

2-m. stainless steel di-*n*-decyl phthalate column (Type A) was employed with hydrogen at 15–20 lb. p.s.i. gauge pressure as the carrier gas. Quantitative estimation of areas was made by tracing the curves on filing cards, cutting out the pertinent section and weighing. In most instances, a correction factor (c.f.) needed to multiply the observed composition to obtain the true composition was determined by calibration with known mixtures.

Photolysis of Diethyl Diazomalonate (I) in 2,3-Dimethylbutane.—A solution of 13.0 g. (0.07 mole) of diazomalonate ester in 550 ml. (5.4 mols) of 2,3-dimethylbutane (Phillips Petroleum Co.; pure grade, > 99%) was irradiated according to the previously described procedure for diazoacetic ester.⁴ The crude malonic esters remaining after distillation of the solvent were refluxed 3 hr. with 125 g. of 10% ethanolic potassium hydroxide. Removal of the ethanol left a solid residue which was dissolved in 50 ml. of water and acidified. Ether extraction afforded the crude malonic acids which were decarboxylated by heating at 160–180°. The resulting monocarboxylic acids were dissolved in ether and extracted with 6 *N* sodium hydroxide. After two ether extractions, the aqueous solution of sodium salts was acidified to liberate the free acids, which were then converted by excess ethereal diazomethane to the methyl esters; 4.09 g. (37.2% of theory), b.p. 56–63° (15 mm.).

G.l.p.c. separation of the liquid esters at 133° gave two fractions, of which the first (67.6%) was isolated and shown to have the same infrared spectrum as methyl 3,3,4-trimethylpentanoate (c.f. 1.03)⁴ and the second (32.4%) had the same infrared spectrum as authentic methyl 4,5-dimethylhexanoate (c.f. 0.97).⁴

Calculation of Reactivity Ratio.—The reactivity ratio of different groups (or types of hydrogen atoms), α_{ia} , is defined as the ratio of the rate of reaction (of the carbene) with the group *i* to that with group *a* taken as standard. The reactivity ratio is therefore equal to $f_i n_a / n_i f_a$ where *f* is the fraction of total product and *n* the number of each type of group.

Photolyses in Isobutane. (a) **Authentic Materials.**—Methyl 2,2-dimethylbutanoate, b.p. 133° (760 mm.), was prepared according to Homeyer, *et al.*¹⁵ Diethyl *t*-butylmalonate was prepared from *t*-butylacetic acid by the procedure of Bush¹⁶; b.p. 102–103° at 11 mm. Methyl 4-methylpentanoate, b.p. 146° (760 mm.), and diethyl isobutylmalonate were prepared by a standard malonic ester synthesis. A mixture of 61.9% of methyl *t*-butylacetate

(15) A. H. Homeyer, F. C. Whitmore and W. H. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933).

(16) M. T. Bush, *ibid.*, **61**, 637 (1939).

and 38.1% of methyl 4-methylpentanoate was analyzed by g.l.p.c. at 100°; three determinations gave relative compositions of 61.9 and 38.1%, 61.6 and 38.4%, and 61.3 and 38.7%. Correction factors (c.f.) of 1.005 and 0.992, respectively, were derived and applied in the analytical procedure.

(b) **Methyl Diazoacetate.**—Irradiation of 10.0 g. of methyl diazoacetate in 1000 ml. of isobutane gave 6.48 g. of product, b.p. 114–117° at 760 mm., which was shown by g.l.p.c. (100°) to consist of 25.4% of methyl *t*-butylacetate and 74.6% of methyl 4-methylpentanoate. The pure compounds were separated by g.l.p.c. and were identified by their infrared spectra.

(c) **Ethyl Diazomalonate.**—The product from irradiating 8.0 g. of ethyl diazomalonate in 1000 ml. of isobutane was saponified with 120 g. of refluxing ethanolic potassium hydroxide. The crude acids were decarboxylated and methylated with ethereal diazomethane giving 2.74 g. of mixed esters, b.p. 150–180°. Separation by g.l.p.c., identification by infrared spectrum and analysis by g.l.p.c. showed the mixture to consist of 70.0% of methyl *t*-butylacetate (c.f. 1.01) and 30.0% of methyl 4-methylhexanoate (c.f. 0.99).

(d) **Validation of Analytical Procedure.**—A synthetic mixture of 2.120 g. (70.0%) of diethyl *t*-butylmalonate and 0.910 g. (30.0%) of diethyl isobutylmalonate was treated in the same manner as above, then saponified, decarboxylated, methylated and analyzed by g.l.p.c. at 100°. The mixture, after applying the correction factor, appeared to consist of 69.3% of methyl *t*-butylacetate and 30.7% of methyl isobutylacetate.

Photolyses in *n*-Butane. (a) **Authentic Materials.**—Methyl *n*-hexanoate (IX) was obtained from commercial hexanoic acid and excess ethereal diazomethane: b.p. 152° (760 mm.), n_D^{25} 1.4038. Methyl 3-methylpentanoate (VIII) was prepared from *sec*-butyl chloride by a standard malonic ester synthesis: b.p. 142° (760 mm.), n_D^{25} 1.4050. Triplicate analyses by g.l.p.c. at 100° of a synthetic mixture of 69.0% of VIII and 31.0% of IX indicated 69.8, 69.8 and 69.5% of VIII, corresponding to c.f. of 0.990 for VIII and 1.022 for IX.

(b) **Methyl Diazoacetate.**—The reaction of 9.5 g. of methyl diazoacetate afforded 6.02 g. (49%) of mixed esters consisting of 60.9% of VIII and 39.1% of IX. The pure products were separated by g.l.p.c. and identified by their infrared spectra.

(c) **Ethyl Diazomalonate.**—The product from 15.0 g. of I was worked in the usual manner to give 2.06 g. of mixed esters, b.p. 75–154°, consisting of 84.8% of VIII and 15.2% of IX (determined by g.l.p.c. with hydrogen at 15 lb. p.s.i. (gauge) and 75°).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Ionic Reactions in Bicyclic Systems. III. Solvolysis of Bicycloöctanyl and Bicycloöctenyl *p*-Toluenesulfonates¹

BY HARLAN L. GOERING AND MARTIN F. SLOAN²

RECEIVED OCTOBER 17, 1960

First-order rate constants for acetolysis and ethanolysis of (a) *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I), (b) bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) and (c) *exo(axial)*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) have been determined. Rate constants for the solvolysis of VII in 80% aqueous acetone and acetolysis of *endo(equatorial)*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI) have also been determined. Ionization of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I), which results in complete rearrangement to the bicyclo[3.2.1]oct-3-en-2-yl system, is anchimerically assisted. Solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) is accompanied by internal return which results in the interconversion (equilibration) of the two isomers during solvolysis. The reactivities of these isomers are consistent with the idea that ionization results in the formation of a common bridged ("non-classical") carbonium ion; *i.e.*, anchimeric acceleration is indicated.

Introduction

In the first paper in this series³ it was shown that acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-

(1) This work was supported in part by the Office of Ordnance Research.

(2) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

toluenesulfonate (I) gives *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate (IX). Deamination of *endo*-5-aminobicyclo[2.2.2]oct-2-ene also results in complete rearrangement to the bicyclo[3.2.1]oct-3-en-2-yl system.^{3,4} On the other hand, solvolysis

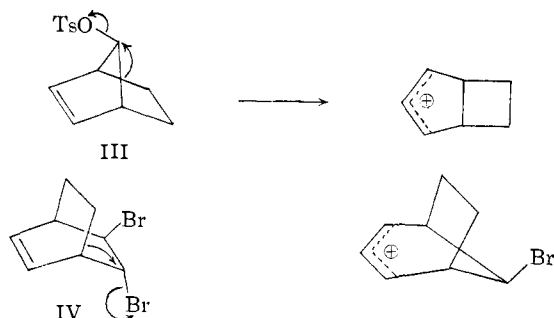
(3) H. L. Goering, R. W. Greiner and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

of the saturated analog, bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII), or deamination of the corresponding amine results in only partial rearrangement to the bicyclo[3.2.1]octan-2-yl system.⁵

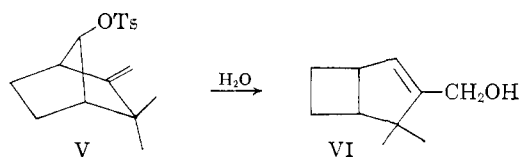
The Wagner–Meerwein conversion of the *endo*-bicyclo[2.2.2]oct-5-en-2-yl system to the bicyclo[3.2.1]oct-3-en-2-yl system is not unexpected. By analogy with related systems, ionization of I would be expected to give the bicyclo[3.2.1]-allylic cation II. Evidence has been presented that *syn*-7-norbornenyl *p*-toluenesulfonate (III)^{6,7}



and *trans*-5,6-dibromobicyclo[2.2.2]oct-2-ene (IV)⁸ ionize in polar media to give the allylic carbonium ions. In each of these cases participation by the methylene group is manifested by a high reactivity. The conversion of *syn*-7-camphenyl *p*-toluene-



sulfonate (V) to 1,1-dimethyl-2-hydroxymethylbicyclo[3.2.0]hept-2-ene (VI) by hydrolysis⁹ indicates that here also ionization may involve direct formation of the allylic carbonium ion. However, in this case there is no apparent rate enhancement—the acetolysis rate of V at 140° is slightly smaller than that of its saturated analog.⁹



In the present work the solvolytic reactivity of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I) in ethanol and acetic acid was determined to obtain information concerning the nature of carbonium ion reactions in this system. To assess the rate enhancement resulting from methylene participation the rates of acetolysis and ethanolysis of the saturated analog, bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII),⁵ were also determined.

(4) W. C. Wildman and D. R. Saunders, *J. Am. Chem. Soc.*, **76**, 946 (1954).

(5) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

(6) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(7) S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

(8) A. Gagneux and C. A. Grob, *Helv. Chim. Acta*, **42**, 1753 (1959).

(9) E. E. van Tamelen and C. I. Judd, *J. Am. Chem. Soc.*, **80**, 6305 (1958).

It was discovered that VII undergoes a reversible stereospecific isomeric rearrangement to *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) during solvolysis and for this reason solvolysis of the latter compound, and its epimer XVI, were also investigated.

Results

endo-Bicyclo[2.2.2]oct-5-en-2-ol, prepared and purified by a method described earlier,¹⁰ gave a *p*-toluenesulfonate derivative which contained a reactive contaminant (probably the *exo* isomer).^{3,11} Pure *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I)³ was obtained by recrystallization of this material from ethanol. When Compound I was derived from pure *endo*-bicyclo[2.2.2]oct-5-en-2-ol³ the ethanol recrystallization was not necessary. Homogeneous samples of I, prepared by either of these ways, showed excellent first-order solvolytic behavior. The *p*-toluenesulfonate derivative I was shown to have the bicyclo[2.2.2]oct-5-en-2-yl structure by conversion (hydrogenation) to bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII).⁵

Specific first-order rate constants for acetolysis (30° and 42°) and ethanolysis (30° and 49°) are given in Table I. In each experiment the reaction was followed to at least 75% completion and nine or more values of the first-order constant were determined from appropriately spaced titrations. No trends in these values were observed and the rate constants were reproducible. A kinetic experiment is included in the Experimental section. With this compound, and all of the others investigated in the present work, the infinity titers corresponded to theory.

With one exception, the constants in Table I are average values (and deviations from the

TABLE I
SOLVOLYSIS OF *endo*-BICYCLO[2.2.2]OCT-5-EN-2-YL *p*-TOLUENESULFONATE (I)^a

Temp., °C.	<i>n</i> ^b	10 ³ <i>k</i> , sec. ⁻¹
Acetolysis		
30.07	2	2.97 ± 0.03
30.07	1 ^c	3.10 ± .02
42.06	2	13.2 ± .05
$\Delta H^\ddagger = 23.1$ kcal./mole; $\Delta S^\ddagger = -3.0$ e.u. at 30°		
Ethanolysis		
30.07	3	0.323 ± 0.002
49.03	2	3.95 ± .05
$\Delta H^\ddagger = 25.0$ kcal./mole; $\Delta S^\ddagger = -1.2$ e.u. at 30°		

^a Initial concentration of I was 0.025 *M* in all experiments. ^b Number of independent kinetic experiments. ^c Contained 0.055 *M* sodium acetate.

average) of two or three independent kinetic experiments. The other is the average of nine determinations made during the single experiment. The activation parameters included in the table

(10) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1953).

(11) This material, even after several recrystallizations from ether-pentane, gave apparent integrated first-order rate constants (ethanolysis and acetolysis) which decreased more than 60% during the first 50% reaction.

were computed in the usual manner.¹² The second entry in Table I shows that 0.055 *M* sodium acetate causes a slight positive salt effect. It was under these conditions that the product was shown to be *exo(axial)*-bicyclo[3.2.1]oct-3-en-2-yl acetate (IX).³

To determine the effect of the double bond in I on the reactivity, the rates of acetolysis and ethanolsis of the saturated analog, bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII), were investigated. The *p*-toluenesulfonate VII was prepared from pure bicyclo[2.2.2]octan-2-ol.⁵ In this case the integrated first-order rate coefficient, *k* (eq. 1), for both acetolysis and ethanolsis decreased during the reaction. Both the initial rate constants (obtained by extrapolating plots of percentage reaction *vs.* integrated first-order rate coefficient to 0% reaction) and the rate and magnitude of the downward drift were reproducible. The integrated constants drifted down throughout the entire reaction. However, plots of log [ROTs] *vs.* time became linear after about 30% reaction for acetolysis and about 40% reaction for ethanolsis. In other words, the instantaneous first-order rate constant, *k*_{inst} (eq. 2) drifted down during the early stages of the reaction and then became constant. In all cases, integrated constants calculated from data for the last 50% of reaction were steady.

$$k = (1/t) \ln ([ROTs]_0/[ROTs]_t) \quad (1)$$

$$k_{inst} = -(d[ROTs]/dt)/[ROTs]_t \quad (2)$$

The pertinent kinetic experiments are summarized in Table II. Two values of the rate constants are given in the table. The first, *k*_{i[2.2.2]}, is the initial rate constant (obtained by extrapolating the integrated coefficients to 0% reaction) and the second, *k*_t, is the average of five or more values (and average deviation) of the integrated first-order constant for the final 50% of the reaction (*i.e.*, the zero-time titer was taken at about 50% reaction). The latter values correspond to the instantaneous first-order rate constant after it becomes steady—if integrated first-order constants are steady, *k*(eq. 1) = *k*_{inst}(eq. 2). The data in Table II show that the acetolysis behavior of VII is not affected by the presence of 0.05 *M* sodium acetate. One rate constant for the hydrolysis of VII in 80% acetone is included in Table II. In this case the rate constant also drifted downward (from 9.1×10^{-5} sec.⁻¹, 0% reaction, to 6.5×10^{-5} sec.⁻¹, 75% reaction). These are the conditions under which the product was shown to be a binary mixture of bicyclo[2.2.2]octan-2-ol and *axial*-bicyclo[3.2.1]octan-2-ol.⁵

The decrease in the rate constants for the solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) is due to rearrangement during solvolysis to the slightly less reactive *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII). That VIII is produced during solvolysis, rather than being present in the *p*-toluenesulfonate (VII) from the outset, was established as follows. The infrared spectrum of VII used in the kinetic experiments did not contain bands characteristic of the bicyclo[3.2.1] isomer VIII. Moreover,

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953.

TABLE II
SOLVOLYSIS OF BICYCLO[2.2.2]OCTAN-2-YL *p*-TOLUENESULFONATE (VII)^a

Temp., °C.	<i>n</i> ^b	Added salt, 10 ² <i>M</i>	10 ⁵ <i>k</i> _{i[2.2.2]} , ^c sec. ⁻¹	10 ⁵ <i>k</i> _t , ^d sec. ⁻¹
Acetolysis				
30.07	2		0.68 ± 0.01	0.448 ± 0.001
49.03	2		7.4 ± .1	5.40 ± .04
49.03	2	2.99 NaOAc	7.6 ± .1	5.42 ± .05
49.03	2	5.50 NaOAc	7.5 ± .1	5.36 ± .01
49.03	1 ^e	5.50 NaOAc	7.7 ± .2	5.35 ± .07
Ethanolsis				
49.03	2		1.32 ± 0.01	0.978 ± 0.004
80% aqueous acetone ^f				
49.03	1		9.1 ± 0.2	

^a Initial concentration of VII was 0.025 *M*. ^b Number of independent kinetic experiments. ^c Initial rate constant. ^d Rate constant after 50% reaction (*i.e.*, zero-point titer taken at about 50% reaction). ^e Sample of VII used in this experiment was prepared by recrystallizing analytically pure material (material used in other experiments) four times. ^f Composition based on volumes of pure components at 25° before mixing.

the acetolysis rate behavior and physical properties of an analytically pure sample of VII were unchanged by four additional recrystallizations (fifth entry in Table II).

The less reactive isomer formed during the solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) was identified as *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) in the following way. Unreacted *p*-toluenesulfonate was isolated from an acetolysis reaction after 50% reaction. After recrystallization, the yield of recovered *p*-toluenesulfonate was 63%. The melting point (11° lower than that of pure VII) and infrared spectrum of this material were indistinguishable from those of a pure synthetic binary mixture of 30% VII and 70% VIII. Bands characteristic of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI) were absent.

The fact that the instantaneous first-order constants become steady after the initial downward drift indicates that a steady-state ratio of concentrations of VII and VIII is obtained; *i.e.*, the rearrangement is reversible and reaches equilibrium. This was confirmed by investigating the solvolytic behavior of *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII).

Pure VIII was prepared from pure *axial*-bicyclo[3.2.1]octan-2-ol.⁵ In this case the integrated first-order coefficients drifted upward for both ethanolsis and acetolysis. As for the solvolysis of VII, plots of log [ROTs] *vs.* time become linear after about 30% acetolysis and 45% ethanolsis. Thus in this case the instantaneous rate constants show initial upward drifts and then become steady. Data for the acetolysis and ethanolsis of VIII are given in Table III.

That the upward drift in the rate was indeed due to isomerization to the more reactive bicyclo[2.2.2] isomer VII was demonstrated by isolation of the unsolvolyzed *p*-toluenesulfonate from an ethanolsis experiment after 50% solvolysis. This material, isolated in 78% yield, had an infrared

TABLE III
SOLVOLYSIS OF *axial*-BICYCLO[3.2.1]OCTAN-2-YL *p*-TOLUENE-SULFONATE (VIII) AT 49.03°^a

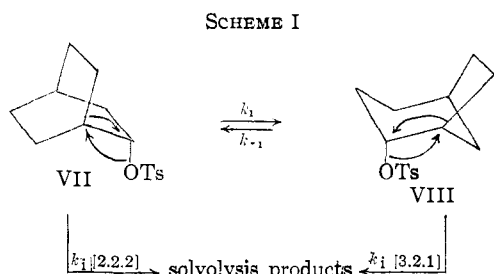
Solvent	10 ⁵ $k_{i[3.2.1]}$, ^b sec. ⁻¹	10 ⁵ $k_{i[2.2.2]}$, ^b sec. ⁻¹
HOAc	4.3	5.23 ± 0.07
HOAc	4.3	5.28 ± .03
EtOH	0.67	0.928 ± .020
EtOH	0.64	0.986 ± .034

^a Initial concentration of VIII was 0.025 M. ^b See footnotes c and d, Table II.

spectrum which corresponded in detail to a binary mixture of 75 ± 5% VIII and 25 ± 5% VII.

The data presented in Tables II and III clearly show that bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) are interconverted during solvolysis. The rate of interconversion (equilibration) is such that starting with either isomer a steady-state ratio of the two isomers is reached by about 30% solvolysis in acetic acid and 40% solvolysis in ethanol. It should be noted that values of k_f (these are the rate constants for the steady-state ratio of VII and VIII) are essentially the same for VII (Table II) and VIII (Table III). The slight differences are probably due to the fact that the zero-point titers were taken a little before equilibration was complete. The following experiment was carried out to check this point more carefully. Solutions of pure VII and VIII in acetic acid were prepared and heated simultaneously in the 49.03° thermostat. The reactions were followed from 75% (zero time) to 95% completion. The integrated rate constants for this portion of the reaction ($5.4 ± 0.2 × 10^{-5}$ sec.⁻¹ for VII and $5.2 ± 0.1 × 10^{-5}$ sec.⁻¹ for VIII) were steady and the same (within experimental error) for the two solutions.

The solvolytic behavior of the isomeric *p*-toluenesulfonates VII and VIII is summarized by the accompanying scheme. From the rate



constants for solvolysis ($k_{i[2.2.2]}$ and $k_{i[3.2.1]}$; Tables II and III) and the values of the first-order constant after equilibration (k_f in Tables I and II) the mole fraction of VII, F , in the equilibrated unsolvolyzed *p*-toluenesulfonate can be determined from eq. 3.¹³ Because both the numerator and

$$(k_f - k_{i[3.2.1]}) / (k_{i[2.2.2]} - k_{i[3.2.1]}) = F \quad (3)$$

denominator are small differences between numbers with rather large uncertainties, the value of F obtained in this way is not very accurate. This treatment indicates that the mole fraction of VII

(13) W. G. Young, S. Winstein and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

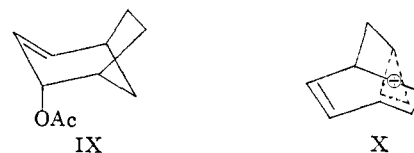
(F) in the equilibrated unsolvolyzed *p*-toluenesulfonate is $0.32 ± 0.04$ for acetolysis at 49° and $0.45 ± 0.04$ for ethanolysis at 49°. These values correspond to equilibrium constants (K_{eq}) of $2.1 ± 0.4$ for acetic acid and $1.2 ± 0.3$ for ethanol for the interconversion of VII and VIII. This steady-state composition differs slightly from the thermodynamic equilibrium composition because the isomers are not consumed (solvolyzed) at equal rates. The equilibrium mixture would contain slightly more of the more reactive isomer VII; *i.e.*, F would be higher and K_{eq} would be lower. From the present data it is clear that the difference in thermodynamic stability between VII and VIII under these conditions is <0.5 kcal.

In principle, the composition of the unsolvolyzed *p*-toluenesulfonate during the equilibration can be determined by eq. 3 (in this case k_f would be replaced by the time-dependent instantaneous rate constant, k_{inst} (eq. 2)).¹³ This would enable determination of the rate constant for equilibration, $k_1 + k_{-1}$ (Scheme I). However, instantaneous rate constants cannot be determined with an uncertainty of less than about 25% of the total range of the drift ($k_{i[2.2.2]} - k_f$). Thus only a rough estimate of the rate of equilibration can be made. Plots of k_{inst} ¹³ vs. time for the early stages of the acetolysis of VII at 49° show that 3000 seconds is an upper limit for a half-life for equilibration (the period required for k_{inst} to drift 50% of the total change). This gives a lower limit of $2 × 10^{-4}$ sec.⁻¹ for ($k_1 + k_{-1}$). From this value and that of the equilibrium constant ($k_1/k_{-1} = 2.1$) it can be determined that under these conditions lower limits for k_1 and k_{-1} are $1.4 × 10^{-4}$ sec.⁻¹ and $0.6 × 10^{-4}$ sec.⁻¹, respectively.

The rate of acetolysis of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI) at 49.03° was also determined for comparison with the rates of the other isomers. In this case excellent first-order behavior was observed and $k = 3.05 ± 0.02 × 10^{-6}$ sec.⁻¹. It is under these conditions that the acetolysis substitution product is *equatorial*-bicyclo[3.2.1]octan-2-yl acetate (*i.e.*, the geometric configuration is retained completely⁶).

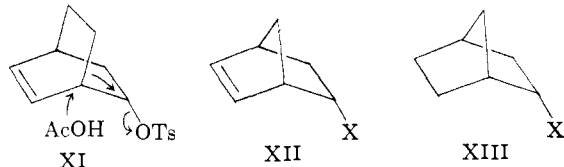
Discussion

As mentioned in the Introductory section, acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl (I) results in complete rearrangement and gives *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate (IX).³ This suggests that ionization of I may involve methylene participation with direct formation of the relatively stable allyl carbonium ion II or possibly a non-classical ion X with substantial allylic character. The bridged or non-classical structure X nicely



accommodates the complete stereospecificity of the reaction (only IX is formed³). However, it is possible that II undergoes exclusive *exo* attack to

give IX.¹⁴ It is significant in this connection that acetate ion results in only a small "normal"¹⁵ positive salt effect and that $k_{\text{HOAc}}/k_{\text{EtOH}} = 9.2$ at 30°. This indicates nucleophilic participation by solvent is not important¹⁶ or, in other words, acetolysis (and probably also ethanolysis) involves a carbonium ion intermediate. Thus concerted processes such as XI (which also would result in the stereospecific conversion of I to IX) seem unlikely.



The most compelling evidence for participation by a neighboring group (in this case methylene) is a greater observed rate of ionization than would otherwise obtain. Relative rates of acetolysis of I, VII, VIII, XVI, *endo*-dehydronorbornyl *p*-toluenesulfonate (XII, X = OTs), *endo*-norbornyl *p*-toluenesulfonate (XIII, X = OTs) and cyclohexyl *p*-toluenesulfonate are given in Table IV. These data are helpful for estimating the unassisted ionization rate for *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I).

TABLE IV
ACETOLYSIS REACTIVITIES OF BICYCLIC SYSTEMS

<i>p</i> -Toluene-sulfonate	Temp., °C.	$10^3 k$, sec. ⁻¹	Relative reactivity ^a
I	30	2.97	105
VII	30	0.68 ^b	24
	49	7.3 ^b	
VIII	49	4.3 ^b	14
XVI	49	0.305	1
Cyclohexyl ²⁶	25	4.7×10^{-3c}	0.34
	30	1.0×10^{-2}	
<i>endo</i> -Norbornyl (XIII) ¹⁹	25	2.8×10^{-3d}	0.20
<i>endo</i> -Dehydronorbornyl (XII) ¹⁸	25	6.3×10^{-3d}	4.5×10^{-3}

^a These values determined from rate constants in preceding column by comparing constants for pairs of compounds at the same temperature. ^b Initial rate constants. ^c Extrapolated from data for other temperatures taken from ref. 26. ^d One-third of the value reported for the corresponding *p*-bromobenzenesulfonate in the indicated reference.

As shown in Table IV, at 30° the rate of acetolysis of I is 4.4 times greater than that of its saturated analog, bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII). However, the unassisted ionization rate would be expected to be lower for the unsaturated analog. The inductive effect of the double bond would lower the unassisted rate in I relative to VII, and non-bonded interactions between the tosyloxy group and the C₅- and C₆-hydrogen atoms (*cis* to the

tosyloxy group) in VII would increase its rate (steric acceleration¹⁷) relative to that of I. It would appear that the relative unassisted rates for I and VII should be comparable to those for *endo*-dehydronorbornyl (XII)¹⁸ and *endo*-norbornyl *p*-bromobenzenesulfonates (XIII, X = *p*-BrC₆H₄-SO₃).¹⁹ Presumably in the latter two systems rates of ionization are not anchimerically assisted. As indicated in Table IV the rate of acetolysis of the saturated analog XIII at 25° is 44 times faster than that of XII. Thus, to a first approximation, in the absence of participation the rate of acetolysis of I would be expected to be about 1/44 as fast as that of VII or about 1/200 the observed rate.

There are several complications involved in this analysis. A minor one concerns the greater stability of bicyclo[2.2.2]octane and -octene systems relative to the corresponding bicyclo[2.2.1]heptane and -heptene systems.²⁰ This difference apparently results from the greater strain associated with rigid bicyclo[2.2.1] systems; or, to put it another way, bicyclo[2.2.2] systems are more flexible.²⁰ This flexibility (twisting) results in a reduction of eclipsed hydrogen-hydrogen interactions which may decrease the driving force for ionization in bicyclo[2.2.2] systems relative to bicyclo[2.2.1] systems (*cf.* rates of ionization of cyclopentyl and cyclohexyl derivatives²¹). Because of factors of this type the difference in the unassisted ionization rates for the saturated (VII and XIII) and unsaturated analogs (I and XII) may not be the same for [2.2.2]- and [2.2.1]bicyclic systems.

Of greater significance is the fact that for two reasons the rate of solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) does not correspond to the rate of unassisted ionization. In the first place, the rate of ionization of VII is apparently anchimerically accelerated. Secondly, because of ion pair return¹⁵ (presumably internal return²²) the rate of ionization of VII is greater than the rate of acetolysis.²³ As will be shown below, the rate of acetolysis of VII (which is about 1/5 of the rate of ionization) is about 100 times greater than that estimated for unassisted ionization. Because of these complications the rate enhancement resulting from methylene participation in the acetolysis of I cannot be determined quantitatively. However, it is clear that the observed rate of acetolysis of I is at least 10² and perhaps over 10³ times greater than if participation were not involved. Perhaps the *endo*-dehydronorbornyl system XII is the best model for estimating the unassisted

(17) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

(18) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(19) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

(20) R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(21) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(22) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

(23) Apparently any ion pair return that might be involved in the acetolysis of I would not affect the rate of solvolysis (*i.e.*, in this case the rate of solvolysis corresponds to the rate of ionization). This is because the expected product of ion pair return, *axial*-bicyclo[3.2.1]oct-3-en-2-yl *p*-toluenesulfonate, would solvolyze immediately. See A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2767 (1956), for a similar situation.

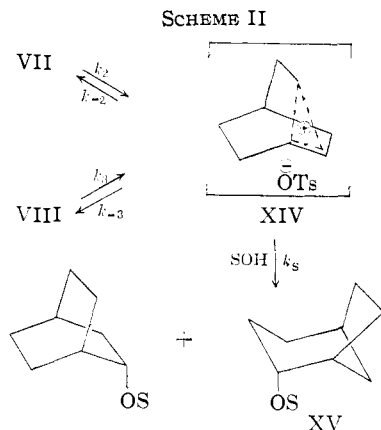
(14) In principle, the two structures for the cation are distinguishable because II has a plane of symmetry whereas X is asymmetric. In another problem evidence is being sought as to whether or not the cation derived from active I (or the corresponding amine) is asymmetric.

(15) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **80**, 459 (1958) and earlier papers in that series.

(16) S. Winstein, *et al.*, *ibid.*, **79**, 4146 (1957); **75**, 147 (1953); **73**, 2700 (1951).

sisted rate for I. On this basis the rate enhancement amounts to a factor of 2.3×10^4 (Table IV).

Evidently, the interconversion of bicyclo[2.2.2]octan-2-yl (VII) and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII), which accompanies solvolysis, involves internal return as illustrated by Scheme II. This is an expansion of Scheme I and includes the "intimate" ion pair intermediate (XIV)²² common to the reversible isomerization and solvolysis. The bridged structure for the cation in XIV has been assigned⁵ to accommodate the stereochemistry of the solvolysis; the bicyclo[3.2.1]product has the *axial* configuration XV.⁵ As will be shown below, the rates of ionization of VII and VIII are consistent with this assignment. Only the internal ion pair intermediate is included in this scheme. Presumably additional intermediates, including the dissociated bridged carbonium ion, are involved in the solvolysis-product forming reaction (k_s).²² It is mechanistically significant that $k_{\text{HOAc}}/k_{\text{EtOH}} = 5.6$ for VII and 6.5 for VIII at 49° (this indicates a carbonium ion mechanism¹⁶) and that the addition of sodium acetate is essentially without effect (there are no indications of special salt effects²⁴ for solvolysis or isomerization).

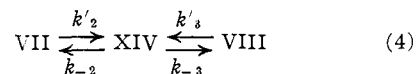


That the intramolecular interconversion of VII and VIII involves an ionic process as illustrated in Scheme II is indicated by the fact that it proceeds slower in ethanol than in acetic acid. Moreover, the data show qualitatively that the rate of equilibration relative to solvolysis is larger for acetolysis than ethanolysis; *i.e.*, $k_{\text{HOAc}}/k_{\text{EtOH}}$ is larger for interconversion ($k_1 + k_{-1}$; Scheme I) than for solvolysis. This means that $(k_{-2} + k_{-3})/k_s$ is smaller for ethanolysis than acetolysis. It has been observed that for other systems the ratio of internal return to solvolysis is greater for acetolysis than ethanolysis.^{15,25}

If a common bridged carbonium ion results from ionization of VII and VIII (*i.e.*, if methylene participation is involved with both isomers) the rates of ionization would be expected to be enhanced (anchimeric assistance). It is clear from the interconversion of VII and VIII (ion pair return) which accompanies solvolysis that the rate of ionization is greater than the rate of solvolysis; *i.e.*, the rate

of formation of XIV (ionization) is greater than that of production of solvolysis products.

The rates of ionization of VII and VIII (k_2 and k_3 in Scheme II) can be estimated as outlined below for VII. The rate of formation of that fraction of XIV which is converted to product is the rate of solvolysis, $k_{i[2.2.2]}$ (Scheme I and Table II). The rate of formation of the fraction of XIV involved in the isomerization can best be determined by considering the interconversion separately from solvolysis (*e.g.*, eq. 4). Two rate constants in eq. 4



(k'_2 and k'_3) differ from the corresponding constants (k_2 and k_3) in Scheme II in that the latter correspond to total rates of ionization and the former (eq. 4) correspond to rates of ionization of that fraction of substrate that is not converted to solvolysis product. Thus

$$k_2 = k'_2 + k_{i[2.2.2]} \quad (5)$$

The value of $k_{i[2.2.2]}$ can be measured directly (Table II) and k'_2 can be estimated as follows. The rate constant for isomerization of VII to VIII, k_1 (Scheme I), is related to the constants in eq. 4 as

$$k_1 = k'_2/[1 + (k_{-2}/k_{-3})] \quad (6)$$

As shown in the preceding section the lower limit for k_1 (Scheme I) is 1.4×10^{-4} . The value of k_{-2}/k_{-3} can be determined from the equilibrium constant for the interconversion ($K_{\text{eq}} = 2.1$) and eq. 7 by assuming that the value of the ratio k'_2/k'_3 corresponds to ratio of the initial rates of solvolysis of VII and VIII; *i.e.*, $k'_2/k'_3 = k_{i[2.2.2]}/k_{i[3.2.1]}$.

$$(k'_2/k'_3)/K_{\text{eq}} = k_{-2}/k_{-3} \quad (7)$$

Thus for acetolysis at 49°

$$k_{-2}/k_{-3} = (7.4/4.3)/2.1 = 0.8$$

and with eq. 6 it can be shown that $k'_2 = 1.4(1 + 0.8) \times 10^{-4} = 2.5 \times 10^{-4}$. Thus the total rate of ionization of VII (k_2 , Scheme II) computed from eq. 5 is $(2.5 + 0.7) \times 10^{-4} \text{ sec.}^{-1}$ or about 5 times larger than the rate constant for solvolysis ($k_{i[2.2.2]}$). A similar treatment for VIII gives a value of $1.7 \times 10^{-4} \text{ sec.}^{-1}$ (acetolysis at 49°) for the total rate of ionization (k_3 , Scheme II) which in this case is 4 times larger than the rate constant for solvolysis ($k_{i[3.2.1]}$).

It is difficult to estimate unassisted ionization rates for VII and VIII. Probably the best model for VII is the *endo*-norbornyl system XIII. In the absence of participation VII would be expected to be less reactive than XIII because of the aforementioned greater flexibility of the bicyclo[2.2.2]-system. From Table IV it can be seen that VII solvolyzes over 10^2 times faster than XIII. This, however, underestimates the difference in ionization rates by a factor of 5 providing that the rate of solvolysis corresponds to the rate of ionization for XIII. Thus, there is little doubt but that methylene participation is involved in the ionization of VII.

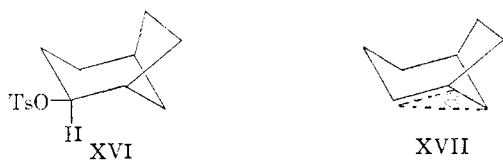
It appears that ionization of *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) is also anchimerically assisted. Its rate of solvolysis is 40 times greater than that of cyclohexyl *p*-toluenesul-

(24) S. Winstein and E. Clippinger, *J. Am. Chem. Soc.*, **78**, 2784 (1956).

(25) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); H. I. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

fonate²⁶ (Table IV). If the rate of solvolysis of cyclohexyl *p*-toluenesulfonate corresponds to its rate of ionization, the difference in rates of ionization is a factor of about 160. Thus the reactivities of VIII and VII appear to be consistent with the idea that each gives rise to a common bridged ion.⁵

Acetolysis of *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI) gives acetate with retained configuration.⁵ This suggests that ionization in this case also gives rise to a bridged ion (XVII).⁵ It is possible that the rate of ionization is greater than that of acetolysis; internal return from the symmetrical "internal" ion pair intermediate would re-form the reactant and thus would not disturb the first-order solvolytic behavior. It is apparent that anchimeric acceleration, if present, is small. However, the present data are not inconsistent with the view that a bridged ion is involved in this case also.



Experimental

Materials.—The preparations and purification of *endo*-bicyclo[2.2.2]oct-5-en-2-yl (I),³ bicyclo[2.2.2]octan-2-yl (VII)⁵ and *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI)⁵ have been described earlier.

axial-Bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) was prepared from the pure parent alcohol³ by the method described for the preparation of VII.⁵ After three recrystallizations from pentane the yield was 92%, m.p. 51.0–52.6°; Infrared bands: 9.50, 10.05, 10.65, 10.90, 11.25, 11.40, 11.75, 12.30, 12.40, 13.55, 13.90, 14.65 and 15.05 μ (carbon disulfide).

Anal. Calcd. for C₁₅H₂₀O₂S: C, 64.25; H, 7.19; solvolysis equiv., 280.4. Found: C, 64.38; H, 7.20; solvolysis equiv., 281.7 \pm 1.2 (4 determinations).

Hydrogenation of *endo*-Bicyclo[2.2.2]oct-5-en-2-yl *p*-Toluenesulfonate (I).—A solution of I³ in ether was hydrogenated at room temperature and atmospheric pressure over 5% palladium-on-barium sulfate. The theoretical amount of hydrogen was absorbed in 30 min., after which the reaction ceased. After removal of the catalyst (filtration) and solvent (distillation) the residual product was recrystallized from pentane. The melting point of this product was 54.6–55.2° (75% yield). Its infrared spectrum was indistinguishable from that of pure bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII), m.p. 54.2–55.0°.⁵

Kinetic Experiments.—The sealed ampule technique was used for the 49° and 42° experiments. The first point was taken as soon as possible after temperature equilibration and the reactions were quenched by cooling the ampules in ice. The ampules (which contained about 5.5 ml.) were then warmed to 25° after which the 5-ml. aliquots were measured and titrated. The reactions at lower temperatures were carried out in volumetric flasks. In these experiments the 5-ml. aliquots were measured at the temperature of the reaction and delivered into a flask cooled in ice-water and titrated immediately. Infinity titers for all experiments were obtained by heating aliquots in sealed ampules to 100° for a period corresponding to at least ten half-lives. In all cases observed infinity titers were within 2% of the calculated values.

A. Acetolysis.—Anhydrous acetic acid was prepared by refluxing reagent grade acetic acid with the calculated amount of acetic anhydride. The reactions were followed by titration of the aliquots with a standard 0.03 *M* solution of sodium acetate in acetic acid to the brom phenol blue end-point. In those experiments in which excess sodium

acetate was present, aliquots were delivered into an excess of standard perchloric acid in acetic acid and back-titrated with the standard sodium acetate solution.

B. Ethanolysis.—Reactions in anhydrous ethanol²⁷ and 80% aqueous acetone were followed by titrating aliquots to the brom thymol blue end-point with 0.03 *M* standard sodium methoxide in methanol. Typical acetolysis and ethanolysis experiments are summarized in Tables V and VI.

TABLE V
ACETOLYSIS OF *endo*-BICYCLO[2.2.2]OCT-5-EN-2-YL *p*-TOLUENESULFONATE (I) AT 30.07°

Time, 10 ⁻³ sec.	[ROTS] (10 ² M)	10 ³ k, sec. ⁻¹
0	2.19	
3.000	2.00	3.00
6.600	1.80	2.93
10.20	1.63	2.92
13.80	1.46	2.93
18.00	1.29	2.93
22.80	1.14	2.93
27.60	0.976	2.93
34.80	.786	2.95
42.00	.650	2.90
49.20	.512	2.95

Av. 2.94 \pm 0.02

TABLE VI
ETHANOLYSIS OF BICYCLO[2.2.2]OCTAN-2-YL *p*-TOLUENESULFONATE (VII) AT 49.03°

Time, 10 ⁻³ sec.	[ROTS] (10 ² M)	10 ³ k, sec. ⁻¹
0	2.44	1.32 ^a
11.52	2.12	1.24
17.28	1.97	1.24
23.04	1.85	1.21
28.80	1.73	1.19
35.22	1.62	1.17
40.80	1.52	1.16
47.82	1.41	1.14
54.90	1.32	1.13
62.10	1.23	1.11
86.22	0.964	1.08
99.90	.853	1.05
112.5	.748	1.05
125.1	.671	1.03
137.7	.590	1.03

Recalculation of data using 47.82 \times 10³ sec. as zero time

0	1.41	
7.080	1.32	1.01
14.28	1.23	0.978
38.40	0.964	.998
52.08	.853	.970
64.68	.748	.985
77.28	.671	.965
89.88	.590	.972

Av. 0.982 \pm 0.012

^a This value obtained by extrapolation to 0% reaction.

Isolation of Unsolvolyzed *p*-Toluenesulfonate. A. Acetolysis of Bicyclo[2.2.2]octan-2-yl *p*-Toluenesulfonate (VII).—A solution of 2.81 g. (0.01 mole) of VII, m.p. 54.2–55.0°, in 50 ml. of anhydrous acetic acid was heated at 49.03° for 190 min. (50% reaction). After cooling, the solution was poured into a flask containing 100 g. of crushed ice, and the resulting mixture was extracted with four 50-ml. portions of ether. The ether extracts were combined, washed with 10% sodium carbonate solution and dried over magnesium sulfate. The volume of ether was reduced to ca. 5 ml. under a stream of air and the resulting solution was diluted with 35 ml. of pentane. Crystallization was

(23) H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956).

(27) R. H. Manske, *ibid.*, **53**, 1104 (1931).

induced by cooling in Dry Ice, and the solvent was removed with a filter stick. Three recrystallizations of the residual material from ether-pentane yielded 886 mg. (63%) of material which melted at 42.5–43.7°. When mixed with VII, m.p. 54.2–55.0°, the mixture melted at 40.6–46.2°; when mixed with VIII, m.p. 51.0–52.6°, the mixture melted at 43.8–50.0°.

The infrared spectrum of the recovered tosylate was an exact composite of the spectra of VII⁵ and VIII. The absence of bands at 10.55 and 12.00 μ showed that *equatorial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI)⁵ was not present. The *equatorial*-tosylate XVI is less reactive than VII or VIII and thus if present would survive the conditions of the isolation.

Quantitative infrared analyses were carried out by the method described in the previous paper⁵ with the exception that synthetic mixtures were not analyzed. The bands used for analysis (0.4 *M* solutions in carbon disulfide) were 10.30 μ (VII) and 13.55 μ (VIII). The percentage transmittance at 2.8 μ was arbitrarily set at 100. The results indicated

that the mixture contained 65 \pm 5% VIII and 35 \pm 5% VII.

B. Ethanolysis of *axial*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (VIII).—A solution of 1.00 g. (0.0036 mole) of VIII, m.p. 51.0–52.6°, in 18 ml. of anhydrous ethanol was heated at 49.03° for 24 hr. (50% reaction). The solution was poured into 100 g. of crushed ice and the resulting mixture was extracted with five 30-ml. portions of ether. The ether extracts were combined, washed with dilute potassium hydroxide solution and water and dried over magnesium sulfate. After removal of the ether the solid residue was recrystallized four times from pentane. This gave 388 mg. (78%) of material which melted at 44.7–45.8°. The infrared spectrum differed from that described in A only in the relative intensities of the peaks. A quantitative infrared analysis indicated that the mixture contained 75 \pm 5% VIII and 25 \pm 5% VII.

A synthetic binary mixture consisting of 70% VIII and 30% VII melted at 42.8–43.8° after one recrystallization from pentane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

Conformational Analysis. XIV. The Use of the Polarograph for the Determination of the Conformations of the 2-Halocyclohexanones^{1,2}

By ARTHUR M. WILSON AND NORMAN L. ALLINGER

RECEIVED OCTOBER 1, 1960

The half-wave potentials for the reduction of a number of 2-halocyclohexanones at the dropping mercury electrode have been measured. With systems of relatively fixed conformation, such as the 2-halo-4-*t*-butylcyclohexanones, the epimer with the axial halogen is reduced more easily. A compound such as 2-chlorocyclohexanone, which contains comparable amounts of two conformations, shows the potential characteristic of the more easily reduced (*axial*) form.

Introduction

The 2-halocyclohexanones have recently been studied in considerable detail by a number of workers, and quite a large amount of information about these compounds has now been accumulated.³ It has been found that the properties of a 2-halocyclohexanone in a more complicated system, such as a steroid, will in general parallel nicely the same properties in a simple system, and methods useful for the determination of conformation in the simple systems can usually be applied to more complicated cases. As it happens the reverse is frequently done also.

In a polyfunctional system it is not always possible to apply criteria such as the location of the carbonyl stretching frequency to determining conformation, since the frequency in question may be obscured by the absorption of other carbonyls in the molecule. Additional methods for

the determination of the axial or equatorial position of a halogen adjacent to a ketone are therefore desirable. It is of particular interest to be able in some way to determine the conformation of a fluorine atom, since the spectral shifts here may be indecisive, chemical methods are difficult to apply, and even the powerful rotatory dispersion method is not generally useful.^{3e}

It is well known that 2-chlorocyclohexanones are polarographically reduced.⁴ It seems likely *a priori* that the reduction potential of such a system will depend on the conformation of the halogen atom. The determination of the reduction potentials of some simple 2-halocyclohexanones was therefore undertaken.

Results and Discussion

The *cis* and *trans* isomers of the 2-halo-4-*t*-butylcyclohexanones (II, X = Br, Cl, F) were available from earlier work. Because of its bulk the *t*-butyl group assumes an equatorial position almost exclusively,⁵ and hence the *cis* isomer has the halogen equatorial (IIe) while in the *trans* isomer it is axial (IIa). These compounds are very nearly conformationally homogeneous,⁶ and

(1) Paper XIII, N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961).

(2) This research was supported in part by a grant from the Atomic Energy Commission and in part by a grant from the Alfred P. Sloan Foundation.

(3) For references to the 2-chlorocyclohexanones see (a) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960). For the 2-bromocyclohexanones see (b) N. L. Allinger, J. Allinger and N. A. LeBel, *ibid.*, **82**, 2926 (1960); (c) N. L. Allinger, J. Allinger, L. E. Geller and C. Djerassi, *J. Org. Chem.*, **25**, 6 (1960). For the 2-fluorocyclohexanones see (d) H. M. Kissman, A. M. Small and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 2312 (1960). For a brief general review of the physical properties of 2-halocyclohexanones see (e) C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 115.

(4) P. J. Elving and R. E. Van Atta, *J. Electrochem. Soc.*, **103**, 676 (1956).

(5) (a) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955); (b) E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5992, 5995 (1957); E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).

(6) Actually calculations have indicated the presence of about 1% of a boat form in such systems: N. L. Allinger, *ibid.*, **81**, 5727 (1959).