mmole of butenes and 0.11 mmole of *sec*-butyl acetate were produced.

Titrations with sodium acetate of the *p*-nitrobenzenesulfonic acid formed in typical solvolyses showed no increase after 6 hr., though only about 87% of the nosylate was accounted for this way. The fate of the remainder was not determined.

**Acknowledgment.**—The work was supported in part by the Sloan Foundation and in part by the National Science Foundation. G. W. B. is also grateful to the U. S. Industrial Chemicals Company for a fellowship for the year 1960–1961. The authors wish to thank Miss Juanita Hillman for preliminary experiments which led to the selection of the system studied.

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# Synthesis and Rates of Acetolysis of *exo-exo* and *exo-endo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-yl *p*-Bromobenzenesulfonates[1,2]

ALLAN K. COLTER AND ROCCO C. MUSSO

*Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania 15213*

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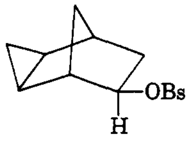
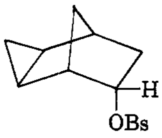
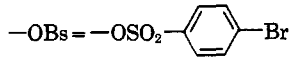
In connection with the ability of the cyclopropane ring to exhibit properties of unsaturation[3] and in particular to stabilize a carbonium ion through direct conjugation,[4] the solvolytic behavior of *exo-exo-* and *exo-endo*-tricyclo[3.2.1.0$^{2,4}$]octan-6-yl *p*-bromobenzenesulfonates (Ia and IIa) are of interest. These compounds are the cyclopropyl analogs of the homoallylic *exo-* and *endo*-dehydronorbornyl *p*-bromobenzenesulfonates, respectively, in which participation of the double bond in solvolysis has been demonstrated.[5] Because of the fixed orientation of the cyclopropane ring in Ia and IIa, the solvolytic behavior of these compounds may help to define the stereochemical requirements for cyclopropane conjugation.[6]



Ia

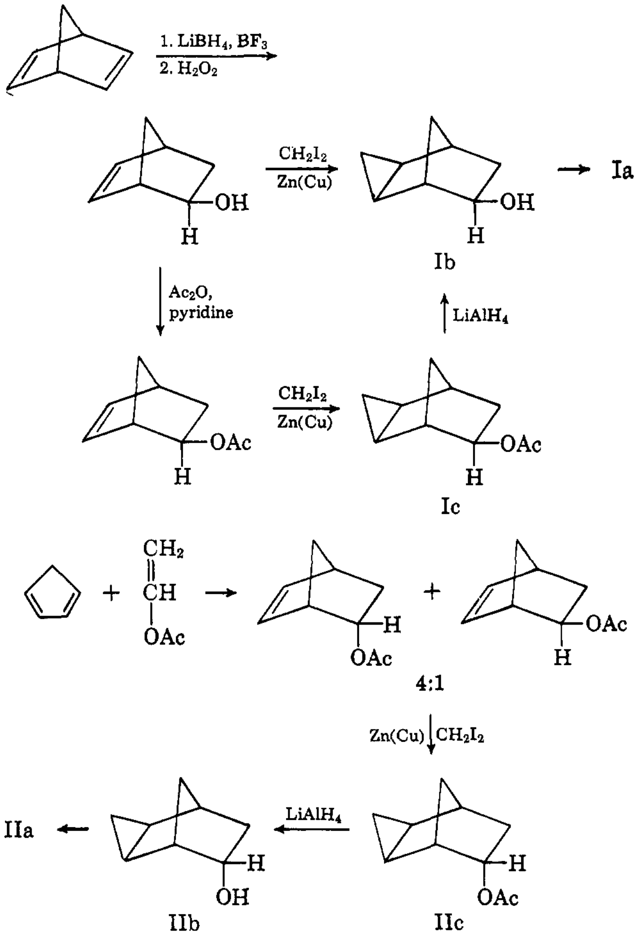


IIa



The title compounds were synthesized as outlined in Chart I. Hydroboration of bicycloheptadiene by a procedure similar to that of Brown[7] led to *exo*-dehydronorborneol containing 8–13% (gas phase chromatography) *endo* isomer, depending on conditions. Pure *exo*-dehydronorborneol, obtained by crystallization and sublimation of the hydroboration product, was treated with methylene iodide and zinc–copper couple according to the Simmons–Smith procedure.[8] Gas phase chromatography (g.p.c.) showed the presence of a single tricyclic alcohol indicating that the methylene addition was at least 95% stereoselective, presumably *exo*.[9] The same alcohol (identical infrared spectrum) was prepared in lower yield through Simmons–Smith addition to *exo*-dehydronorbornyl acetate, followed by lithium aluminum hydride reduction, as outlined in Chart I. Treatment of the alcohol Ib with *p*-bromobenzenesulfonyl chloride in pyridine led to the brosylate Ia as an oil.

CHART I



A mixture of dehydronorbornyl acetates (*exo–endo*, *ca.* 1:4) was treated according to the Simmons–Smith procedure to give a product which, on distillation, yielded a single (>95%) tricyclic acetate (g.p.c.). Lithium aluminum hydride reduction yielded a single tricyclic alcohol having a longer retention time (Ucon

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[1] Abstracted from a portion of the Ph.D. Thesis of R. C. M., Carnegie Institute of Technology, June 1963.

[2] Supported in part by a Frederick Gardner Cottrell Grant from the Research Corp.

[3] For leading references, see M. Yu. Lukina, *Usp. Khim.* (Engl. Trans.), **31**, 419 (1962); M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955); R. S. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); E. N. Trachtenberg and G. Odian, *ibid.*, **80**, 4018 (1958); R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963).

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[6] N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953); E. M. Kosower, *Proc. Chem. Soc.*, 25 (1962); A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

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[9] (a) Completely stereoselective methylene addition, also assumed to be *exo* on the basis of steric considerations, was observed with bicyclo[2.2.1]heptene: H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964). (b) R. R. Sauers and J. A. Beisler [*Tetrahedron Letters*, **No. 32**, 2181 (1964)] have reported the formation of Ia through solvolytic and deamination reactions of compounds in the 3-nortricyclylcarbinyl system and by methylene addition to *exo*-dehydronorborneol. No experimental details have been reported.

Polar on Chromosorb, Wilkins Instrument and Research, Inc.) than Ib. The brosylate IIa was obtained by the usual procedure as a crystalline solid, m.p. 82.5–83.5°.

Since highly stereoselective methylene addition occurred in the reactions of both *exo*-dehydronorborneol and *endo*-dehydronorobonyl acetate, it is reasonable to assume *exo* addition in both cases. Further evidence of the *exo* ring fusion was obtained in the case of IIa. Treatment of this ester with potassium *t*-butoxide in dioxane led to an olefin having an infrared spectrum (9–11 $\mu$) identical with that published[10] for the product of the Simmons–Smith reaction with bicycloheptadiene and different from that reported[11] for the Diels–Alder adduct of cyclopentadiene and cyclopropene.[11] Infrared spectral data were consistent with the structural assignments for Ia, b, and c and IIa, b, and c (Experimental). The high-resolution infrared spectrum of IIb in the C–H stretching region has bands at 3067 (w), 3016 (m), 2943 (s), and 2886 cm.$^{-1}$ (w). The frequencies of the first two bands appear to be somewhat higher than normal,[12,13] possibly owing to opposition between the cyclopropylmethylene and the bridge methylene.[14] This conclusion must await high-resolution infrared spectral examination of the corresponding *endo*-cyclopropyl compounds, however.

The results of a kinetic study of acetolysis of Ia and IIa are summarized in Table I.

TABLE I

RATES OF ACETOLYSIS OF *exo-exo* AND *exo-endo*-TRICYCLO[3.2.1.0$^{2,4}$]OCTAN-6-YL *p*-BROMOBENZENESULFONATES[a]

| Compound | Temp., °C. | $10^5k$, sec.$^{-1}$ [b] |
|---|---|---|
| *exo-exo*, Ia | 25.00 ± 0.03 | 1.69 ± 0.03 |
| *exo-endo*, IIa | 85.07 ± 0.03 | 3.44 ± 0.08 |
| | 75.07 ± 0.03 | 1.05 ± 0.02 |
| | 65.00 ± 0.03 | 0.333 ± 0.004 |
| | 25.00 | 0.0012[c] |

[a] In glacial acetate acid–0.04 *M* sodium acetate. [b] Rate constants listed with average deviations. [c] Extrapolated from data at higher temperatures.

In all cases, calculated first-order rate constants showed no regular drift through three half-lives. The data for the *exo-endo* brosylate lead to the following activation parameters.

$$\Delta H^* (65.0°) = 27.3 \text{ kcal. mole}^{-1},$$
$$\Delta S^* (65.0°) = -3.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

From the data in Table I, $k_{exo}/k_{endo} = 1.4 \times 10^3$ at 25°. This value falls between the ratio of $7.9 \times 10^3$ for acetolysis of *exo*- and *endo*-dehydronorbornyl brosylates[15] and $3.50 \times 10^2$ for acetolysis of *exo*- and *endo*-norbornyl brosylates.[16] Thus, there appears to be some evidence for participation of the C-2–C-4 bond in the cyclopropane ring analogous to that of the double bond in the dehydronorbornyl system. Rates of ionization, however, provide a better measure of anchimeric acceleration and such rates are not known for Ia and IIa; the appropriate ratio for the norbornyl system[17] is $1.6 \times 10^3$.

The infrared spectra of the acetolysis products from Ia and IIa at 75.0° were essentially identical and were similar in most major features to that of *exo-exo*-tricyclo[3.2.1.0$^{2,4}$]octan-6-yl acetate, indicating that this acetate was the major product. On learning of a similar study of the products of acetolysis of Ia and IIa in the laboratories of Dr. Kenneth B. Wiberg, these investigations were discontinued.

## Experimental

***exo*-Dehydronorborneol.**—When this compound was prepared as described by Brown, *et al.*,[7] a crude product containing 87% *exo*- and 13% *endo*-dehydronorborneol (g.p.c.) was obtained. Sublimation led to a 35% yield of *exo*-dehydronorborneol, m.p. 89–91°, lit.[7] m.p. 89–90°. Two crystallizations from pentane raised the melting point to 91–92°. When the oxidation step was carried out using ethanolic sodium hydroxide and 30% hydrogen peroxide at 0° (rather than aqueous sodium hydroxide at 25–40° as described by Brown), the crude product was 92% *exo* but the over-all yields of crude product were somewhat lower.

***exo*-Dehydronorbornyl Acetate.**—*exo*-Dehydronorborneol (11.6 g., 0.105 mole) was heated for 1 hr. on the steam bath with 15 ml. (150% of theory) of acetic anhydride and 40 ml. of dry pyridine. The mixture was added to 245 ml. of pentane, washed three times with 2 *N* hydrochloric acid, three times with aqueous sodium carbonate, and once with water, and dried over anhydrous potassium carbonate. Evaporation of the pentane gave 14 g. (87%) of product, $n^{25}$D 1.4490.

*Anal.* Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.94; H, 8.13.

***exo-exo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-ol (Ib).**—A mixture of 233 g. (0.871 mole) of methylene iodide, 73.1 g. of zinc–copper couple,[18] and 0.41 g. (0.0016 mole) of iodine in 500 ml. of anhydrous ether was refluxed for 1 hr. After the mixture was cooled, 45 g. (0.41 mole) of pure *exo*-dehydronorborneol in about 20 ml. of ether was added dropwise, with stirring. The mixture was then refluxed for 100 hr., cooled, and filtered; the filtrate was washed with 5% hydrochloric acid, aqueous bicarbonate, and water. After this was dried over magnesium sulfate, the ether was evaporated leaving a liquid residue. Excess methylene iodide and other nonalcoholic materials were separated by chromatography on alumina. An ether solution of the alcoholic materials was washed with saturated aqueous silver nitrate to remove unreacted dehydronorborneol. After the solution was washed with water and dried over magnesium sulfate, the ether was evaporated leaving 20 g. of liquid product (39% of theory). G.p.c. showed a single peak (>95%) of much larger retention time (Ucon Polar on Chromosorb) than *exo*-dehydronorborneol and slightly shorter retention time than IIb (see below). The infrared spectrum showed no absorption in the region of 6.38 $\mu$, characteristic of the strained double bond in bicyclo[2.2.1]heptene derivatives,[19] and showed peaks at 2.91 (s) (O–H stretching), 3.30 (sh), characteristic of a cyclopropane methylene, and 3.35 (s) and 9.79 $\mu$ (s), characteristic of the cyclopropane ring.

Ib was also prepared by lithium aluminum hydride reduction of the acetate, Ic, as described below for IIc. G.p.c. again indicated >95% purity.

***exo-exo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-yl Acetate (Ic).**—A mixture of 36.4 g. (0.136 mole) of methylene iodide, 9.90 g. of zinc–copper couple,[18] and 2.0 g. (0.0079 mole) of iodine in 102 ml. of anhydrous ether was refluxed for 45 min. External heating was discontinued and 14.0 g. (0.092 mole) of *exo*-dehydronorbornyl acetate in 6 ml. of anhydrous ether was added dropwise, with stirring. The mixture was then refluxed for 75 hr., cooled, and filtered; the filtrate was washed with 5% aqueous hydrochloric acid, aqueous bicarbonate, and saturated aqueous sodium chloride. After drying this over anhydrous magnesium

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(17) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(18) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

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sulfate, filtration, and evaporation of the ether, distillation (b.p. 60° at 1 mm.) led to 1.9 g. (12% of theory) of product, $n^{25}\text{D}$ 1.4626, shown by g.p.c. to be >95% pure. The infrared spectrum showed no absorption in the 6.38-μ region, characteristic of the strained double bond, and showed absorption at 3.25 (sh), 3.31 (sh), and 9.72 (s), characteristic of the cyclopropane ring, and at 5.70 (s) and 8.00 μ (s), due to the acetate group.

***exo-exo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-yl *p*-Bromobenzenesulfonate (Ia).**—A mixture of 4.18 g. (0.0337 mole) of Ib and 8.62 g. (0.0337 mole) of *p*-bromobenzenesulfonyl chloride was dissolved in as little dry pyridine as possible and placed in the refrigerator for 50 hr. The solid material was then pulverized and the contents of the flask were transferred to a separatory funnel containing 100 ml. of 1 *M* hydrochloric acid at 0° and extracted into methylene chloride. The extracts were washed with cold aqueous bicarbonate and ice–water and dried over anhydrous potassium carbonate. Filtration, followed by evaporation of solvent under vacuum, gave a liquid brosylate which solidified on long standing in the refrigerator. The infrared spectrum showed characteristic cyclopropane absorption at 9.83 (m) and at 7.38 (s), 8.46 (s), and 8.53 μ (sh), due to the sulfonate group.

***exo-endo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-yl Acetate (IIc).**—The Simmons–Smith reaction of 60.9 g. (0.40 mole) of a 4:1 mixture of *endo*- and *exo*-dehydronorbornyl acetates[20] was carried out as described for *exo*-dehydronorbornyl acetate with a reflux time of 120 hr. Fractional distillation under reduced pressure led to 10.6 g. (16% of theory) of liquid tricyclic acetate, b.p. 60° at 1 mm., $n^{20}\text{D}$ 1.4813, shown by g.p.c. to be >95% pure. The infrared spectrum showed absorption at 3.24 (s) and 9.65 (s), characteristic of the cyclopropane ring, and at 5.75 (s) and 8.02 μ (s), due to the acetate group. In addition, the near-infrared spectrum showed a band at 1.67 μ, characteristic of the cyclopropane ring.[21]

*Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 9.07.

***exo-endo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-ol (IIb).**—A 4.5-g. (0.027-mole) quantity of IIc was added to a slurry of 1.01 g. (0.027 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether. After refluxing for 1 hr., 2 ml. of water, followed by 1.56 ml. of 10% sodium hydroxide, was added, with stirring. After standing for 12 hr., the resulting white precipitate was filtered off and the filtrate was dried over anhydrous magnesium sulfate. Filtration and evaporation led to 2.9 g. (86% of theory) of product. G.p.c. showed a single peak (>95%) having a retention time (Ucon Polar on Chromosorb) slightly longer than that of Ib. Sublimation and crystallization from petroleum ether gave material of m.p. 60–63°. The infrared spectrum showed absorption at 2.94 (s) (O–H stretching), and at 3.23 (sh), 3.29 (sh) and 9.71 μ (m), characteristic of the cyclopropane ring. The high-resolution spectrum (Perkin-Elmer Model 112 spectrophotometer, calcium fluoride optics, on supercooled liquid film) showed bands at 3067 (w), 3016 (m), 2943 (s), and 2886 cm.$^{-1}$ (w).

***exo-endo*-Tricyclo[3.2.1.0$^{2,4}$]octan-6-yl *p*-Bromobenzenesulfonate (IIa).**—This compound was prepared as described for Ia. Two recrystallizations gave material of m.p. 81.5–82.5°. The infrared spectrum showed characteristic cyclopropane absorption at 3.21 (sh), 3.27 (sh), 9.66 (m), and 9.86 (s), and characteristic sulfonate group absorption at 7.21 (s), 8.40 (s) and 8.51 μ (m).

*Anal.* Calcd. for $C_{14}H_{15}BrO_3S$: C, 48.98; H, 4.40. Found: C, 49.01; H, 4.38.

**Conversion of IIa to *exo*-Tricyclo[3.2.1.0$^{2,4}$]oct-6-ene.**—A solution of 1.37 g. (0.004 mole) of IIa and 0.9 g. (0.008 mole) of potassium *t*-butoxide (incompletely dissolved) in 80 ml. of dioxane was heated at 60° for 12 hr. and then at 80° for 12 hr., with stirring. The solution was added to a large volume of saturated sodium chloride and extracted twice with pentane. The combined pentane extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the pentane left a liquid residue from which some unreacted IIa crystallized on standing in the refrigerator. The infrared spectrum was superimposable upon that published[10] (9–11 μ) for the Simmons–Smith adduct of bicycloheptadiene and had sharp bands at 6.25 and 6.70 μ, characteristic[11] of the *exo* adduct, while bands at 9.54 and 11.3 μ, characteristic of the *endo* adduct,[11] were absent.

**Kinetic Measurements.**—Kinetic solutions were 0.03 *M* in ester (Ia or IIa), 0.04 *M* in sodium acetate in glacial acetic acid containing 0.02 *M* excess acetic anhydride. Rates at 25° were followed by periodic withdrawal of 5-ml. aliquots of kinetic solution directly from a volumetric flask immersed in a constant-temperature bath, quenching by addition to a 20-ml. volume of dioxane. For rates at the higher temperatures sealed ampoules were used and points quenched thermally. The extent of the reaction was followed by potentiometric titration of the excess sodium acetate using standard 0.03 *M* perchloric acid in glacial acetic acid. Rate constants were calculated by the expression $k = 2.303/t \log V_0 - V_\infty/V_t - V_\infty$, where $t$ is the time and $V_0$, $V_t$, and $V_\infty$ are the volumes of standard acid consumed initially (after thermal equilibrium), after time $t$, and after ten half-lives. Infinity titers for IIa were close to 100% of theory. The sample of Ia used in the kinetic measurements contained some unreacted alcohol and gave an infinity titer of 72% of theory.

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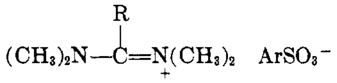
## A Novel Preparation of Amidinium Arenesulfonates

HARRIS E. ULERY

*Contribution No. 380 from the Jackson Laboratory,*
*Organic Chemicals Department,*
*E. I. du Pont de Nemours and Company,*
*Wilmington, Delaware*

*Received February 2, 1965*

We would like to report a novel reaction between arenesulfonyl chlorides and dimethylformamide (DMF). When benzenesulfonyl chloride was refluxed for several hours in an excess of DMF, large colorless crystals could be isolated on cooling. Although exceedingly hygroscopic in this form, recrystallization from DMF or MeOH gave a nearly quantitative yield of material, the elemental analysis of which required the empirical formula $C_{11}H_{18}N_2O_3S$. This material was quite soluble in water, alcohol, and formamide, slightly soluble in hot acetone, and insoluble in ether, benzene, chloroform, and carbon tetrachloride. This suggested an ionic composition. The infrared spectrum revealed the presence of the benzenesulfonate anion, and in addition, possessed a strong absorption at 1710 cm.$^{-1}$ (DMF has a band at 1640 cm.$^{-1}$). The only reasonable structure consistent with these data is that of tetramethylformamidinium benzenesulfonate (I, R = H; Ar = $C_6H_5$). The infrared data agree well with that reported[1] for the corresponding chloride. This structure was firmly established on the basis of the n.m.r.



$$(CH_3)_2N\text{—}\overset{\overset{\displaystyle R}{|}}{C}\text{=}\underset{+}{N}(CH_3)_2 \quad ArSO_3^-$$

I

spectrum in $D_2O$ (TMS as internal reference), which displayed a single methyl resonance (3.16 p.p.m., 12 protons), a vinyl-like singlet (7.52 p.p.m., one proton), and a multiplet characteristic of a monosubstituted benzene ring (centered at about 7.8 p.p.m., five protons). The splitting of the methyl signal observed in some amidinium systems[2] and in the related octamethyloxamidinium cation[1] is absent, possibly owing to a strong "inside–outside" interaction.

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