4-Bromo-2-methyl-3-phenyl-2-cyclopentenone (16).—A solution of 100 mg of 2-methyl-3-phenyl-2-cyclopentenone in 3 ml of carbon tetrachloride was treated with 103 mg of *N*-bromosuccinimide. After 1 hr refluxing, a rapid reaction was observed; the succinimide which separated was collected and the filtrate was evaporated to an oil which crystallized to give 140 mg (96%) of off-white solid, mp 68–75°. Recrystallization from ether–pentane and sublimation gave **16** as white crystals: mp 89–91°; ν^{KBr} 1705 cm^{-1}; δ^{CCl_4} 1.88 (d, 3, J = 1.5 Hz), 3.01 (m, 2), 5.45 (m, 1), 7.45 ppm (s, 5).

Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.61; H, 4.27. Found: C, 57.39; H, 4.41.

2-Methyl-3-phenylcyclopentadienone Dimer (17).—A solution of 46 mg of bromo ketone **16** in 2 ml of triethylamine was refluxed for 1 hr. The mixture was diluted with benzene and 32 mg of triethylammonium bromide was collected by filtration. Removal of solvent gave a colorless oil which crystallized from ether–pentane to give 12 mg (38%) of colorless crystals, mp 161–163°. Recrystallization from methylene chloride–ether gave the dimer **17**, mp 163–164°; for spectral data, see structure.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.86; H, 5.90.

Hydrogenation of 2-Acetyl-5-methyl-6-phenyl-1,2-diazabicyclo[3.2.0]-6-hepten-4-one.—A solution of 900 mg of ketone **1** (R = Ac) in 90 ml of ethyl acetate and 90 mg of 10% Pd–C catalyst was shaken with hydrogen at atmospheric pressure until the uptake of 1 mol of H_2 (1 hr). After filtering off the catalyst, the solution was evaporated to a colorless oil. The nmr spectrum of this oil showed that the starting ketone was absent; the C-5 methyl peaks of the two isomeric dihydro ketones were of essentially equal size. The oil was seeded with a crystal of product from a previous hydrogenation (the initial crystallization required several weeks). A first crop of 380 mg, mp 103–105°, was collected. Recrystallization twice from ether and then sublimation at 105° (1 mm) gave colorless crystals of 2-acetyl-5-methyl-6-*exo*-phenyl-1,2-diazabicyclo[3.2.0]heptanone (**19**): mp 114–115°; ν^{KBr} 1750, 1670 cm^{-1}; δ^{CDCl_3} 0.89 (s, 3), 2.30 (s, 3), 3.5–4.7 (m, 5), 7.42 ppm (s, 5).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.97; H, 6.56; N, 11.52.

The mother liquor from **19** was concentrated, and 290 mg of crystals, mp 94–96°, was obtained after standing at 0°. Recrystallization of this material and final sublimation gave 2-acetyl 5-methyl-6-*endo*-phenyl-1,2-diazabicyclo[3.2.0]-4-heptanone (**20**) as white crystals: mp 94–96°; ν^{KBr} 1760 cm^{-1}; δ^{CDCl_3} 1.47 (s, 3), 2.21 (s, 3), 3.6–4.6 (9 lines, combination of C-3 CH_2, H-6 and C-7 CH_2), 6.9–7.4 ppm (m, 5).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.08; H, 6.78; N, 11.37.

Thermal Behavior of 1 (R = Ac), 2, and 19.—Solutions of 15 mg of the three ketones in 0.3 ml of $CDCl_3$ were sealed under nitrogen in nmr tubes and then heated in an 80° bath and spectra were recorded at intervals. **1** (R = Ac): After 48 hr, conversion to the diazepinone **22** (R = Ac), was 30% complete; after 90 hr, conversion was about 50%; after 310 hr the spectrum was essentially that of **22** (R = Ac) with about 5% of **2** (R = Ac) and negligible impurity peaks. **2**: After 260 hr, the only sharp peaks in the spectrum were those of unchanged **2**; very broad signals comprising about half of the total integral were present at δ 1.8–2.2 and 7.2–7.6. **19**: The spectrum was unchanged after 270 hr at 80°.

Registry No.—**1b**, 26439-91-8; **2**, 21039-49-6; **2** semicarbezone, 26439-93-0; **3**, 17831-34-4; **4a**, 26439-95-2; **4b**, 26439-96-3; **7**, 26439-97-4; **16**, 26439-98-5; **17**, 26439-99-6; **19**, 26440-00-6; **20**, 26440-01-7.

Models for the Stepwise Solvolysis of Unsaturated Ditosylates

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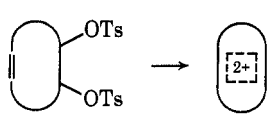
The solvolytic behavior of *cis*-4,5-cyclohexanediol ditosylate (I) has been studied as a model for the stepwise ionization of unsaturated ditosylates. Double ionization to form a bishomocyclobutenium ion is stereoelectronically prohibited in I. For comparison, the solvolyses of *trans*-4,5-cyclohexanediol ditosylate (II), *cis*-1,2-cyclohexanediol ditosylate (III), *trans*-1,2-cyclohexanediol ditosylate (IV), 4-cyclohexenyl tosylate (V), and cyclohexyl tosylate (VI) have also been studied. The rates of all the compounds are compared at 160°. Activation parameters and product analyses are reported. It is found that the double bond in I or II conveys no significant acceleration relative to III or IV, and that the unsaturated *cis*-ditosylate I reacts even more slowly than the *trans*-ditosylate II. These results are taken to be characteristic of the stepwise mechanism. Properties required of a mechanism involving double ionization to a dication are discussed.

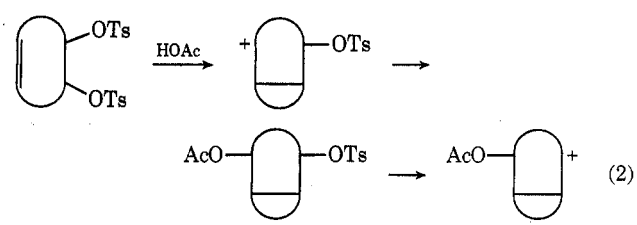
Part A

In this series of papers,[2] it has been our object to examine systems that could give rise to a doubly charged species as a transient intermediate under normal solvolytic conditions. The two positive charges are to be produced by solvolysis of adjacent tosylate groups, and the requisite stabilization is to be provided by an appositely positioned double bond (eq 1). The



(1)

novel intermediate so formed would be termed a bishomocyclobutenium ion and would receive its stabilization by possession of a planar bishomocyclic structure with $4n + 2$ electrons (n = 0). We have previously studied a system[2] that is stereochemically ideal for formation of a bishomo dication, but the kinetic data could not differentiate between the double ionization mechanism of eq 1 and pathways exemplified



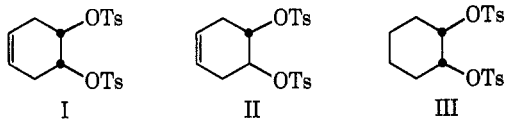
(2)

by eq 2, in which ionization is stepwise and an acetoxy tosylate intermediate intervenes. In the present work, we have examined the solvolysis of *cis*-4,5-cyclo-

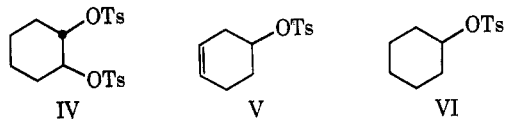
(1) (a) Alfred P. Sloan Foundation Fellow, 1968–1970. This work was supported by the National Science Foundation, Grant GP-9257, and by the Petroleum Research Fund, administered by the American Chemical Society, Grant 2970-A4,5. To whom correspondence should be addressed. (b) National Science Foundation Trainee, 1968–1969; NDEA Fellow, 1969–1970. (c) NDEA Fellow, 1967–1969.

(2) For the first paper, see J. B. Lambert and A. G. Holcomb, *J. Amer. Chem. Soc.*, **91**, 1572 (1969).

hexenediol ditosylate (I), in which participation of the double bond in a double ionization is conformationally disfavored. Examination of the solvolytic properties of I and the related compounds II–VI should therefore



I II III



IV V VI

produce data characteristic of the stepwise pathway (eq 2). This information will serve to clarify the mechanistic analysis of those systems that do offer a stereoelectronically favorable relationship for production of a bishomo dication.

The solvolyses of compounds I–VI were carried out in acetic acid containing an equivalent amount of potassium acetate. Kinetic studies were performed for at least three temperatures in order to obtain activation parameters. The rates adjusted to 160° for all compounds are given in Table I. Products were

TABLE I

SOLVOLYTIC RATES FOR CYCLOHEXYL TOSYLATES (160°)

Compd	Rate, $sec^{-1} \times 10^5$
I	3.92[a]
II	10.0[b]
III	4.15[b]
IV	6.07[b]
V	9420[a]
VI	11900[a]

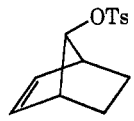
[a] Calculated from the Arrhenius plot. [b] Measured at 160°.

isolated after acetolysis at 170° for 24 hr (100° for VI) and identified by their spectrometric and chromatographic properties.

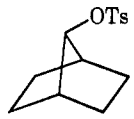
Comparison of the saturated (III) and unsaturated (I) *cis*-ditosylates shows that the double bond slows the reaction by a factor of I/III = 0.94. The deceleration for the monotosylates is similar (V/VI = 0.79). Introduction of the second tosylate group in a cis position slows the reaction with respect to that of the monotosylate by a factor of V/I = 2400 for the unsaturated pair or VI/III = 2900 for the saturated pair. The cis compound solvolyzes more slowly than the trans compound in both the unsaturated (I/II = 0.39) and the saturated (III/IV = 0.68) series. These rate comparisons show that (1) the double bond produces a small inductive retardation of the rate, so there is little anchimeric assistance; (2) the second tosylate group produces the expected large decelerative effect; (3) a cis relationship between the two leaving groups does not convey a rate acceleration. It would have been expected of a dication mechanism that the double bond produce a rate enhancement, the cis relationship a rate enhancement, and the second tosylate group only a small rate retardation. The observed results are considered to define the behavior of the stepwise mechanism.

Part B

Solvolysis of *anti*-7-norbornenyl tosylate (VII) occurs

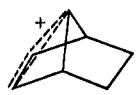


VII

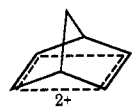


VIII

about eleven powers of ten more rapidly than that of the corresponding saturated tosylate (VIII).[3] This acceleration has been attributed to transition state stabilization leading to the bishomocyclopropenium ion intermediate IX. Isoelectronic to IX

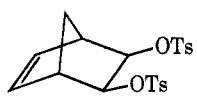


IX

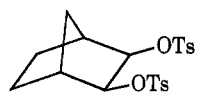


X

is the bishomocyclobutenium dication X, which could be formed by solvolysis of the ditosylate XI. A recent study, however, showed that XI acetolyzes

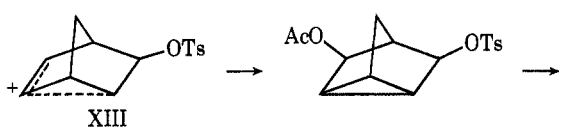


XI

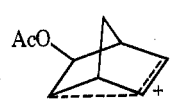


XII

only 500 times more rapidly than the saturated analog XII. The kinetic and product analysis could not differentiate between a concerted or nearly concerted pathway proceeding to the dication X and a stepwise pathway (eq 3), which contains only monocationic intermediates such as XIII and XIV.

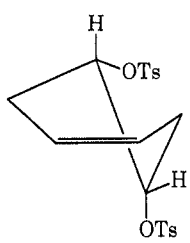


XIII



XIV (3)

In the most favorable situation for formation of a bishomo dication, the two tosylate groups must be cis to each other and anti to the double bond. The molecule XI was chosen for the initial studies because the bicyclic structure rigidly maintains these requirements. In the present study, we have examined the solvolytic behavior of *cis*-4,5-cyclohexenediol ditosylate (I), in which the stereoelectronic requirements for formation of a bishomocyclobutenium dication are not fulfilled. The conformation probably resembles structure Ia. Because the double bond is positioned for



Ia

(3) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).

assistance with the leaving of no more than one tosylate group, the reaction must proceed by the stepwise pathway. The conformation obtained by reversal of the cyclohexene ring is the mirror image of Ia, and identical considerations apply. Compound I differs from XI only in the absence of the methano bridge. Since inductive effects should be almost the same in the two systems, compound I can serve as a model for the stepwise mechanism in analyzing the behavior of XI. The present studies were therefore initiated to characterize the properties of the stepwise mechanism.

For a complete investigation of the cyclohexyl system, the cis-unsaturated ditosylate should be compared to the cis-saturated ditosylate (III), the trans-unsaturated ditosylate (II), and the unsaturated monotosylate (V) in order to define the effect of the double bond, of the cis stereochemistry, and of the second tosylate group in I. To complete the series, the trans-saturated ditosylate (IV) and the saturated monotosylate (VI) have also been included. Previous studies have been reported on the acetolysis and hydrolysis of V[4] and on the acetolysis of the brosylates corresponding to III and IV.[5] In order to ensure common conditions, we have examined the solvolytic properties of the entire series I–VI. A study of analogous cyclooctyl brosylates has been reported by Closson, *et al.*[6]

Results and Discussion

The acetolyses of compounds I–VI were carried out at three temperatures. The kinetics are given in Table II and the activation parameters in Table III.

TABLE II
RATE CONSTANTS FOR ACETOLYSIS

Compd	Temp, °C	Rate, sec^{-1} × 10^5
I	169.7	8.29
	174.8	12.1
	180.8	18.9
II	154.2	6.03
	160.0	10.0
	165.4	14.2
III	154.2	2.92
	160.0	4.15
	169.6	10.5
IV	154.2	3.54
	160.0	6.07
	165.4	9.15
V	77.3	4.75
	90.2	19.7
	100.2	54.1
VI	91.2	28.9
	96.2	46.1
	100.2	72.4

Rates measured or calculated for a common temperature (160°) are listed in Table I. Product studies are described in the Experimental Section.

(4) M. Hanack and K. Keberle, *Ber.*, **96**, 2937 (1963); M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 674 (1967).

(5) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948).

(6) W. D. Closson, J. L. Jernow, and D. Gray, *Tetrahedron Lett.*, 1141 (1970). We are endebted to Professor Closson for informing us of his results prior to their publication.

TABLE III
ACTIVATION PARAMETERS FOR ACETOLYSIS

Compd	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$ (25°), kcal/mol	$\Delta S^{\ddagger}$, eu
I	29.7	10.6	29.1	32.7	−12.2
II	28.5	10.4	28.0	31.8	−13.0
III	31.8	11.7	31.2	33.3	−7.1
IV	31.6	11.7	31.0	33.1	−6.9
V	27.6	12.9	27.0	27.5	−1.4
VI	27.5	12.9	28.9	27.3	−1.4

The ratio of the solvolysis rate for an unsaturated tosylate to that for the corresponding saturated tosylate gives some indication of the anchimeric assistance provided by the double bond. A double bond that is two carbon atoms removed from the reaction site inductively reduces the rate by a factor of 5 or 10.[4] The extent of π participation, which is superimposed upon this inductive retardation, depends on the geometry of the system, with large accelerations observed in favorable cases such as VII. There is little evidence for double bond participation in the present cases, presumably because the double bond is poorly oriented with respect to the leaving group. The unsaturated/saturated ratios are 0.94 for I/II, 0.79 for V/VI, and 1.65 for II/IV. In the stepwise mechanism for I or II, the inductive retardation and the participative acceleration must approximately cancel each other. The dication mechanism would have exhibited a considerable anchimeric acceleration by the double bond.

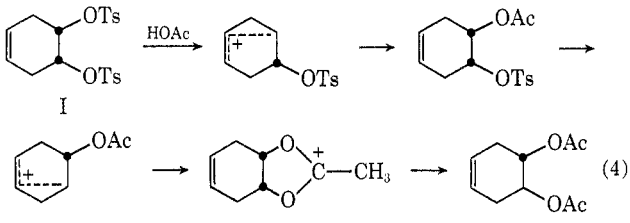
Introduction of a second tosylate group should be appreciably rate retarding, since any electron-deficient intermediate will be destabilized by the electron-withdrawing group. Thus the monotosylate/ditosylate ratios are 2900 for VI/III, 2000 for VI/IV, 940 for V/II, and 2400 for V/I. These ratios would become much smaller in a dication mechanism.

For a double ionization to occur, the leaving groups must be cis to each other and equivalently oriented with respect to the double bond. In the trans form a stepwise mechanism is therefore obligatory. If in the cis isomer the double ionization is to occur more rapidly than the stepwise mechanism, it must convey a rate enhancement. Operationally, the presence of the double ionization therefore requires that the cis isomer react more rapidly than the trans isomer. The cis/trans ratios are 0.39 for I/II and 0.68 for III/IV. The cis isomers thus do not display a rate acceleration. Of the cases examined in the present study, none were expected to show double ionization; so these low cis/trans ratios are in accord with a stepwise mechanism in all cases.

Since little or no anchimeric acceleration is observed in I, II, and V, a participative k_Δ component of the rate is probably small, though not negligible. Limiting carbonium ion behavior (k_c) with neither solvent nor neighboring-group participation is unlikely in these simple secondary systems.[7] The relative contributions of the k_Δ (double bond participation) and k_s (solvent displacement) mechanisms cannot be assessed. The

(7) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

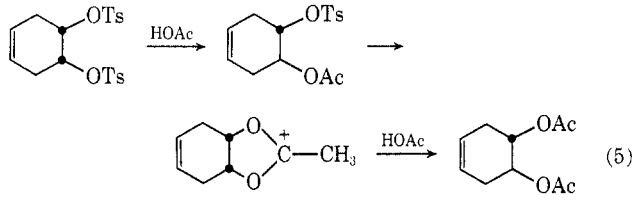
k_Δ component of the rate for the unsaturated compounds would derive from a process such as that in eq 2, or in particular for I, eq 4. The frequent occur-



I

(4)

rence of *trans*-diacetate products may be suggestive of acetoxonium ion intermediates in the final stages of the reaction.[8] For the k_s component, the first stage of the stepwise mechanism would be modified so that the acetoxy tosylate is produced directly from the ditosylate (eq 5).



(5)

Experimental Section

Nmr spectra were taken on Varian Model A-60 and T-60 spectrometers; infrared spectra were recorded on Beckman IR-5 and IR-10 spectrophotometers. Gas chromatographic analyses were performed on F & M Model 700 and Varian Model 1520B chromatographs. Elementary analyses were provided by Micro-Tech Laboratories, Skokie, Ill.

Tosylates were prepared by the usual treatment of alcohols with recrystallized *p*-toluenesulfonyl chloride in dry pyridine at 0°. Purification was effected by crystallization from ethanol or methanol. Rates were measured in dry acetic acid containing an equivalent of potassium acetate. Aliquots were titrated with standardized perchloric acid in acetic acid with crystal violet indicator. Temperatures were read from a Beckman thermometer calibrated against an Anschütz thermometer. The temperature was constant within 0.1 degree for any run. For product studies, about 2 g of a tosylate was treated with 10 ml of acetic acid 1 *N* in KOAc, and this solution was diluted with acetic acid to 100 ml. This solution was heated in a sealed tube at 170° (100° for cyclohexyl tosylate) for 24 hr. The tube was opened and the contents diluted with about 5 vol of H_2O. This mixture was extracted five times with ether. The extracts were shaken with saturated $NaHCO_3$ solution and dried over $MgSO_4$–Na_2CO_3. After the ether was removed, the products were separated by preparative gas chromatography. Diacetates were isolated from a $^1/_2$ in. × 10 ft silicone column and monoacetates from a $^3/_8$ in. × 12 ft Carbowax column. Various acetates were prepared for comparative purposes by treatment of the corresponding alcohol with acetic anhydride.

cis-**Cyclohexene-4,5-diol** was prepared in four steps from cyclohexadiene by the method of Ali and Owen.[9] The product was recrystallized from hexane (mp 79.5–80.5°) and converted to the ditosylate (I, mp 90–91°). *Anal.* Calcd for $C_{20}H_{22}O_6S_2$: C, 56.84; H, 5.26; O, 22.72; S, 15.18. Found: C, 56.83; H, 5.33. The major component (>70%) of the solvolysis was *trans*-4,5-cyclohexenediol diacetate. The nmr and ir spectra were identical with those of an authentic sample.

trans-**Cyclohexene-4,5-diol** was prepared in two steps from cyclohexadiene by the method of Ali and Owen.[9] The material was recrystallized from heptane and converted to the ditosylate (II, mp 80–81°). *Anal.* Calcd for $C_{20}H_{22}O_6S_2$: C, 56.84; H, 5.26; O, 22.72; S, 15.18. Found: C, 57.25; H, 5.25. Over 80% of the acetolysis product was *trans*-4,5-cyclohexenediol acetate. There were no other major components.

cis-**Cyclohexane-1,2-diol** was prepared by treatment of cyclohexene with $KMnO_4$. The product was recrystallized twice from toluene (mp 99–100°) and converted to the ditosylate (III, mp 128–129°). *Anal.* Calcd for $C_{20}H_{24}O_6S_2$: C, 56.57; H, 5.71; O, 22.61; S, 15.11. Found: C, 56.18; H, 5.65. The major components (~50%) of the acetolysis products were *cis*- and *trans*-1,2-cyclohexane diacetates.

trans-**Cyclohexane-1,2-diol** was obtained from Aldrich Chemical Co. The ditosylate IV was recrystallized from ethanol (mp 110–112°). *Anal.* Calcd for $C_{20}H_{24}O_6S_2$: C, 56.57; H, 5.71; O, 22.61; S, 15.11. Found: C, 55.93; H, 5.51. The major acetolysis product (~50%) was the *trans* diacetate. Other products included unsaturated monoacetates.

Cyclohexene-4-ol was prepared by the dehydration of cyclohexane-1,4-diol (Aldrich Chemical Co.) with sulfuric acid or alumina. The product was purified by fractional distillation, with the desired material boiling at 160–163°. Product studies from the solvolysis of the tosylate have been discussed elsewhere.[4]

Cyclohexanol was purchased from Aldrich Chemical Co. The only major ester product from the solvolysis of the tosylate was cyclohexyl acetate.

Registry No.—I, 26431-17-4; II, 26419-16-9; III, 5433-22-7; IV, 5433-21-6; V, 26431-20-9; VI, 953-91-3.

(8) S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 816 (1948).

(9) M. E. Ali and L. N. Owen, *J. Chem. Soc.*, 1066 (1958).