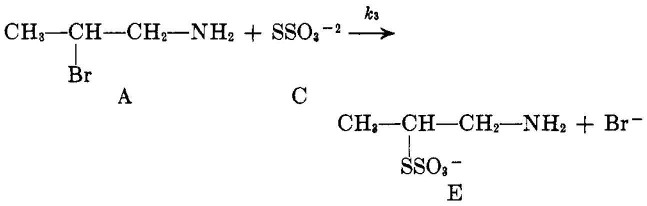

$$CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_2{-}NH_2 + SSO_3^{-2} \xrightarrow{k_3} CH_3{-}\underset{\displaystyle SSO_3^-}{\underset{|}{CH}}{-}CH_2{-}NH_2 + Br^-$$

A C E

$$-(\mathrm{d}[\mathrm{A}]/\mathrm{d}t) = k_1[\mathrm{A}] + k_3[\mathrm{A}][\mathrm{C}] \quad (1)$$

$$-(\mathrm{d}[\mathrm{B}]/\mathrm{d}t) = -k_1[\mathrm{A}] + k_2[\mathrm{B}][\mathrm{C}] \quad (2)$$

$$-(\mathrm{d}[\mathrm{C}]/\mathrm{d}t) = k_2[\mathrm{B}][\mathrm{C}] + k_3[\mathrm{A}][\mathrm{C}] \quad (3)$$

$$(\mathrm{d}[\mathrm{D}]/\mathrm{d}t) = k_2[\mathrm{B}][\mathrm{C}] \quad (4)$$

$$(\mathrm{d}[\mathrm{E}]/\mathrm{d}t) = k_3[\mathrm{A}][\mathrm{C}] \quad (5)$$

An analytical solution is not possible since one is not justified in invoking the steady-state approximation with regard to the intermediate ethylenimonium ion.[2a,b] A graphical solution for obtaining k_1 and k_3 was employed instead. Values for $(\mathrm{d}[\mathrm{A}]/\mathrm{d}t)$, $(\mathrm{d}[\mathrm{D}]/\mathrm{d}t)$ and $(\mathrm{d}[\mathrm{E}]/\mathrm{d}t)$ were obtained from the respective plots of [A], [D], and [E] (determined from the n.m.r. spectrum) *vs.* time. The values of [C] at different times were obtained from the relationship, $[\mathrm{C}]_t = [\mathrm{C}]_0 - [\mathrm{E}]_t - [\mathrm{D}]_t$, where subscript 0 represents initial concentration and subscript t represents concentration at time t. From eq. 5 the linear plot of $(\mathrm{d}[\mathrm{E}]/\mathrm{d}t)$ *vs.* $[\mathrm{A}]_t[\mathrm{C}]_t$ gave k_3 as the gradient $= 7.9 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$.

From eq. 1 and 5, $-(\mathrm{d}[\mathrm{A}]/\mathrm{d}t) = k_1[\mathrm{A}] + (\mathrm{d}[\mathrm{E}]/\mathrm{d}t)$, or $-(\mathrm{d}[\mathrm{A}]/\mathrm{d}t) - (\mathrm{d}[\mathrm{E}]/\mathrm{d}t) = k_1[\mathrm{A}]$.

A plot of $-[(\mathrm{d}[\mathrm{A}]/\mathrm{d}t) + (\mathrm{d}[\mathrm{E}]/\mathrm{d}t)]$ *vs.* $[\mathrm{A}]_t$ was linear with a gradient (k_1) of 1.14×10^{-5} sec.$^{-1}$. Therefore, for the reaction of I with sodium thiosulfate at 36.5° the ratio

$$\frac{\text{rate of intramolecular displacement}}{\text{rate of intermolecular displacement}} = k_1/k_3 = \frac{1.14 \times 10^{-5}}{7.9 \times 10^{-6}} = 1.45 \frac{\text{sec.}^{-1}}{\text{l. mole}^{-1}\ \text{sec.}^{-1}}$$

Discussion

Recently, there has been interest shown in the comparison of the rates of intra- and intermolecular displacement reactions and hydrolyses.[16] The present results bear on this problem. While it is generally accepted that nucleophilic attack on 1,2-(secondary-amino)-haloalkanes is preceded by the formation of an intermediate ethylenimonium ion,[2a] most kinetic data are restricted to compounds bearing a tertiary-amino group. No similar conclusion has been reached regarding displacements occurring in primary- and secondary-amino compounds.

The work reported here indicates that ring closure occurs less readily when a primary-amino group acts as the neighboring group, allowing some direct displacement by an external nucleophile. This is probably due to the lower nucleophilicity of the primary-amino group[17] since steric hindrance effects in the formation of three-membered rings are not important and are overridden by polar effects.[17] If I reacted exclusively through the 2-methylethylenimonium ion, then only the rearranged thiosulfuric acid, IV, would result since it has been shown that this cyclic ion opens only at the primary carbon atom. The direction of opening of unsymmetrical cyclic imines is usually given by analogy with ordinary bimolecular nucleophilic displacement[18] where the rate sequence for attack on carbon is primary > secondary > tertiary. We have shown that once the cyclic ion has been formed it is attacked exclusively in the primary position, in accordance with the above conclusion.

This is believed to be the first observation of the concurrent displacement and rearrangement occurring in the nucleophilic attack on an aminohaloalkane. The ratio of the rate constants indicates that the intramolecular displacement is dominant when thiosulfate is the nucleophile. When the weaker nucleophile, sulfite, was substituted, intramolecular displacement occurred to the exclusion of the intermolecular displacement.

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[16] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960); T. C. Bruice and S. J. Benkovic, *J. Am. Chem. Soc.*, **85**, 1 (1963).

[17] A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 106.

[18] S. Gabriel and H. Ohle, *Ber.*, **50**, 804 (1917); G. H. Coleman and J. E. Cullen, *J. Am. Chem. Soc.*, **68**, 2006 (1946); A. H. Nathan and M. T. Bogert, *ibid.*, **63**, 2361 (1941).

The Solvolytic Behavior of Tricyclo[3.2.1.0^{2,4}]octane Derivatives[1]

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The four possible tricyclo[3.2.1.0^{2,4}]octan-6-ols have been prepared and converted to their respective brosylates. Acetolysis of three of the four isomers gave identical products, *exo-exo*-tricyclo[3.2.1.0^{2,4}]octan-6-yl acetate, *exo*-bicyclo[3.2.1]oct-3-en-6-yl acetate, and nortricyclane-3-methyl acetate. The related nortricyclane-3-methyl brosylate gave qualitatively the same products. The isomerization of *endo-exo*-tricyclo[3.2.1.0^{2,4}]octan-6-yl brosylate to the *exo-exo* isomer during the course of solvolysis leads to the conclusion that a "norbornyl-type ion" is produced in this system. A consideration of the products and their ratios along with the kinetic data leads to a tentative scheme for the solvolysis of these compounds.

In many instances a cyclopropane ring behaves in a fashion similar to that of a double bond.[3] The observation that a double bond may participate in a solvolytic reaction as with the norbornenyl tosylates[4] and the demonstration that the cyclopropane ring in bicyclo-[3.1.0]hexane may participate in a solvolytic reaction[5]

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[1] This work was supported in part by the Army Research Office (Durham).

[2] National Science Foundation Postdoctoral Fellow, Yale University, 1962–1963.

[3] *Cf.* M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955); R. S. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. S. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

[4] S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); S. Winstein and E. T. Stafford, *ibid.*, **79**, 506 (1957).

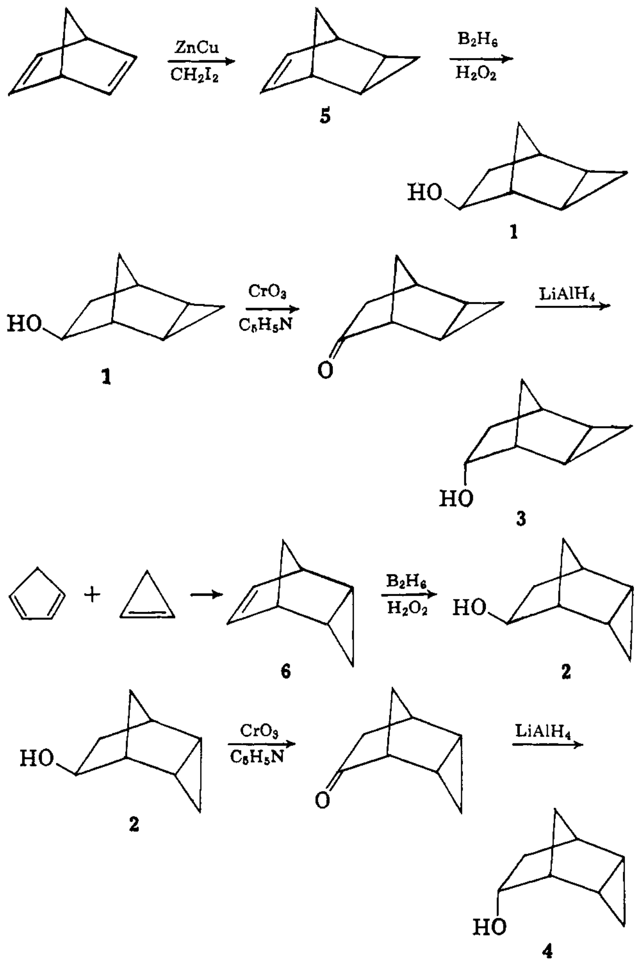
[5] S. W. Winstein and J. Sonnenberg, *ibid.*, **83**, 3231 (1961); **83**, 3244 (1961).

make it interesting to examine the stereochemical requirements for participation in such cases. Whereas the requirements for the interaction of a double bond with another center of unsaturation are moderately well defined,[6] the restrictions on the interaction of cyclopropyl rings with electron-deficient centers appear to be the subject of conflicting views.[7]

Since the question of the stereochemical requirement for the interaction of cyclopropyl rings seemed to be open, a study of the tricyclo[3.2.1.0^{2,4}]octane derivatives, **1–4**, was of interest. Such a study might allow one to estimate the ability of the cyclopropane ring to interact with the developing cationic center across the ring system in a solvolytic reaction. Further, if an interaction did exist, the availability of the four isomers would allow an assessment of any stereochemical preference to the interaction.

Alcohol Synthesis.—The alcohols used in this work were prepared by standard methods shown in Chart I. These syntheses required the two tricyclo[3.2.1.0^{2,4}]-2-octenes (**5** and **6**), both of which are known compounds. The isomer having an *exo*-cyclopropyl ring was obtained from bicycloheptadiene through the Simmons–Smith reaction.[8] The other isomer was obtained *via* the facile Diels–Alder reaction between cyclopropene and cyclopentadiene.[9]

CHART I



The configuration of the two olefins **5** and **6** are known with certainty. The product of the Simmons–Smith procedure has been shown to have the cyclopropyl ring in the *exo* position by the conversion to *exo*-2-2-methylnorbornane.[10] A conversion of **6** to *endo*-2-methylnorbornane has also been effected.[10] Previous to this demonstration, the configurations of the two olefins were assigned on the basis of the n.m.r. data pertaining to the relative complexity of the signals for the bridgehead hydrogens, and by analogy with the stereochemical course of related reactions.[8,9]

The conversion of the tricyclic olefins to the related alcohols **1** and **2** was readily achieved *via* hydroboration using diborane generated from sodium borohydride and boron trifluoride etherate.[11] This procedure was found to be superior to that of *in situ* generation of diborane using lithium aluminum hydride and boron trifluoride etherate in diethyl ether.[12] The hydroboration led to mainly one product as was indicated by g.l.p.c. In each case the product appeared to be greater than 95% pure *exo* alcohol. The exact *exo–endo* ratio is not known due to the lack of clear separation of the chromatographic peaks. The configuration of the major alcohol formed would be expected to be *exo* and this could be demonstrated by consideration of the n.m.r. signals due to the hydrogen on the carbon bearing the alcohol oxygen.[13]

The oxidations of the two *exo* alcohols using the Sarett reagent[14] were found to give nearly pure ketones when pentane was used in the extraction of the reaction mixture. In this case, the impurities were apparently not extracted. The final reductions with lithium aluminum hydride produced the alcohols having the *endo*-hydroxyl group. The degree of stereoselectivity of this reduction is not known. Again, however, g.l.p.c. analysis indicated approximately 95% of the *endo*-hydroxyl compounds.

All four alcohols, **1**, **2**, **3**, and **4**, could be converted to crystalline brosylates using standard methods. In each case these esters were recrystallized to a constant melting point. The remaining alcohols used in this work were prepared as shown in Chart II. The nortricyclane-3-methanol (**7**) was readily prepared from the acid obtained by the carbonation of nortricyclomagnesium bromide.[15] The synthesis of bicyclo[3.2.1]octan-6-ol (**8**) deserves some comment since it represents a reasonably facile preparation of this substance on a moderate scale The thermal isomerization of cyclopropanes has been studied rather extensively.[16] Thus it appeared that a process such as that in Chart II would be successful. The conditions given in the Experimental section of this paper probably are not

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(6) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(7) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964); R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963); E. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962); N. H. Cromwell, F. H. Schumaker, and J. L. Adelfand, *J. Am. Chem. Soc.*, **83**, 974 (1961).

(8) H. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(9) K. B. Wiberg and W. Bartley, *ibid.*, **82**, 6375 (1960).

(10) W. von E. Doering and W. Grimme, unpublished results.

(11) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 93–94; H. C. Brown and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

(12) S. Wolfe, M. Nussin, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(13) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962); H. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

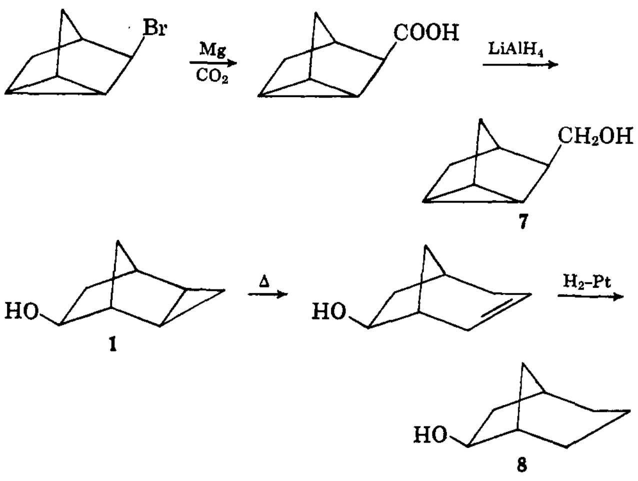
(14) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 423 (1953).

(15) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(16) W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963), and references cited therein.

optimal since no attempt was made to study the reaction variables. The structure of the alcohol formed in the pyrolysis rests upon its facile hydrogenation to a solid alcohol which forms a crystalline phenylurethan melting at 123.5–124.5°, as well as its conversion to the known bicyclo[3.2.1]octan-6-one. The melting point of the latter agreed with the literature value as does the melting point of the semicarbazone derivative.[17]

CHART II



Results

The three tricyclic brosylates derived from compounds **1**, **2**, and **3** will be considered along with nortricyclane-3-methyl brosylate. The brosylate from **4** will be considered at another time, since it represents a somewhat unusual case and gives different products than the other brosylates. Both the rates and products of acetolysis of the brosylates were studied. Chart III and Table I supply the qualitative and quantitative information regarding product distribution.

CHART III

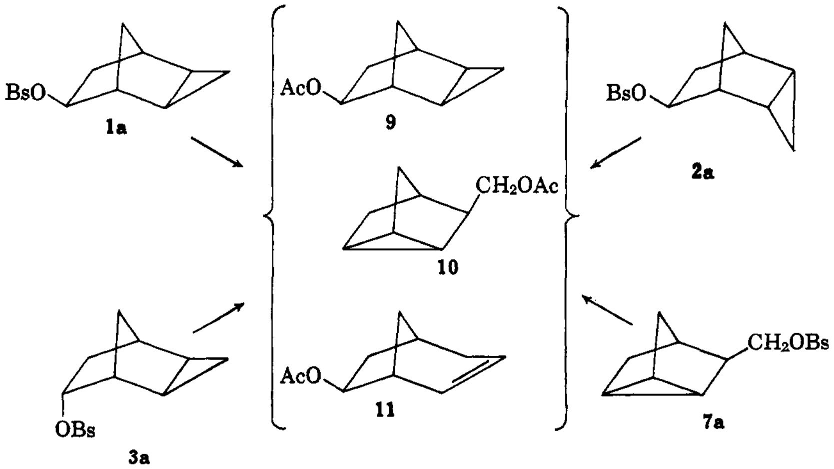


TABLE I

SOLVOLYSIS OF TRICYCLIC BROSYLATES

Brosylate	% [3.2.1.0^{2,4}] acetate (**9**)	% minor acetates	Composition of minor acetates: % bicyclooctenyl (**11**)	% nortricyclane-3-methyl (**10**)
1a, *exo-exo*	67.5 ± 0.8[a]	32.5	77.9 ± 1.4[a]	22.1
2a, *endo-exo*	68.5 ± 0.1	31.5	79.2 ± 1.0	20.8
3a, *exo-endo*	67.5 ± 0.1	32.5	78.0 ± 0.6	22.0
7a, nortricycl	58.2 ± 0.5	41.8	78.1 ± 0.1	21.9

[a] Average deviation.

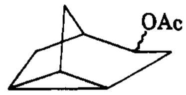
TABLE II

ABSOLUTE YIELDS AND INFINITY TITERS[a]

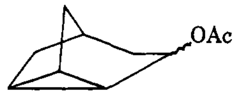
Brosylate	Yield of acetate, %	Infinity value
1a, *exo-exo*	83	0.85–0.86[b]
2a, *endo-exo*	89	0.90[b]
3a, *exo-endo*	94	0.93
7a, nortricyclane-3-methyl	81[c]	1.00

[a] 85°, 0.04966 M potassium acetate in glacial acetic acid. [b] Determined after 12 half-lives at 40°. [c] Determined after 8 half-lives at 85°.

As can be seen, all of the brosylates, **1a**, **2a**, **3a**, and **7a**, give qualitatively the same products. The identities of these products were ascertained by comparison with authentic samples with the exception of the bicyclooctenyl acetate (**11**), which was identified after hydrogenation to bicyclo[3.2.1]octanol. No product acetates of structures **12** and **13** were isolated; however, it is possible that small amounts of these may have escaped detection. The three tricyclo[3.2.1.0^{2,4}]octyl brosylates give similar or identical product mixtures, while the fourth isomer, **7a**, gives more minor acetates **10** and **11**. The ratio of **9** to the sum of **10** and **11** was about 2:1 for the acetolyses of **1a**, **2a**, and **3a**. Within the accuracy of the analytical data these ratios must be taken as equal.[18] Whereas nortricyclane-3-methyl brosylate gave more of the minor acetates than any of the tricyclic compounds **1a**, **2a**, or **3a**, it should be noted that the ratio of nortricyclane-3-methyl acetate to bicyclooctenyl acetate is the same as that for the



12



13

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[17] G. Kommpa, T. Hirn, W. Rohrmann, and S. Beckman, *Ann.*, **521**, 242 (1936).

[18] These values are not so accurate as ideal g.l.p.c. data, since there was a slight but real overlap of the peaks of the major and minor acetates

TABLE III

RATES OF ACETOLYSIS[a]

Brosylate	$k_{25} \times 10^5$ sec.$^{-1}$	$k_{40} \times 10^4$ sec.$^{-1}$	$k_{85} \times 10^5$ sec.$^{-1}$	$k_{100} \times 10^4$ sec.$^{-1}$	ΔH^*	ΔS^* (°C.)
1a, *exo-exo*	1.36	1.00			24.2 ± 0.7	1.3 ± 2.6 (25°)
2a, *endo-exo*	0.68[b]					
3a, *exo-endo*			3.35	1.64	27.7 ± 0.7	−2.6 ± 1.4 (85°)
4a, *endo-endo*			3.36	1.58	26.7 ± 0.6	−5.4 ± 1.7 (85°)
7a, nortricyclane-3-methyl			0.653			

[a] In 0.04966 *M* potassium acetate in glacial acetic acid. [b] Initial rate.

other brosylates. These ratios were determined as is described in the Experimental section of this paper.

The product acetates were accompanied by *very* small amounts of lower boiling materials which were not identified but which probably were traces of olefinic materials. The absolute yields of acetates were determined by g.l.p.c. analysis using an internal standard. The results are given in Table II. It is estimated that the values are good to ±2%. Within the accuracy of the method used the first three compounds in Table II gave the same absolute yield of acetate after considering infinity values (96–98% *exo-exo*, 99% *endo-exo*, and 100% *exo-endo*). Nortricyclocarbinyl brosylate seems to give a lower yield of acetates. However, this value is somewhat doubtful experimentally.

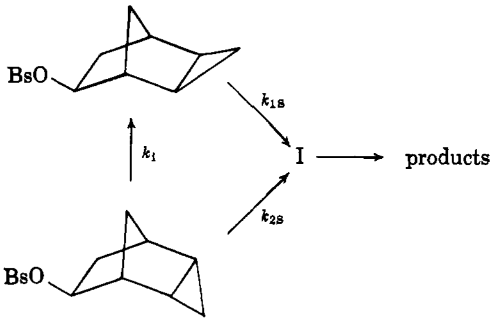
The rates of acetolysis were determined giving the data shown in Table III. Compounds **1a**, **2a**, and **3a** did not give theoretical values for acid liberated, therefore the infinity titer was used in the evaluation of the rate constants. The lack of theoretical production of acid was due to the formation of nortricyclane-3-methyl brosylate during the course of solvolysis. This brosylate is far less reactive than any of the tricyclo[3.2.1.0^{2,4}]octyl brosylates. In each case crystalline nortricyclane-3-methyl brosylate could be isolated from the solvolysis mixtures after the completion of the solvolysis. Good first-order behavior was obtained with compounds **1a**, **3a**, and **7a**. In the case of the *endo-exo* isomer **2a**, the titrimetric rate constant was found to drift upward during a run. This drift was reproducible and resulted from an isomerization to the *exo-exo* isomer **1a**. The formation of the latter was demonstrated by the isolation of the *exo-exo* brosylate after an approximate one-half life of solvolysis of the *endo-exo* isomer. The rate of the isomerization could be determined using the change in the n.m.r. spectrum with time. This gave the rate constant ~2.5 × 10^{-5} sec^{-1}.

Discussion

In considering the nature of the reactions which occur, we shall first treat the isomerization of **2a** to **1a**. The rate of isomerization was found to be ~2.5 × 10^{-5} sec.$^{-1}$, following the reaction *via* n.m.r. spectroscopy. In the solvolysis of **2a**, the value of the first-order rate constant in a given run would drift from about 0.7 × 10^{-5} to 1.3 × 10^{-5} sec.$^{-1}$ at which time it would become steady. The latter value is identical with that observed for the brosylate **1a**.

This type of isomerization has been encountered in the acetolysis of a number of tosylates or brosylates.[19]

CHART IV



One can analyze the rate data according to the simplified scheme given in Chart IV. A commonly used approach is that given by Young, Winstein, and Goering.[19] Somewhat higher accuracy in evaluating the rate constants was obtained by incorporating the independently determined data on the rate of isomerization. The details are given in the Experimental part of this paper and lead to the rate constants given in Table IV.

TABLE IV

RATE CONSTANTS FOR THE ISOMERIZATION REACTION[a]

$$k_i + k_{2S} = (3.25 \pm 0.11) \times 10^{-5}\ \text{sec.}^{-1}$$
$$k_{2S} = 0.68 \times 10^{-5}\ \text{sec.}^{-1}$$
$$k_{1S} = 1.36 \times 10^{-5}\ \text{sec.}^{-1}$$
$$k_i = 2.57 \times 10^{-5}\ \text{sec.}^{-1}$$

[a] 25°; glacial acetic acid, 0.04966 *M* in potassium acetate.

At this point it is necessary to consider whether a significant amount of **2a** is present in equilibrium with **1a**. This type of behavior has been previously noted by Goering and Sloan.[19] A number of experimental observations bear on this possible equilibrium. The fact that both the instantaneous and integrated rate constants for the last 40% of the solvolysis of **2a** are identical with the value for the *exo-exo* brosylate **1a** indicates that less than 5% of **2a** is present in equilibrium. The n.m.r. results also indicate that less than 5% of isomer **2a** is present during the solvolysis of **1a**. Thus within the accuracy of the data there is no evidence for a significant amount of **2a** in equilibrium with **1a**.

Next, one may ask does the solvolysis of **2a** proceed entirely by isomerization to **1a** and then reaction to form products? This appears not to be correct, since the initial rate of solvolysis of **2a** is much too rapid to be explained by prior isomerization to **1a**.

The observed data may be summarized as follows. (1) Each of the four brosylates give the same products. (2) Each of the three tricyclo[3.2.1.0^{2,4}]octyl isomers give identical products ratios. (3) The nortricyclane-3-methyl brosylate, while giving more "minor acetates,"

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[19] W. T. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951); H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961); S. Winstein and H. H. Fainberg, *ibid.*, **80**, 459 (1958); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952); J. Meinwald and P. G. Gassman, *ibid.*, **85**, 57 (1963).

CHART V

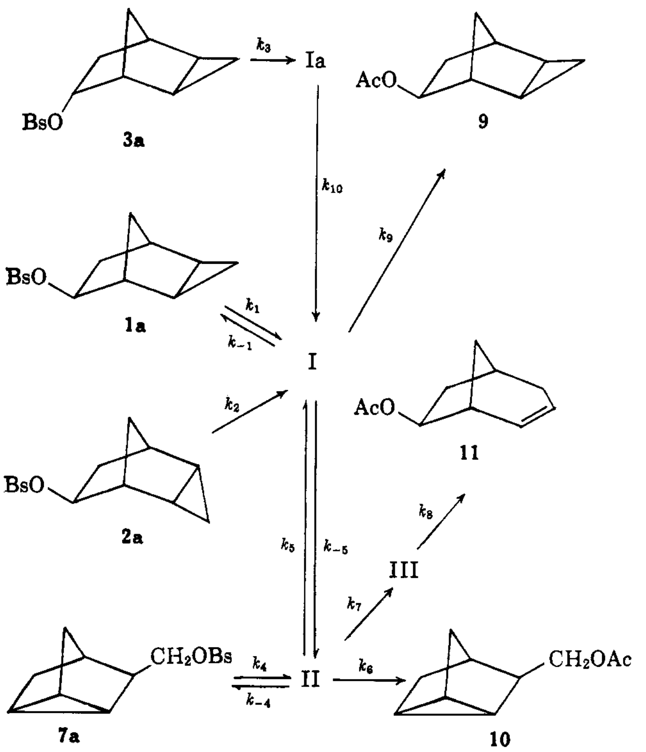
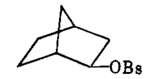
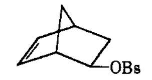
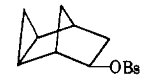
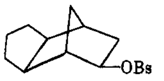
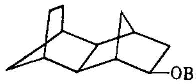


TABLE V

	Compounds	k_{25}, sec.$^{-1}$	Solvent	k_{exo}/k_{endo}	Ref.
A,		8.9×10^{-5}	AcOH, NaOAc	350	*a*
B,		4.5×10^{-5}	AcOH	7700	*b*
C,		1.36×10^{-5}	AcOH, KOAc	1250	
D,		1.02×10^{-6c}	AcOH	13	*d*
F,		3.76×10^{-8e}	AcOH	20	*f*

[a] See ref. 21. [b] S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956). [c] Estimated as three times the reported solvolysis rates for tosylates. [d] P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956. [e] Extrapolated from data at higher temperatures. [f] L. De Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960).

nevertheless produces the same ratio of nortricyclane-3-methyl acetate to bicyclo[3.2.1]octyl acetate as to the other three isomers. (4) The absolute yield of product acetates is identical for the three tricyclooctyl derivatives and may be somewhat less for the nortricyclane-3-methyl brosylate.

A scheme which will accommodate the above observations is shown in Chart V. All of the steps shown correspond to experimental observations recorded herein. The steps starting with the brosylate **7a** were first observed by Sauers and Beisler who determined the products of the solvolysis of nortricyclane-3-methyl tosylate.[20]

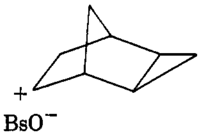
The reactions involving the ion-pair intermediates Ia and I appear to be counterparts of the corresponding reactions of *exo*- and *endo*-norbornyl tosylates.[21] Ia is presumably the classical *endo* ion pair which rearranges to the ion pair I. The acetate product arising directly from this ion is **9.**

It is interesting to compare the results with those for related norbornyl-type systems. The data are summarized in Table V. The effect of fusing a carbocyclic ring between C-5 and C-6 is usually a marked reduction in rate of solvolysis for the *exo* isomer and a marked reduction in the k_{exo}/k_{endo} ratio. Thus, the importance of carbon participation in the rate-determining step is decreased by this type of substitution.

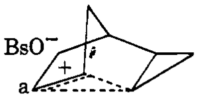
In the case of the *exo*-cyclopropyl derivatives studied herein (C in Table V), the rate reduction is significantly less, and the k_{exo}/k_{endo} ratio compared with norbornyl has increased rather than decreased. One possible explanation is that the normal effect of ring fusion is counterbalanced by weak participation of the cyclopropane ring in a fashion similar to the double bond in norbornenyl brosylate. This would lead to the increased k_{exo}/k_{endo} ratio which was observed. However, as with most solvolytic reactions, the rate of product formation may not equal the rate of ionization, and it is this latter quantity which is of importance.

The formation of **10** from **7a** does not involve a nucleophilic displacement since the ratio of **10** to **11** derived from **7a** was the same as that derived from **1a.** Since the proportions of **9** and **10** from **7a** were different from that from **1a,** the ion pairs I and II must be different. They are, however, almost equilibrated under the conditions of the solvolysis.

In view of the similarity between the present case and the norbornyl brosylates, it is suggested that I and Ia have the structures shown. Attack on I by acetate



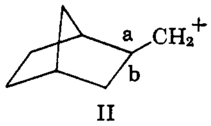
Ia



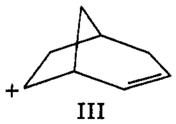
I

ion or internal return to a brosylate will occur principally at bond a, since this results in the presumably more stable *exo*-cyclopropane ring.[22]

It seems probable that II and III are different. If bond a migrates, II may be converted to III without a hydrogen migration, whereas migration of bond b must be followed by such a migration. The simplest hypothesis involves the classical structures shown. Based



II



III

on the rate constants of Winstein, *et al.*,[23] the constant expected for the solvolysis of neopentyl brosylate at 85° is $\sim 1 \times 10^{-6}$ sec.$^{-1}$. The nortricyclane-3-methyl brosylate is the nabouts even times as reactive, suggesting that there may be some carbon participation in the

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[20] R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964).

[21] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).

[22] *Cf.* K. Alder and G. Stein, *Ber.*, **67**, 613 (1934); S. J. Cristol, W. F. Seifert, D. W. Johnson, and J. B. Jumle, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

[23] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

rate-determining step. Similarly, it is not unlikely that the double bond in III will interact with the positive charge in order to reduce the energy of the ion.

In order to give a more definitive statement concerning the nature of the ions, it will be necessary to finish a detailed investigation of the solvolysis of the fourth of the tricyclic brosylates (**4a**) and to obtain information on the primary ionization process rather than just product-forming steps. Such studies are in progress.

Experimental

exo-exo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-ol** (**1**).—Diborane, generated from 20.6 g. of boron trifluoride etherate in 150 ml. of purified diglyme and 4.22 g. of sodium borohydride in 150 ml. of diglyme according to the procedure of Brown[11] was passed into a solution of 38 g. of *exo*-tricyclo$[3.2.1.0^{2,4}]$-2-octene in 150 ml. of tetrahydrofuran over a period of 2.5 hr. The mixture was allowed to stand under nitrogen for an additional 2 hr. followed by the addition of 70 ml. of 10% sodium hydroxide after cooling to 0°. The resulting solution was treated dropwise with 65–70 ml. of 30% hydrogen peroxide with stirring. After stirring for 3.3 hr. at 0° and 1 hr. at 25°, the phases were separated and the aqueous layer was extracted with 250-ml. portions of pentane. The combined organic layers were washed with water, dried over magnesium sulfate, and distilled giving 25 g. (63%) of *exo-exo*-tricyclo$[3.2.1.0^{2,4}]$octan-6-ol, b.p. 93° at 12 mm., $n^{25}D$ 1.5070.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.4; H, 9.7.

A 3,5-dinitrobenzoate was prepared in pyridine solution. After recrystallization from ethanol, it had m.p. 98–100°.

Anal. Calcd. $C_{15}H_{14}N_2O_6$: C, 56.5; H, 4.4. Found: C, 56.5, 56.7; H, 4.7, 4.7.

endo-exo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-ol** (**2**).—This alcohol was prepared from *endo*-tricyclo$[3.2.1.0^{2,4}]$-2-octene (b.p. 86° at 140 mm., m.p 30°) using the procedure given above, with the exception of the distillation. After removal of the solvents a mushy solid, m.p. 45–50°, was obtained. This material was used directly for further reactions since g.l.p.c. indicated greater than 95% purity. From 20 g. of olefin there was obtained 21.8 g. (94%) of the crude product. Further purification of a small sample gave material having m.p. 75–79.5°.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.2; H, 9.7.

A dinitrobenzoate was formed in pyridine solution. Recrystallization from ethanol gave plates, m.p. 129–131°.

exo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-one.**—To a stirred suspension of chromium trioxide–pyridine complex prepared from 47 g. of chromium trioxide and 260 ml. of pyridine was added 13 g. of *exo-exo*-tricyclo$[3.2.1.0^{2,4}]$octan-6-ol in 70 ml. of pyridine. The mixture was stirred at room temperature for 23 hr.; then 400 ml. of cold water was added. The solution was extracted with ten 200-ml. portions of pentane. The pentane solution was washed with 10% hydrochloric acid and with water. After drying over magnesium sulfate, distillation gave 8.0 g. (63%) of the ketone, b.p. 113–116° at 52 mm. In another run, 79% of the ketone was obtained.

Anal. Calcd. for $C_8H_{10}O$: C, 78.7; H, 8.3. Found: C, 78.6; H, 8.1.

The 2,4-dinitrophenylhydrazone was prepared and had m.p. 170–173° dec.

endo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-one.**—The oxidation of *endo-exo*-tricyclo$[3.2.1.0^{2,4}]$octan-6-ol was effected as described above giving the ketone as a mushy solid in 85% yield. A small sample purified by g.l.p.c. (7-ft. Carboxwax 20M, 170°) had a melting point of 87–88° with softening at 80°.

Anal. Calcd. for $C_8H_{10}O$: C, 78.7; H, 8.3. Found: C, 78.6; H, 8.1.

exo-endo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-ol** (**3**).—A solution of 7.5 g. of *exo*-tricyclo$[3.2.1.0^{2,4}]$octan-6-one in 30 ml. of dry ether was added to 0.65 g. of lithium aluminum hydride in 100 ml. of dry ether. After the usual work-up there was obtained 6.8 g. of the alcohol. After purification by g.l.p.c. (7-ft. Carbowax 20M, 188°), it had m.p. 62–64.5°.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.2; H, 9.8.

endo-endo-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-ol** (**4**).—The reduction of 10.0 g of *endo*-tricyclo$[3.2.1.0^{2,4}]$octan-6-one gave 8.7 g. of the alcohol. After purification by g.l.p.c., it had m.p. 136–138°.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.1; H, 9.4.

With the alcohols described above, the n.m.r. signal for the hydrogen on the alcohol carbon at τ 5.8 could be used to indicate the configuration of the hydroxy group. For the *exo* alcohols, it was found that the signal for this proton approximates the X portion of an ABX pattern and, hence, is a somewhat broadened quartet which sometimes collapses to a triplet in certain derivatives. The *endo* alcohols showed a more complex pattern, normally a sextet. These relationships have been observed with similar compounds[13] and arise as a result of the approximately 90° dihedral angle between the bridgehead hydrogen and the hydrogen in question in the *exo* compounds.

Bicyclo[3.2.1]octan-6-ol. A. From Solvolysis Mixture.—The acetate fraction from a large-scale solvolysis of *exo-cis* brosylate was subjected to preparative g.l.p.c. (7-ft. Carbowax 20M, 180°). The peaks corresponding to the desired acetates (retention times, 8.0 and 9.3 min.) were collected and subjected to reductive hydrolysis with lithium aluminum hydride to yield a mushy solid which was directly hydrogenated using platinum oxide in ethanol. Removal of the solvent followed by g.l.p.c. purification gave a solid, m.p. 147–149°.

B. Pyrolysis of *exo-exo*-**Tricyclo$[3.2.1.0^{2,4}]$octan-6-ol.**—The alcohol (3.5 g.) was slowly dropped through a vertical column of glass helices (washed with ammonia), 13 in. long and 0.75 in. in diameter, which was held at 425–450°. A stream of nitrogen was passed through the tube during and after the duration of the addition (0.5 hr.). The crude straw-colored pyrolysate was subjected to preparative g.l.p.c. which indicated a 50% conversion to olefinic alcohol, the remainder of the materials being starting materials and lower boiling fragments. The mixture of olefinic bicyclooctanols thus obtained was hydrogenated as above. The resulting product after g.l.p.c. (7-ft. Carbowax 20M, 180°) was a solid, m.p. 138–140°. The infrared spectra of preparations A and B were identical.

A phenylurethan was prepared in boiling benzene. Recrystallization from ethanol and then pentane gave needles, m.p. 123.5–124.5°. It may be noted that the urethan from the epimeric *endo*-bicyclo[3.2.1]octan-6-ol melted at 133° and the alcohol melted at 170°.[17]

Bicyclo[3.2.1]octan-6-one.—The corresponding alcohol was oxidized with chromic acid–pyridine complex[14] to give a solid ketone. The ketone after g.l.p.c. purification melted at 157–159° (lit.[17] m.p. 157–158°). A semicarbazone formed in ethanol had m.p. 183.–185° (lit.[17] m.p. 183–183.5°).

Nortricylane-3-methanol (**7**).—The reduction of nortricyclane-3-carboxylic acid[15] was effected with lithium aluminum hydride to give the alcohol, b.p. 92–92.5° at 9.5 mm., $n^{25}D$ 1.4977.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.1; H, 9.4.

p-**Bromobenzenesulfonates.**—To a cold solution of 1.0 g. of the alcohol in 10 ml. of anhydrous pyridine was added 2.2 g. of *p*-bromobenzenesulfonyl chloride. The mixture was maintained at −5° for 15 hr., after which time water (10–15 ml.) was added and the material was induced to crystallize by scratching. After filtering, the crude brosylate was dried under vacuum for 3–4 hr. at 1 mm. All brosylates were recrystallized from pentane unless otherwise specified. The data obtained are summarized in Table VI.

TABLE VI

Alcohol	Yield of brosylate	M.p., °C.	%[a] C	%[a] H	%[a] S
exo-exo (**1**)	82	38–40	48.8	4.4	
endo-exo (**2**)	89	83.5–84.5	49.1	4.3	
exo-endo (**3**)	95	77.5–79 (EtOH)	49.3	4.2	
endo-endo (**4**)	86	75–76.6	49.0	4.3	9.4
Nortricyclane-3-methanol (**7**)	98	59–61	49.2	4.3	9.5

[a] Calcd.: C, 39.0; H, 4.4; S, 9.3.

Acetates.—To a solution of 250 mg. of the alcohol in 2 ml. of pyridine was added 7 ml. of acetic anhydride. The mixture was allowed to stand for 4–5 hr.; then 5 ml. of cold water was added. The mixture was extracted four times with 10 ml. of pentane. After washing the pentane solution with dilute hydrochloric acid

TABLE VII

Acetate	$n^{25}D$	B.p., °C. (mm.)	%[a] C	H
exo-exo (**1**)	1.4780	99 (13)	71.8	8.2
endo-exo (**2**)	1.4810		72.3	8.5
exo-endo (**3**)	1.4785		72.4	8.3
endo-endo (**4**)	1.4833		72.5	8.5
Nortricyclane-3-methanol (**7**)	1.4686		72.0	8.5

[a] Calcd. for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5.

and with water, it was dried over magnesium sulfate and the pentane was removed to give an essentially quantitative yield of the acetate. The data are summarized in Table VII.

Kinetic Method.—The rates of acetolysis were determined in a conventional fashion using a set of sealed vials for each run. The vials were removed at known times; a measured portion of the contents was removed and titrated with *p*-toluenesulfonic acid in glacial acetic acid to determine the remaining acetate.

The rate constants for the reactions of **2a** were obtained using an analysis similar to that of Young, Winstein, and Goering, except that the *F* values were not obtained from the solvolysis data but rather from the independently measured rate of isomerization. The reaction solution was made up as for the other kinetic runs and 20–30-ml. aliquots were removed at specified times and quenched by pouring into excess pentane. Each pentane solution was extracted twice with water and with 15% sodium carbonate solution. The pentane was removed and the residual mixture was kept at 10^{-3}-mm. pressure until no product acetates were present as was indicated by the absence of the CH_3CO peaks in the n.m.r. spectrum. The mixture of brosylates was dissolved in carbon tetrachloride and the n.m.r. spectrum was obtained. Since brosylate **1** exhibits a peak at τ 9.08 which is not present in **2**, it is possible to calculate the *F* values directly. The titrimetric and n.m.r. data are summarized in Table VIII. The x' values in the table were obtained from the x values (amount of acid liberated at time t) by multiplication by 1/0.90. The correction factor takes into account the production of about 10% of unreactive nortricyclane-3-methyl tosylate in the solvolysis. The rate constant was evaluated graphically by plotting $\ln a/(a - x)F$ against time.

TABLE VIII

RATE OF SOLVOLYSIS AND ISOMERIZATION OF BROSYLATE 2

Time × 10^{-3}, sec.	$(H_\infty - H_t)$[a]	x[b]	x'	F	$(a - x')F$
7.6	0.990	0.00427	0.00459	0.81	0.04252
18.9	0.898	0.00884	0.00950	0.60	0.02857
25.8	0.854	0.01102	0.01185	0.56	0.02536
34.6	0.752	0.01609	0.01730	0.50	0.01993
44.0	0.683	0.01952	0.02098	0.43	0.01556
57.4	0.592	0.02404	0.02584	0.25	0.00784

[a] *H* is the milliliters of 0.04966 *N* acid required per 2-ml. aliquot: $H_0 = 1.984$, $H_\infty = 0.910$. [b] Amount of acid formed.

The product composition was determined by carrying out the solvolysis to at least three half-lives, diluting with water, and extracting with pentane. The pentane solution was concentrated and analyzed *via* g.l.p.c. The products were identified both by using the retention times independently measured using authentic samples and by collection of the various fractions followed by a comparison of the n.m.r. spectra with those of authentic samples. In the case of the bicyclooctenyl acetate, the identification of the g.l.p.c. fraction was made after hydrogenation and hydrolysis to bicyclo[3.2.1]octanol-6.

Trialkoxyalkylidenephosphoranes from the Reaction of Trialkyl Phosphites with *cis*- and *trans*-Dibenzoylethylene. P^{31} Nuclear Magnetic Resonance Spectra[1,2]

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Trimethyl phosphite reacts with *cis*- and *trans*-dibenzoylethylene at 20° in methylene chloride to give a moderately stable *trialkoxyalkylidenephosphorane.* This *phosphitemethylene* or *ylide* undergoes a methyl group translocation which results in an enol phosphonate methyl ether. The ylide reacts with benzyl bromide and gives an enol phosphonate benzyl ether. The enol ethers are converted into a furylphosphonate on heating. The ylide is capable of reacting with a second molecule of dibenzoylethylene; the structure of the products varies with the nature of the solvent; in alcohol the products are mainly 1,2-dibenzoylethane, 1,2,3,4-tetrabenzoylbutane, and trimethyl phosphate. The main product of the reaction of trimethyl phosphite with dibenzoylethylene in boiling xylene is 2,5-diphenylfuran. The compound with pentavalent phosphorus, said to be formed in this reaction, was not observed.

Kukhtin and Orekhova[3] isolated a noncrystalline material from the reaction of *trans*-dibenzoylethylene (DBE) with triethyl phosphite in ether solution. They ascribed to this material the structure of a cyclic tetraalkoxyalkylphosphorane Ia, but gave no analysis and offered no proof of structure. When the reaction of DBE with the phosphite was carried out at elevated temperatures, the products were 2,5-diphenylfuran and triethyl phosphate (31%).

Other cyclic oxyalkylphosphoranes have been postulated as intermediates in reactions of trialkyl phosphites with α,β-unsaturated carbonyl compounds.[4,5]

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[2] This investigation was supported by the National Science Foundation (G 19 509), and by Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute.

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[4] (a) G. Kamai and V. A. Kukhtin, *ibid.*, **27**, 2431 (1957); (b) *ibid.*, **27**, 2436 (1957); (c) *ibid.*, **31**, 1621 (1961); (d) *cf. Chem. Abstr.*, **52**, 7127*d* (1958); **52**, 9948*f* (1958).

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