than the *para* as indicated. Since yields were not quantitative, however, such reactions cannot be ruled out.

Experimental[8]

4-Benzyl-6-hydroxy-7-methoxyisoquinoline (**4**).—Vanillin (3.04 g., 0.02 mole) was dissolved in a minimum amount of absolute ethanol, combined with 2.66 g. (0.02 mole) of aminoacetaldehyde diethylacetal, diluted to 15 ml. with absolute ethanol and hydrogenated at atmospheric pressure[9] and room temperature over 200 mg. of previously reduced platinum oxide. Hydrogen consumption stopped at about 90% completion after about 3 hr. The catalyst was removed by filtration and the solvent was evaporated under vacuum. The residual oil was dissolved in 50 ml. of concentrated hydrochloric acid. The solution which had become hot was cooled and washed with three 30-ml. portions of 3:2 ether–benzene to remove starting aldehyde. A twofold excess of benzaldehyde (4.24 g., 0.04 mole) dissolved in 50 ml. of ethanol was added to the acidic solution which was subsequently boiled for 30 min. The cooled solution was diluted with an equal volume of water and washed with three 50-ml. portions of ether to remove the excess benzaldehyde. The solution was made basic with ammonium hydroxide to pH 8. The precipitate was removed by filtration and crystallized once from water–ethanol to give 3.33 g. of product, m.p. 185–190°, 63%. The analytical sample, m.p. 192–193°, was recrystallized three more times and dried.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.94; H, 5.91; N, 5.49.

A **picrate** was prepared in ethanol and recrystallized twice from the same solvent to give the analytical sample, m.p. 235–238°.

Anal. Calcd. for $C_{23}H_{18}N_4O_9$: C, 55.87; H, 3.67; N, 11.33. Found: C, 55.64; H, 3.81; N, 11.59.

4-Benzyl-7-hydroxy-6-methoxyisoquinoline (**5**).—These reactions were carried out exactly like those leading to **4**. The starting material was isovanillin. The crude product, m.p. 200–205°, amounted to 2.88 g., 54%. The analytical sample, m.p. 207–209°, was recrystallized four times from water–ethanol.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.61; H, 5.79; N, 5.25.

A **picrate** was prepared in ethanol–benzene and recrystallized three times from the same solvents to give an analytical sample, m.p. 204–206°.

Anal. Calcd. for $C_{23}H_{18}N_4O_9$: C, 55.87; H, 3.67; N, 11.33. Found: C, 56.08; H, 3.69; N, 11.38.

4-Benzyl-8-hydroxy-7-methoxyisoquinoline (**6**).—The reduction and acid treatment steps were the same as those described above leading to **4**. The starting material was *o*-vanillin. When the acid–benzaldehyde–isoquinoline mixture was cooled (to 5°), however, the product precipitated as a hydrochloride salt and was removed by filtration. It amounted to 3.68 g., m.p. 204–207°, 61%. The analytical sample, m.p. 207–209°, was recrystallized three times from 6 *N* hydrochloric acid.

Anal. Calcd. for $C_{17}H_{16}ClNO_2$: C, 67.73; H, 5.33; Cl, 11.77; N, 4.64. Found: C, 67.45; H, 5.57; Cl, 11.61; N, 4.78.

The **free base** was prepared by passing an ethanolic solution of the hydrochloride over a column of 50 g. of basic alumina (Woelm). The main fraction of the eluate was yellow and gave, on evaporation, the free base. The analytical sample, m.p. 220–222°, was recrystallized three times from acetone–water.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.86; H, 5.85; N, 5.21.

A **picrate** was prepared from the hydrochloride by neutralization of an aqueous solution, filtration of the solid base, and final salt formation in ethanol. The analytical sample, m.p. 220–223°, was recrystallized three times from acetone–ethanol.

Anal. Calcd. for $C_{23}H_{18}N_4O_9$: C, 55.87; H, 3.67; N, 11.33. Found: C, 56.03; H, 3.77; N, 11.24.

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[8] Melting points were recorded on a Kofler hot stage microscope and are corrected. The n.m.r. spectra were measured on a Varian A-60 instrument. The microanalyses were performed by Mr. H. Fröhofer of the Organic Chemistry Institute, University of Zürich, Zürich, Switzerland.

[9] Pressures up to 10 p.s.i. or so were safe, but decomposition sometimes occurred at higher pressures.

Absence of Direct Participation of *sec*-Butyl Chloride in Acetolysis of Isopropyl *p*-Nitrobenzenesulfonate

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The nucleophilic character of covalent organohalogen compounds is strongly suggested both by the existence of stable diarylhalonium salts[1] and by the commonplace neighboring-group participation by halogen in carbonium ion reactions, both from the β position[2] and from greater distances.[3] There are nevertheless still no reports of stable dialkylhalonium ions, nor is there definitive evidence for intermolecular participation by an alkyl halide in a carbonium ion reaction. This Note reports an attempt to detect such participation in one system, chosen as fairly typical and easy to deal with experimentally, and not necessarily the optimum case for dialkylhalonium ion formation.

When isopropyl nosylate was solvolyzed in a 12:1 mixture (mole ratio) of *sec*-butyl chloride and acetic acid at 95°, the initial products were isopropyl acetate and propene, and only secondarily did other products (*sec*-butyl acetate, isopropyl chloride, and butenes) appear. Thus from 1.85 mmoles of nosylate after various reaction times were observed the product distributions shown in Table I.

TABLE I

SOLVOLYSIS PRODUCTS FROM 1.85 MMOLES OF ISOPROPYL NOSYLATE

	Products, mmoles[a]				
Time, hr.	Propene	*i*-PrOAc	*i*-PrCl	*sec*-BuOAc	Butenes
0.5	0.025	0.031	...	...	...
3	0.23	0.80	0.05	0.009	0.054
6	0.09	1.12	0.18	0.08	0.11
12	0.06	0.98	0.42	0.23	0.21

[a] The numbers are averages of several runs at each time. The scatter in the data[7] indicates precisions of 5–10% for the saturated products and 10–30% for the volatile olefins.

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[1] (a) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Am. Chem. Soc.*, **82**, 2948 (1960); (b) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *ibid.*, **81**, 342 (1959); (c) R. B. Sandin and A. S. Hay, *ibid.*, **74**, 274 (1952); (d) A. N. Nesmeyanov and T. P. Tolstaya, *Dokl. Akad. Nauk SSSR*, **105**, 94 (1955); (e) A. N. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva, *ibid.*, **104**, 872 (1955).

[2] (a) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1576, 2845 (1939); (b) S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946); (c) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948); (d) E. Grunwald, *ibid.*, **73**, 5458 (1951).

[3] (a) P. E. Peterson and J. E. Duddey, *ibid.*, **85**, 2865 (1963); (b) P. E. Peterson and G. Allen, *ibid.*, **85**, 3608 (1963); (c) R. E. Glick, Ph.D. Thesis, University of California at Los Angeles, 1954.

The conclusion is that to no major extent does *sec*-butyl chloride participate directly in solvolysis to form a *sec*-butylisopropylchloronium ion (I), which would

$$sec\text{-}C_4H_9\text{-}\overset{+}{Cl}\text{-}i\text{-}C_3H_7$$

I

have been expected to yield significant amounts of isopropyl chloride, *sec*-butyl acetate, and butenes as *primary* products. Rather, these must form from side reactions, such as acid-catalyzed solvolysis of *sec*-butyl chloride and reaction of isopropyl acetate and propene with HCl. A quantitative estimate of the relative nucleophilic participating abilities of *sec*-butyl chloride and acetic acid can be obtained by the reasonable assumption that the former, reacting through I, would give isopropyl chloride as a major product. In early stages of the solvolysis, the ratio of isopropyl acetate to isopropyl chloride is at least 90 (from data at 1.5 hr., not shown in Table I). From the 12:1 composition of the solvent, the acetic acid is at least 1000 times as nucleophilic toward the nosylate as *sec*-butyl chloride.

Control experiments showed that the solvent mixture does indeed undergo *p*-nitrobenzenesulfonic acid catalyzed decomposition to give butenes and *sec*-butyl acetate, and that addition of extra HCl to the solvolysis reaction mixture does indeed increase the yield of isopropyl chloride.

Experimental[4]

Materials.—Acetic acid, Du Pont reagent grade, was purified by the method of Fieser.[5] Approximately 1.5 l. of acetic acid and 100 g. of crude triacetyl borate were placed in the pot for the final distillation which was carried out through a 3-ft. column packed with $^3/_{16}$-in. glass helices. An intermediate fraction boiling sharply at 117° was collected.

Isopropyl chloride and isopropyl acetate, Eastman Kodak Co. reagent grade, were dried over sodium sulfate and distilled through a 1-ft. wire-spiral column. The materials were collected at 35 and 88°, respectively.

Octane, Phillips Petroleum Co. 99 mole % pure, was distilled from calcium hydride through a 1-ft. wire-spiral column and collected at 125°.

sec-Butyl acetate was washed with sodium bicarbonate and water, dried over sodium sulfate, and distilled through a 1-ft. wire-spiral column. The material boiled sharply at 111°.

sec-Butyl chloride, Eastman Kodak Co. reagent grade, was found by v.p.c. analysis to contain sufficient impurities to hinder the analyses, when one considers the quantity of *sec*-butyl chloride used as a solvent during the reaction runs. Careful distillation through a 2-ft. spinning-band column brought about the removal of these impurities. The distillation was always followed by v.p.c. analysis. No *sec*-butyl chloride was collected until these minor impurities had been eliminated. The *sec*-butyl chloride was collected at 67–68°. It should be noted that *sec*-butyl chloride decomposes very slightly under the conditions used for v.p.c. analysis. (These conditions are given further in this section.)

p-Nitrobenzenesulfonic acid, Eastman Kodak Co. technical grade, was dried by azeotropic distillation of the water with benzene. During the drying process the acid changed color from white to black. The dried acid was collected by filtration and the excess solvent was removed by drying in an Abderhalden apparatus under vacuum. The grayish white powder was used directly. The material is very hygroscopic.

All the liquid reagents used showed greater than 99% purity when subjected to vapor phase chromatography.

Isopropyl *p*-Nitrobenzenesulfonate.—Isopropyl alcohol (12.2 g., 0.203 mole) and pyridine (100 ml., Merck reagent grade which had been distilled from potassium hydroxide) were cooled in an ice–salt bath to −5°. *p*-Nitrobenzenesulfonyl chloride (Eastman Kodak Co. research grade was used without further purification; 50.0 g., 0.226 mole) was added in *ca.* 10-g. lots; the temperature was kept around 0°. The solution was then kept at −5° for 45 min. A yellowish precipitate formed during this period. Water (200 ml.) was added and the aqueous solution was extracted with methylene chloride. The methylene chloride solution was washed with cold 20% hydrochloric acid until the aqueous solution was less than pH 1. The methylene chloride was washed with cold 10% sodium bicarbonate and water. The solution was dried with sodium sulfate and the solvent was removed by the use of a rotary evaporator. The oily residue was chromatographed on Florisil with chloroform as the eluent. The resulting oil was crystallized from cyclohexane–ether to give 30.3 g., m.p. 49–53° (plus some higher melting material). Recrystallization from methylcyclohexane–ether gave 28.3 g., m.p. 49–51° (some higher melting material present). Chromatography on Florisil followed by crystallization from methylcyclohexane–ether gave 22.5 g. (45%), m.p. 51.5–53° (lit.[6] m.p. 50–51°).

Anal. Calcd. for $C_9H_{11}NO_5S$: C, 44.10; H, 4.52. Found: C, 43.83; H, 4.71.

To prevent decomposition this material was stored at −20°. Caution should also be exercised in handling the substance, which apparently causes a dermatitis.

Solvent.—When the term solvent is used, it refers to a mixture of *sec*-butyl chloride and acetic acid in the ratio 12.0 moles to 1.00 mole, respectively. The solvent was transferred and delivered by means of a 5-ml. automatic pipet, and was stored at −20°.

Vapor Phase Chromatographic Analysis.—The vapor phase chromatographic analyses were done on an F and M Model 300 machine with helium as the carrier gas. The separations were carried out using an 8-ft. column of F and M Ucon Water Insoluble on Chromosorb P. The operating parameters were usually as follows: block temperature, 220°; injection port temperature, 175°; column temperature, 90°; helium flow, 40 cc./min.; and attenuation, 4, 8, 16, 32, or 64 as conditions warranted. Peak area integrations were made by means of a Disc chart integrator. In general, clean separations of all components were observed. Typical retention times are as follows: propene, 1 min.; butenes, 1.9 min.; isopropyl chloride, 3.9 min.; *sec*-butyl chloride, 7.1 min.; isopropyl acetate, 11.9 min.; octane, 18.4 min.; and *sec*-butyl acetate, 23.2 min.

Thermal conductivity corrections were determined by analysis of known mixtures[7] of all products except propene, which was assumed to have the same thermal conductivity as the butene mixture.[8]

Isopropyl *p*-Nitrobenzenesulfonate Solvolyses.—Isopropyl *p*-nitrobenzenesulfonate, octane, and 5.0 ml. of solvent were sealed in a tube and heated to 95.0° for a specified length of time. The tube was cooled and the contents were transferred by bulb-to-bulb distillation for 1.5 hr. at 0.15-mm. pressure with liquid-nitrogen cooling of the receiver. The distillate was washed with 5 ml. of cold 20% sodium hydroxide solution which had been saturated with sodium chloride, followed by four 5-ml. portions of cold saturated sodium chloride solution, dried over magnesium sulfate, and filtered by gravity into a 12 × 35 mm. screw-cap vial which was then equipped with a silicone rubber septum. The sample for analysis was removed through the septum and injected into the gas chromatograph.

Known mixtures were run through the entire procedure to eliminate the possibility of systematic errors, and it was shown necessary to make some corrections for volatility losses of the olefins in the transfer step.

When the solvent used had been brought to 0.175 *M* in hydrogen chloride before the reaction, the average yields after 6 hr. follow: propene, 0.05 mmole; butenes, 0.12 mmole; isopropyl chloride, 0.37 mmole; isopropyl acetate, 1.02 mmoles; and *sec*-butyl acetate, 0.08 mmole (compare with Table I).

When 5 ml. of solvent was heated with 380 mg. of *p*-nitrobenzenesulfonic acid for 24 hr. at 95°, an average (four runs) of 0.12

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[4] Melting points and boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer grating instruments, Models 237 and 521. Microanalysis was by Mr. Josef Nemeth and associates.

[5] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 281.

[6] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

[7] G. W. Burton, Ph.D. Thesis, University of Illinois, 1964.

[8] H. J. Lucas and D. Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 152.

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.

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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]

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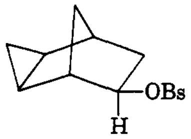
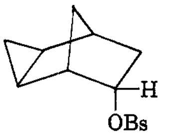
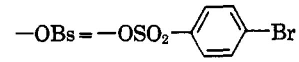
In connection with the ability of the cyclopropane ring to exhibit properties of unsaturation[3] and in particular to stabilize a carbonium ion through direct conjugation,[4] the solvolytic behavior of *exo-exo-* and *exo-endo*-tricyclo[3.2.1.0^{2,4}]octan-6-yl *p*-bromobenzenesulfonates (Ia and IIa) 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



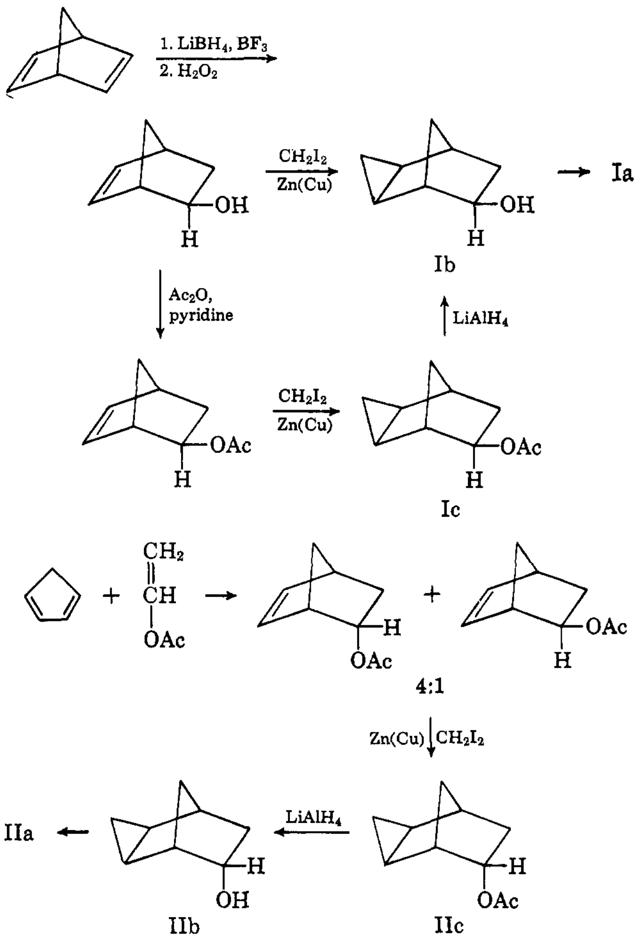
IIa



$-\mathrm{OBs} = -\mathrm{OSO_2}-\mathrm{C_6H_4}-\mathrm{Br}$

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).

[4] N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962); H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964).

[5] S. Winstein, H. M. Walborsky, and K. C. Schreiber, *ibid.*, **72**, 5795 (1950).

[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).

[7] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

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

[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.