reported. In the first method, I is prepared from 1,4-dinitrobutene-2 (II), *via* the 2,3-dichloro-1,4-dinitrobutane.[1] In the second method, 2,3-dihydroxy-1,4-dinitrobutane is prepared from nitromethane and glyoxal, converted into the diacetate and deacylated to give I.[2] A simple one step, high yield reaction for the

$$\text{OHCCHO} \xrightarrow{CH_3NO_2} O_2NCH_2CHOHCHOHCH_2NO_2 \longrightarrow$$
$$NO_2CH_2CHOAcCHOAc\ CH_2NO_2 \xrightarrow{KHCO_3} \text{I}$$

preparation of I is now reported. It has been found that the treatment of II with potassium hydroxide and bromine gives a 79% yield of I. A probable mechanism for the formation of I is given in eq 1. Perekalin and

$$\text{II} \xrightarrow{KOH} \left[KCCH(NO_2)=CHCK(NO_2) \right] \xrightarrow{Br_2} \left[KCCH(NO_2)=CHCBr(NO_2) \right] \longrightarrow \underset{\text{I}}{NO_2CH=CH-CH=CHNO_2} + KBr \quad (1)$$

Lerner[2] reported that I was a highly stable compound and that it was only slowly brominated to a dibromide. We found that 2 mol of bromine can be added to I to yield 1,4-dinitro-1,2,3,4-tetrabromobutane (III). Treatment of III with aqueous methanol quantitatively yielded yellow needles (mp 126–127.5°). This product was identified by elemental and infrared analysis as 1,4-dibromo-1,4-dinitro-1,3-butadiene (IV). Infrared analysis indicated the compound was the 1,4-dibromo isomer as opposed to the 2,3-dibromo isomer by comparison of the wavelengths of its nitro absorptions to those of other analogous nitro compounds.[3] Compound IV was apparently obtained by the facile dehydrohalogenation of the tetrabromo derivative (III), similar to the dehydrohalogenations of analogous aromatic substituted compounds.[4]

$$\text{I} \xrightarrow{2Br_2} \underset{\text{III}}{NO_2CH(Br)-CH(Br)-CH(Br)-CH(Br)NO_2} \xrightarrow[CH_3OH]{H_2O} \underset{\text{IV}}{NO_2CBr=CHCH=CBrNO_2}$$

Experimental Section

Melting points are uncorrected. The infrared spectra were taken on mulled samples with a Perkin-Elmer Infracord.

1,4-Dinitro-1,3-butadiene.—Methanolic potassium hydroxide (28.6 ml, 0.98 *N*) was added in small portions with stirring to 1,4-dinitrobutene-2 (2.05 g, 14 mmol) slurried in 15 ml of methanol, cooled to −10°. A small amount of precipitated dipotassium salt was dissolved by the addition of 15 ml of water to yield a dark solution. This cold solution and an equivalent volume of methanolic bromine solution (2.46 g, 15.4 mmol, 10% excess) were added dropwise simultaneously to 90 ml of water stirred at 0°. The solution became yellow and a yellow solid precipitated after several minutes. An excess of bromine was maintained at all times and the temperature was maintained at or somewhat below 0°. Stirring was continued for 1 hr after the final addition followed by pouring the mixture into 300 ml of water. The yellow solid was filtered, washed with several portions of water, and dried *in vacuo* to yield 1.60 g (79%) with a decomposition melting point of 133–142°. Recrystallization from chloroform yielded pale yellow needles with a decomposition melting point of 145.5–147.5° (lit.[1] mp 147–148°). This compound is light sensitive and was stored in the dark, λ_{max}^{Nujol} 6.7, 7.5 μ.

Anal. Calcd for $C_4H_4N_2O_4$: C, 33.34; H, 2.80. Found: C, 33.09, 32.96; H, 2.72, 2.89.

1,4-Dinitro-1,2,3,4-tetrabromobutane.—1,4-Dinitro-1,3-butadiene (10.79 g, 75 mmol) and bromine (26.4 g 165 mmol, 10% excess) were refluxed 1 hr in 125 ml of chloroform. (The reaction was protected from light by wrapping with aluminum foil.) An orange syrup was obtained on evaporation of solvent and excess bromine under reduced pressure. This syrup was extracted with multiple portions of boiling hexane until a small quantity of dark residue remained. Evaporation of the hexane under reduced pressure yielded an amber syrup (32.05 g, 92%). The syrup crystallized very slowly in the icebox after being seeded. Two recrystallizations from hexane yielded the analytical sample as colorless prisms: mp 83.5–84.5°; λ_{max}^{Nujol} 6.4, 7.4 μ.

Anal. Calcd for $C_4H_4Br_4N_2O_4$: C, 10.36; H, 0.87. Found: C, 10.48, 10.37 H, 0.89, 0.76.

1,4-Dibromo-1,4-dinitro-1,3-butadiene.—1,4-Dinitro-1,2,3,4 tetrabromobutane (11.6 g, 25 mmol) was dissolved in 50 ml of methanol and 5 ml of water was added. The resulting yellow solution was allowed to stand 20 hr at ambient temperature. The yellow needles which had crystallized from solution were washed once with a small quantity of methanol and dried to yield 5.41 g, mp 125.5–127°. A second crop (0.72 g, mp 124.5–126.5°) was obtained by concentration of mother liquor to yield a total of 6.13 g (81%). One recrystallization of the first crop from methanol yielded the following analytical sample: mp 126–127.5°; λ_{max}^{Nujol} 6.6, 7.7, 10.6, 12.7 μ.

Anal. Calcd for $C_4H_2Br_2N_2O_4$: C, 15.91; H, 0.67; N, 9.28. Found: C, 15.80, 15.76; H, 0.76, 0.65; N, 9.38.

Registry No.—I, 929-11-3; III, 868-21-3; IV, 868-79-1.

Acknowledgment.—The sponsor of this work was Air Force Armament Laboratory (AFATL), ATWT, Eglin AFB, Fla. 32542.

(1) V. V. Perekalin and O. M. Lerner, *D. Acad. Nauk SSR*, **129**, 1303 (1959).

(2) S. S. Novikov, I. S. Korsakova, and K. V. Babievskii, *Izv. Acad. Nauk SSSR*, 994 (1960).

(3) J. F. Brown, *J. Amer. Chem. Soc.*, **77**, 6341 (1955).

(4) P. Ruggli, *Helv. Chem. Acta.*, **23**, 718 (1940).

Solvolysis of Optically Active Tricyclo[3.2.1.$0^{2,7}$]octan-4-yl *p*-Toluenesulfonate

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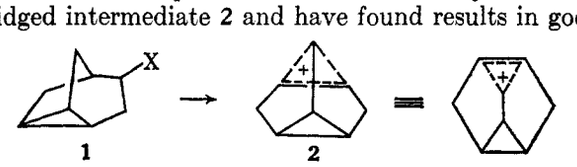
Recent communications by Berson and coworkers regarding the solvolytic nature of optically active tricyclo[3.2.1.$0^{2,7}$]octan-4-yl *p*-bromobenzenesulfonate[1] prompted us to report our results of similar studies. We have studied the kinetics and stereochemistry of solvolysis of the optically active *p*-toluenesulfonate **1a** to determine the possible existence of the symmetrical bridged intermediate 2 and have found results in good



1 2

a, X = OTs
b, X = OH
c, X = $O_2CC_6H_4CO_2H$
d, X = OAc

(1) (a) J. A. Berson, R. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **90**, 3236 (1968); (b) *ibid.*, **90**, 3238 (1968).

agreement with those reported by Berson for the *p*-bromobenzenesulfonate.

The tricyclo[3.2.1.0^{2,7}]octan-4-ol (**1b**) used in these studies was prepared by the procedure of Lumb and Whitham[2] and resolved into its optical isomers by recrystallization of the brucine salt of the corresponding acid phthalate (**1c**).[3] Two individual resolutions gave samples of **1b** having $[\alpha]^{24}$ −21.9° and $[\alpha]^{28}$ −21.1°.[4] The similarity of these rotations suggests that the first sample of **1b** is essentially optically pure.[5] Recrystallization of second crops of salt gave **1b** with $[\alpha]^{25}$ −18.4° which was converted into *p*-toluenesulfonate **1a** having $[\alpha]^{26}$ −3.9° (−4.6° in acetic acid).

First-order rate constants for acetolysis of **1a** (k_c) were determined conductometrically in unbuffered media at several temperatures and are summarized in Table I along with the activation parameters determined in the usual way. Polarimetric rate constants for acetolysis (k_α) were determined at 24.91° and are also listed in Table I. The low activity of the *p*-toluenesulfonate necessitated the use of higher concentrations than used in the conductometric runs. In all cases good first-order behavior was observed and optical activity was completely lost.[6] (Products were shown to be stable to conditions of buffered acetolysis.)

TABLE I

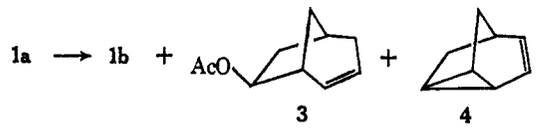
FIRST-ORDER RATE CONSTANTS FOR ACETOLYSIS OF TRICYCLO[3.2.1.0^{2,7}]OCTAN-4-YL *p*-TOLUENESULFONATE (**1a**)

Temp, °C	ROTs *M*	NaOAc *M*	10^4k,[a] sec^{-1}
	Conductometric Rates		
			k_c
50.29	0.049	None	6.10 ± 0.08
50.29	0.014	None	6.10 ± 0.06
40.00	0.012	None	1.82 ± 0.03
40.02	0.012	None	1.80 ± 0.03
30.15	0.012	None	0.502 ± 0.007
30.07	0.012	None	0.490 ± 0.007
24.91	0.012	None	0.256 ± 0.003
$\Delta H^{\pm}$ = 24.2 kcal/mol		$\Delta S^{\pm}$ = +1.4 eu (at 50.27°)	
	Polarimetric Rates		
			k_α
24.91	0.132	0.146	0.68 ± 0.03
24.91	0.163	0.164	0.73 ± 0.03
24.91	0.162	0.178	0.70 × 0.01
24.91	0.163	None	0.63[b]

[a] Rate constants are the average (and average deviation) of the 10–20 values for each run determined from the integrated form of the first-order rate equation. [b] Determined graphically.

A comparison of k_α and k_c shows that the rate of loss of optical activity exceeds the rate of formation of product by a factor of 2.5. As noted in previous studies of this kind[1b,7] this results from an excess racemization of substrate by ion pair return. That ion pair return results in the reformation of **1a** was confirmed by carrying out a partial acetolysis (*ca.* 35%) and recovering unreacted ester. Recovered material was identical in structure to starting material as shown by its melting point and nmr spectrum.

Sauers[8] has reported recently that the acetolysis product from **1a** is composed of acetate of retained structure **1d**, rearranged product, bicyclo[3.2.1]oct-2-en-7-yl acetate (**3**), and a small amount of a hydrocarbon identified as tricyclo[3.2.1.0^{2,7}]oct-3-ene (**4**). We have found the same product spectrum in our work.



3 4

At 25° in buffered acetic acid **1d** and **3** were formed in relative amounts of 40 and 60%, respectively, along with about 6–7% of hydrocarbon, as shown by gas chromatography (gc). In 80% (by volume) aqueous acetone at 25° ($CaCO_3$ buffer) the composition was 67% tricyclic alcohol **1b** and 33% bicyclic alcohol **3-OH**. In both solvents none of the isomeric tricyclo[3.2.1.0^{2,7}]octan-3-yl product was found.[9]

Although some residual rotation was observed in the polarimetric rate studies of **1a**, no activity could be detected either in the mixture of acetate products isolated from these experiments or in the individual acetates obtained by preparative gc. Likewise, no activity could be detected in the mixture of hydrolysis products. The solvolysis products therefore appear to be completely racemic.[10] A consideration of the maximum amount of activity which could have been retained under solvolysis conditions[7a] and the accuracy of the polarimeter used would set a lower limit to the detection of optical activity lost in the ionization process at about 95% in acetolysis and greater than 95% in hydrolysis.

The present results can be accounted for by the mechanism shown in the following scheme (only half of the enantiomers are shown) which indicates racemization of **1a** by ion pair return from the symmetrical bridged ion **2**. Apparently the ion can also react to form racemic tricyclic acetate **1d** or undergo a hydride shift to give the cyclopropylcarbinyl-type ion **5** (or the mesomeric ion related to **5** and **6**) (Scheme I). This hydride shift should be a facile process and it seems likely that this is the reason for the low k_α/k_c ratio (2.5) observed here. These ratios are usually in the range of 4–5 for *p*-toluenesulfonate esters.[7a,c,d,f] Hydride shift would effectively diminish ion pair return in this case.

An alternative route to loss of optical activity in solvolysis involving ionization to the symmetrical classicial ion **7a** is possible. However, if this occurs it must be of minor importance, since solvolysis experi-

(2) J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965).

(3) Attempted resolutions using other optically active bases were unsuccessful; these gave a salt which could not be induced to crystallize (cinchonine) or no detectable resolution on recrystallization of the salt (cinchonidine and α-phenylethylamine).

(4) Rotations are for chloroform solution (*c* 1.6) unless otherwise noted and were measured using the 546-mμ wavelength of mercury.

(5) Berson, *et al.*,[1b] calculate as a maximum rotation for **1b** $[\alpha]_D$ 24.4–31.7° ($CHCl_3$).

(6) In each case some residual (+) activity was observed at the completion of the kinetic run, but product studies indicated this was apparently due to contamination of the *p*-toluenesulfonate by a (+) rotating impurity. See the subsequent discussion of solvolysis products.

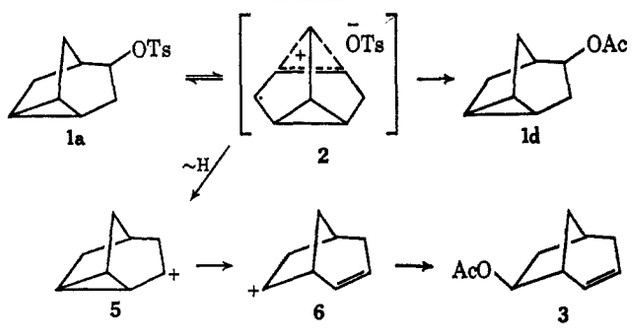
(7) For example see (a) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1154 (1952); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (d) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (e) S. Winstein and D. Heck, *ibid.*, **74**, 5584 (1952); (f) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848 (1968); (g) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964), and earlier papers in that series.

(8) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

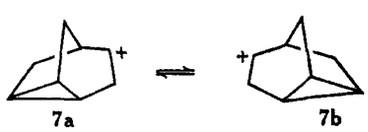
(9) Berson[1b] reports about 30% of the tricyclic isomer in buffered acetic acid at 50° and none at 100°. The differences in the amouts of the tricyclic acetate found apparently result from instability of the compound.[1b]

(10) Berson[1] reports about 3% net inversion in the tricyclic acetate **1d**. This is within the experimental error of the present work.

SCHEME I



ments using sulfonate labeled at C-4 with deuterium show the tricyclic product **1d** has the label approximately equally spread over C-4 and C-5.[1b,8] In addition, the solvolysis of **1a** appears somewhat accelerated, that is, **1a** undergoes acetolysis about eight times faster at 50° than the bicyclo[2.2.2]octan-2-yl system[11] which has been calculated to have an acceleration factor of 9.5.[12,13] Thus, the data seem more consistent with ionization to the bridged ion **2**.



An alternative representation for the bridged ion should also be considered, that is, a rapidly equilibrating pair of classical ions **7a** ⇌ **7b**, as has been suggested for similar cases.[14] Because of the symmetry of the pair of ions in this case (that is **7a** ≡ **7b**) one cannot detect a loss or preservation of stereochemistry at the reacting carbon and thus a stereochemical argument cannot be used to distinguish between the alternative formulations.

Experimental Section[15]

Materials. **Tricyclo[3.2.1.0^{2,7}]octan-4-ol (1b)** was prepared by the method of Lumb and Whitham;[2] the alcohol melted at 140.3–141.1° (lit. mp 123.5–124.5°,[2] 136–138°,[8] 140–141°).[1b]

Resolution of Tricyclo[3.2.1.0^{2,7}]octan-4-ol (1b).—1b (24 g) was converted into the acid phthalate (**1c**) using the procedure of Walborsky, *et al.*[16] Crystalline **1c** melting at 97–100° was obtained in 87% yield.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.42; H, 5.82.

1c (23.2 g, 0.0853 mol) was dissolved in 90 ml of acetone and 33.6 g (0.0853 mol) of anhydrous brucine was added at reflux. Reflux was continued until solution of solid was complete. After cooling, the solution was seeded and 75 ml of ether was added. After a few days at room temperature 47 g of brucine salt was collected, $[\alpha]^{25}$ −31.6°. The salt was recrystallized twice from about 120 ml of a 2:1 acetone–chloroform solution, allowing several days at room temperature for crystallization. This gave 3.4 g of salt, $[\alpha]^{25}$ −42.8°, mp 163–165°. Decomposition of the salt with 10% hydrochloric acid and carbonate purification gave 1.31 g (94% yield) of active **1c**, $[\alpha]^{22}$ −22.9° mp, 88–94°.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92°. Found: C, 70.40; H, 5.87.

Saponification of the acid phthalate in 10 ml of 1.5 *M* methanolic–potassium hydroxide (1.5 hr reflux) gave (after one sublimation) 376 mg (64% yield) of (−)-**1b** as a waxy solid melting at 140.5–141.7°, $[\alpha]^{24}$ −21.9°. In a second resolution brucine salt having $[\alpha]$ −42.7° was obtained in the first crop of crystals. This provided **1c** with $[\alpha]^{28}$ −22.2° and, after saponification, **1b** melting at 139.9–141.1°, $[\alpha]^{28}$ −21.1°.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.52; H, 9.83; mass spectrum (70 eV) *m/e* (relative intensity) 124 (37, M^+), 106 (64, $M^+ - H_2O$).

Concentration of mother liquors gave second crops of brucine salt which were similarly recrystallized several times from acetone–chloroform. This gave 13 g of salt having $[\alpha]^{23}$ −40.6°. Decomposition of the salt gave 4.8 g (93% yield) of **1c** and, after saponification, 2.1 g (95% yield) of **1b**, $[\alpha]^{25}$ −18.4°, mp 140.3–141.3°.

To establish the rotational relationship between active **1b** and its corresponding acetate, about 250 mg of **1b**, $[\alpha]^{28}$ −21.1°, was acylated by a previously described method.[7f] Microdistillation (80–100° bath, 22 mm, no boiling point obtained) gave 247 mg (68% yield) of colorless liquid acetate **1d**, $[\alpha]^{22}$ − 16.9°, −19.0° in acetic acid.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.65; H, 8.15.

A good elemental analysis was not obtained for the acetate due to the difficulty in purifying the small amount of material at hand; however, the structure is confirmed by the mass spectrum (12 eV) *m/e* (relative intensity) 164 (<0.1, M^+), 106 (100, $M^+ - HOAc$).

(±)-Tricyclo[3.2.1.0^{2,7}]octan-4-yl *p*-Toluenesulfonate (1a).—To a magnetically stirred solution of 0.75 g (6.05 mmol) of **1b** in 5 ml of anhydrous pyridine cooled in an ice bath there was added all at once 1.37 g (7.18 mmol) of *p*-toluenesulfonyl chloride. The solution was allowed to stand in a refrigerator overnight; then 1 ml of water was added dropwise over a brief period to the cold (ice bath), stirred solution to decompose excess acid chloride. The resulting solution was poured into 25 ml of cold water and the aqueous solution was extracted with ether. The extract was washed successively with 5% hydrochloric acid, water, 5% sodium carbonate, water, brine, and dried ($MgSO_4$). Removal of solvent on a rotary evaporator left a clear oil which could not be induced to crystallize. Crystallization was finally achieved from ether–pentane using Dry Ice–acetone bath cooling. This gave 1.23 g (73% yield) of white crystalline **1a**, mp 45.5–48.6° (lit.[8] reported **1a** as an oil). The melting point was unchanged after two recrystallizations from ether–pentane. (Elemental analyses were not obtained for the sulfonate esters because of their general instability at room temperature.)

(−)-Tricyclo[3.2.1.0^{2,7}]octan-4-yl *p*-Toluenesulfonate (1a) was prepared from 2.1 g (0.017 mol) of (−)-**1b** ($[\alpha]^{25}$ −18.4°) in 72% yield by the procedure described above. This gave an oil which crystallized from ether–pentane on standing in a freezer. Filtration gave 2.8 g of (−)-**1a**, mp 50.4–52.2°, $[\alpha]^{27}$ −3.9°. From the mother liquors there was obtained 0.6 g of tan ester having $[\alpha]^{26}$ −3.9°. Crystallization of the active ester apparently does not fractionate optical isomers.

Kinetic Studies. A. Conductometric studies were carried out by weighing ester **1a** (*ca.* 50 mg) into a dried flask and adding 15 ml of preheated anhydrous acetic acid.[7f] After thorough mixing the solution was placed in a Freas-type conductance cell and the cell was allowed to come to thermal equilibrium in a constant-temperature bath. Conductance readings were then taken for two to three half-lives, with the value after ten half-lives being taken as the "infinity" reading. Measurements were made with an Industrial Instruments Model RC16B2 conductivity bridge, equipped with an electric eye null point indicator.

(11) (a) H. L. Goering and M. F. Sloan, *J. Amer. Soc.*, **83**, 1992 (1961); (b) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2862 (1968).

(12) P. von R. Schleyer, *ibid.*, **86**, 1856 (1964).

(13) The bicyclo[2.2.2]octyl system seems to be a good one for comparison with **1a** since the related ketones have almost identical stretching frequencies: tricyclo[3.2.1.0^{2,7}]octan-4-one 1730 cm^{-1},[12] bicyclo[2.2.2]octan-2-one 1731 cm^{-1}.[12]

(14) (a) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965), and references contained therein; (c) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3900 (1967), and earlier communications in the series by Brown and coworkers; (d) however, see G. A. Olah, A. Commeyras, and C. Y. Liu, *ibid.*, **90**, 3882 (1968), for recent evidence favoring the bridged ion interpretation for the norbornyl cation.

(15) Melting points are corrected. Sealed capillaries were used for the tricyclic alcohols, which were sublimed (*ca.* 90°, 25 mm) prior to the determination of melting points and optical rotations. Rotations were measured with a Franz Schmid and Haensch polarimeter (readings to 0.01°), using a 2-dm polarimeter tube. Nuclear magnetic resonance (nmr) spectra were measured at 60 MHz, using tetramethylsilane as internal standard. Mass spectra were obtained with an LKB 9000 gas chromatograph–mass spectrometer (1% OV-17 stationary phase).

(16) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961).

Both the bridge and bath had to be effectively grounded to obtain a distinct null point reading. A plot of conductance *vs.* concentration of *p*-toluenesulfonic acid was found to be linear in the range studied, 0.003–0.01 *M*.

B. Polarimetric studies were performed by dissolving (−)-**1a** (*ca.* 0.5 g) and a 10% molar excess of anhydrous sodium acetate in 11.0 ml of anhydrous acetic acid and transferring the solution to a 2 dm × 8 mm jacketed polarimeter tube through which water from a 25° constant-temperature bath was circulated. Rotations were measured periodically through about two half-lives for change in optical activity. Initial readings were about −0.4°. Infinity readings (after ten half-lives) showed some positive rotation (*ca.* +0.6°) which product studies indicated was apparently due to a contaminant in the (−)-**1a**.

Product Studies. A. Acetolysis.—Products from the polarimetric rate studies of **1a** were recovered after ten half-lives for acetolysis in about 80% yield by dilution of the solution to 100 ml with water and continuous extraction with pentane for 24 hr. The extract was washed with 5% sodium carbonate and water and dried ($MgSO_4$). The extract was carefully concentrated to a few milliliters by distillation and analyzed by gc. Analysis of the products from three kinetic runs on a 5 ft × 0.25 in. column packed with 5% FFAP[17] on Chromosorb P, operating at 145°, helium flow 40 ml/min, showed two major products at 6.0 and 7.2 min retention time in the respective relative amounts by area (disk integrator) of 59.7 ± 0.4 and 40.3 ± 0.4% (average of the three compositions). A few per cent of an unidentified component with a retention time of 8.3 min was also observed, in addition to about 6–7% of a hydrocarbon (1.2 min retention time), presumed to be tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**4**).[8] Measurement of the rotation of the acetate mixture from one of the kinetic experiments (180 mg in 11.0 ml of pentane) showed no detectable activity (detectable to 0.01°).

Samples of the two acetate products were obtained by preparative gc for infrared and nmr analysis, using a 20 ft × $^3/_8$ in. column packed with 5% FFAP[17] on Chromosorb P, operating temperature 202°, helium flow 150 ml/min. This gave 105 mg of the major product (retention time 12.6 min, pure by gc) and 90.6 mg of the minor product (retention time 14.3 min) which contained a trace of the major product and about 3% of a contaminant having a retention time of 16.0 min. In agreement with Sauers' results,[8] a comparison of spectra with those of authentic samples or with reported data[8] showed the major product is the bicyclic acetate **3**, the minor product is the tricyclic acetate **1d**. Both of the acetate samples in 11.0 ml of pentane showed no optical activity.

The absence of tricyclo[3.2.1.$0^{2,7}$]octan-3-yl acetate in the product was determined by analysis of an nmr spectrum (neat) of the acetolysis mixture. A comparison of the integration for the methinyl protons centered at δ 4.6 (due to **1d**) and 4.95 (due to **3**) *vs.* that for the vinyl protons centered at 5.6 and the cyclopropyl centered at 0.7 indicated only a mixture of **1d** and **3** was present.

Structural and optical stability of **1d** to buffered acetolysis conditions was determined in the following way. (−)-**1d** (205 mg) and 10.4 mg of anhydrous sodium acetate were dissolved in 11.0 ml of anhydrous acetic acid and the solution was placed in the 2-dm jacketed polarimeter tube maintained at 25°. Rotations were measured periodically, and after 30 hr (ten polarimetric half-lives) the rotation was the same as at the outset (−0.71°). Gc analysis of the acetate recovered as described above also showed no structural change had occurred. Likewise, the bicyclic acetate **3** was recovered unchanged (by gc analysis) after being subjected to the conditions of buffered acetolysis at 25° for 74 hr.

B. Hydrolysis.—(−)-**1a** (203 mg, 0.728 mmol) and 81.7 mg (0.817 mmol) of calcium carbonate were weighed into a 10-ml volumetric flask and 80% (by volume) aqueous acetone was added to the mark. After heating the solution at 25.0° for 80 hr, acetone was distilled from the solution using a steam bath. The residue was diluted to 100 ml with water and the solvolysis products were isolated by continuous extraction with pentane (48 hr). After drying, the extract was concentrated to a few milliliters and analyzed by gc. Analysis on a 150 ft × 0.01 in. Ucon 50 LB 550 X capillary column (temperature 120°, N_2 pressure 40 psi) showed 33% **3-OH** (retention time 11.8 min) and 67% **1b** (retention time 13.8 min) by comparing retention times with those of authentic samples. The rotation of the mixture of alcohols in 11.0 ml of pentane was measured. No activity could be detected. Because of the similarity in retention times of **3-OH** and tricyclo[3.2.1.$0^{2,7}$]octan-3-ol the mixture of hydrolysis products was analyzed by nmr to determine if the latter alcohol was present. The nmr spectrum (CCl_4) of the mixture (34 mg after removal of pentane and sublimation) was a composite of those for **1b** and **3-OH**.

Stability of tricyclo[3.2.1.$0^{2,7}$]octan-3-ol to hydrolysis conditions was shown by heating 100 mg of the alcohol[18] in 10 ml of 80% aqueous acetone with 207 mg of calcium carbonate at 25° for 84 hr. The alcohol was recovered as described above and analyzed by nmr (after sublimation). The spectrum (CCl_4) was identical with that of the starting tricyclic alcohol.

Partial Acetolysis of Tricyclo[3.2.1.$0^{2,7}$]octan-4-yl *p*-Toluenesulfonate (1a).—A 401-mg sample of **1a** was dissolved in 5.0 ml of anhydrous acetic acid preheated to 40° and the solution was maintained at 40° in a constant-temperature bath for 41 min (35% acetolysis). The reaction was quenched by cooling the solution in an ice bath and then pouring it into 20 ml of cold water. After extracting the aqueous solution thoroughly with ether, the extract was washed with 5% sodium carbonate, water, and brine and dried ($MgSO_4$). The solvent was removed on a rotary evaporator, pentane was added to the residue, and the recovered ester was allowed to crystallize in a freezer. The mother liquors were decanted and the solid was recrystallized twice from ether–pentane to remove acetate contaminant. This gave 140 mg of tan crystals having a slight acetate odor, mp 45–47°. The nmr spectrum of the material ($CDCl_3$) was identical with that of the starting ester **1a**.

Registry No.—**1a** (±), 19740-91-1; **1a** (−), 19740-92-2; **1b** (−), 19740-93-3; **1c** (±), 19740-94-4; **1c** (−) (brucine salt), 19789-50-5; **1c** (−), 19740-95-5; **1d** (−), 19740-96-6.

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(17) FFAP is a modified Carbowax 20M stationary phase available from Varian Aerograph, Walnut Creek, Calif.

(18) Prepared from the corresponding ketone[2] by lithium aluminum hydride reduction.[8]