in. layer of glass wool.

The collection system consisted of three T-shaped three-way stopcocks joined in series to the exit end of the detector cell. This connection was originally made by means of a glass-to-metal seal, but this proved fragile and was replaced by a short piece of silicone rubber tubing. The stopcocks were connected by ball joints to cold traps partially filled with glass beads. The outlet manifold was maintained at about 200° by means of electrical heating tape. The collected samples were removed from the traps in a vacuum line.

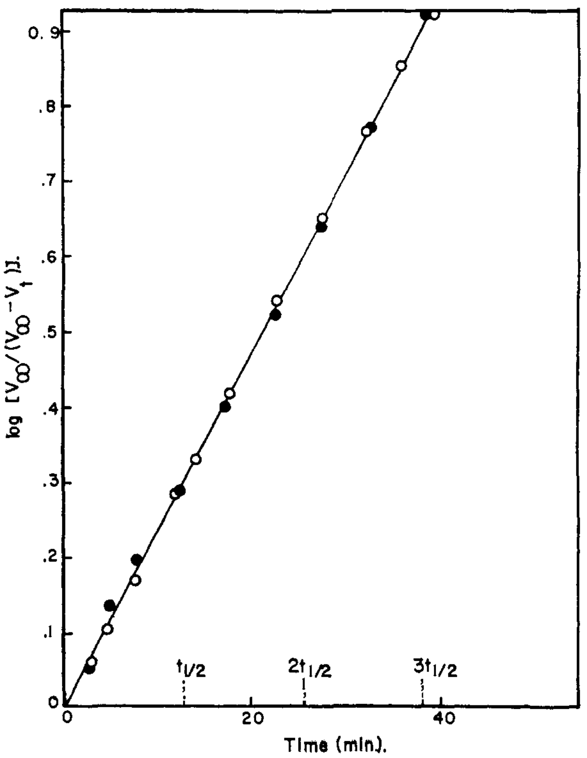

Fig. 2.—Decomposition of III in *n*-hexadecane at 269.5°; duplicate runs at 1.00 × 10^{-2} *M* initial concentration.

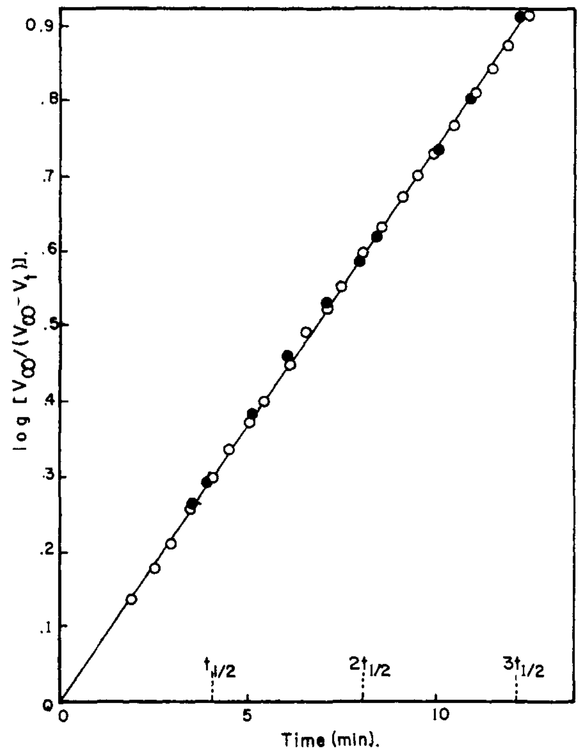

Fig. 3.—Decomposition of III in *n*-hexadecane at 286.5°; open circles represent data at 5.63 × 10^{-3} *M* initial concentration; filled circles at 1.91 × 10^{-2} *M* initial concentration.

Trial experiments showed that essentially quantitative trapping was achieved when the traps were held at −78° even with helium flow rates as high as 1500 ml./min.

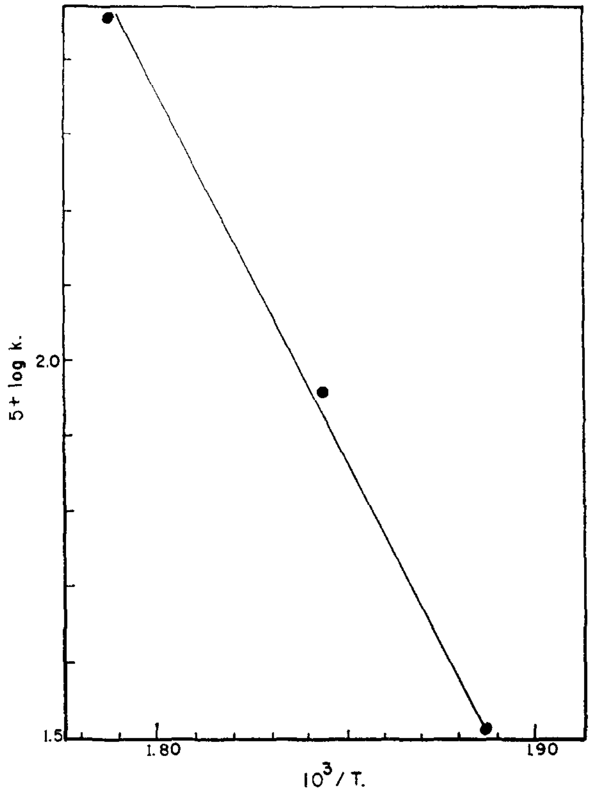

Fig. 4.—Arrhenius plot; decomposition of 2-azobornane (III) in *n*-hexadecane.

Each fraction was examined by analytical vapor chromatography and by infrared spectroscopy. In a typical run, a fraction separated by preliminary vacuum line manipulation and trapped at −45° weighed 3.97 g. and was further fractionated by vapor chromatography into six fractions. These were: (A) 0.7 g., 13.5% unidentified components, 46.5% nonane, 31.6% octane, 8.4% bornene (bornene spectrum was masked by the companion substances); (B) 0.23 g., 1.2% bornene, 45.4% tricyclene and olefin IX, 53.5% bornane (characteristic peaks of olefin IX and bornane in the infrared); (C) 2.03 g., 100% bornane (infrared spectrum identical with that of bornane); (D) 0.07 g., 1.2% bornane, 98.8% isocamphane and decane (infrared showed all the characteristic peaks of isocamphane in the proper relative intensities; decane present as judged by a few extra infrared peaks; (E) 0.09 g., 60.6% decane, 30.4% unidentified component, infrared like that of an *n*-alkane; (F) 0.33 g.; 96% 1-*p*-menthene; 4% unidentified component; infrared spectrum identical with that of 1-*p*-menthene; total recovery 3.45 g. (87%).

Kinetics.—First-order rate behavior was observed for the decomposition of azo compound X at low initial concentrations. The rates were followed by measuring gas evolution. Volume readings were corrected for the partial pressure of the water used in the buret. Short induction periods were observed when time zero was taken as the time of insertion of the sample, and presumably were due to the accompanying brief drop in temperature. The effective zero time volumes were determined by extrapolation of early volume readings to zero time. This procedure gave values of V_∞ which checked with the calculated values and to plots of log $[V_\infty/(V_\infty - V_t)]$ *vs.* time that were straight lines passing through the origin. An illustrative set of data is given in Table III. The first-order rate constant k is given by

$$k = \frac{2.3}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

In duplicate runs, we observed the rate constants 6.01 × 10^{-4} sec.$^{-1}$ and 5.81 × 10^{-4} sec.$^{-1}$.

Table III

Illustrative Kinetic Data for Decomposition of X in *n*-Hexadecane at 285.5 ± 0.5°[a]

Time sec. × 10^{-2}	Vol. of gas V_t, ml.	$k \times 10^4$, sec.$^{-1}$
1.8	3.1	4.94
2.4	4.6	5.60
3.0	5.7	5.65
3.6	7.1	6.01
4.2	8.1	5.96
5.4	10.1	5.94
8.4	14.4	5.96
11.4	18.2	6.05
17.4	23.8	6.05
26.4	28.4	5.83
35.4	31.2	5.50
47.4	33.9	5.58
54.0	35.3	5.71
∞	36.5	..

Mean k = 5.81 ± 0.19

[a] Initial concentration 0.0192 *M*; stoichiometric V_∞ = 37.3 ml.

The rate constants for the decomposition of 2-azobornane (III) at three temperatures (257 ± 0.5°, 269.5 ± 0.5°, 286.6 ± 0.5°) were determined graphically from plots of log $[V_\infty/(V_\infty - V_t)]$ *vs.* time. Two determinations were made at each temperature. Since the V_∞ values did not correspond to stoichiometric values (see Table I), the value of V_∞ was chosen in each case to give the best straight line representation of the data. The choice was facilitated by a procedure in which arbitrarily chosen V_∞ values were checked for consistency with the condition that $V_{t^{1/2}} = V_\infty/2$ and $V2t_{t^{1/2}} = 3V_{t^{1/2}}/2$ (where $t_{1/2}$ = the half-life) by consulting a plot of the raw data V_t *vs.* t. The rate constants k, determined from the slopes (k/2.303) of the log $[V_\infty/(V_\infty - V_t)]$ graphs were independent of initial concentration over a threefold variation (5.63 − 19.1 × 10^{-3} *M*) as is shown in Figs. 1 and 3, representing data at 257° and 286.6°. Reproducibility of the kinetic runs is demonstrated by Fig. 2, representing data at 269.5°. Even at higher concentrations (0.173 *M*, not plotted here) the initial rate "constants" were the same as for the lower concentrations. Linear first-order behavior to 2.5–3 half-lives, however, was observed only at the lower concentrations.

An alternative method[37] of treating the data involves plotting log $(V_t + \Delta_t - V_t)$ *vs.* t, where $\Delta t \geq 2t_{1/2}$. The rate constants found by this method were within 4% of the values obtained by the previous one. Because of the emphasis that the second method placed upon volumes at long reaction times (where the differences between successive volume measurements approached experimental error) the values obtained by the first method are considered more reliable.

The quantities of activation given in Table II were obtained from the Arrhenius plot (Fig. 4).

Acknowledgment.—We are indebted to Professor C. G. Overberger for helpful discussions of the chemistry of azo compounds.

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[37] E. Guggenheim's method as described by A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 48.