

Experimental Section¹⁰

Kinetic Measurements.—The acetolysis conditions and procedure were the same as previously reported.^{2b,6}

Materials.—5,8-Dimethoxybenzonorbornadiene (I) was prepared according to the procedure of Meinwald and Wiley.⁸

5,8-Dimethoxybenzornorbornen-2(*exo*)-ol (II).—To a suspension of 9.8 g of I and 1.83 g of sodium borohydride in 150 ml of tetrahydrofuran there was added a solution of 9.15 g of boron trifluoride etherate in 20 ml of tetrahydrofuran at $\sim 0^\circ$ with stirring under nitrogen atmosphere; this was allowed to stand overnight at room temperature. Oxidation with 3 *N* sodium hydroxide and 30% hydrogen peroxide gave a crude alcohol which was, for purification, converted into the *p*-nitrobenzoate, mp 146–147° (from ethyl acetate). Hydrolysis of the ester with sodium bicarbonate in aqueous dioxane gave 4 g of the pure II: bp 128° (0.07 mm); $\nu_{\text{max}}^{\text{OH}}$ 3618 (OH) cm^{-1} . Its brosylate was a viscous oil.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ (alcohol): C, 70.89; H, 7.32. Found: C, 70.82; H, 7.40.

Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_6\text{N}$ (*p*-nitrobenzoate): C, 65.03; H, 5.19; N, 3.79. Found: C, 65.15; H, 5.30; N, 3.86.

5,8-Dimethoxybenzornorbornen-2-one (III).—The Oppenauer oxidation of II (4.0 g) with aluminum tri-*t*-butoxide (8.95 g) and *p*-benzoquinone (2.11 g) in benzene (230 ml) afforded a crude ketone (4.2 g). Recrystallization from ether gave the pure material, mp 93–94°. The infrared spectrum (in CCl_4) showed $\nu_{\text{C=O}}$ 1760 and 1748 cm^{-1} (a little stronger).

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$: C, 71.54; H, 6.47. Found: C, 71.62; H, 6.60.

5,8-Dimethoxybenzornorbornen-2(*endo*)-ol (IV).—Treatment of III with 4 equiv of lithium aluminum hydride in ether followed by the usual work-up yielded II and IV in an approximate ratio of 9:1. Elution chromatography over standard alumina gave pure IV: mp 91.5–92.5°; $\nu_{\text{max}}^{\text{OH}}$ 3612 (free OH) and 3582 (associated OH . . . π). The retention time of the *endo*-acetate on vpc (in a 1-m column of SE-30, 200°, and 2.0 kg of He) was 12 min, while that of the *exo* acetate was 14 min.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$: C, 70.89; H, 7.32. Found: C, 70.60; H, 7.14.

The brosylate had mp 95.5–96.5° (from *n*-hexane).

Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{O}_6\text{BrS}$: C, 51.94; H, 4.36. Found: C, 52.13; H, 4.47.

Registry No.—II, 14123-80-9; *p*-nitrobenzoate of II, 14123-81-0; II-OBs, 14123-82-1; III, 14123-83-2; IV, 14123-84-3; IV-OBs, 14123-85-4.

(10) Melting points were taken by capillary and are corrected. Infrared spectra were recorded on a Nippon Bunko DS-201-B spectrometer, except for the measurement of an internal interaction between a hydroxyl group and π electrons which was carried out by a Nippon Bunko DS-402-G (grating).

Partial Acetolysis of Neopentyl Tosylate-sulfonyl-¹⁸O. An Attempt to Trap Neopentyl Cation

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Opposing views have been expressed on the timing of the ionization and rearrangement steps in reactions of neopentyl substrates which give derivatives of *t*-amyl cation. In a recent study,¹ which includes a critical review of the previous literature, the rates of several solvolyses of 1-adamantylcarbinyl arenesulfonates were found to be essentially the same as those of the cor-

responding neopentyl compounds, indicating the slow step in each case to be simple ionization to the primary carbonium ion. More recently, Kirmse and Horn² have isolated substantial to predominant yields of neopentyl products from reactions of diazoneopentane with acetic acid, trifluoroacetic acid, and thiophenol. These results strongly suggest the formation of neopentyl cations in tight ion pairs, which collapse to products at rates comparable to those of methyl migration. On the other hand, Saunders and co-workers have preferred an interpretation in terms of concerted ionization-rearrangement for the rates and migration aptitudes found in solvolysis of a series of *p*-substituted β -benzylisobutyl tosylates³ and of neopentyl brosylate and its γ -methylated analogs.⁴ In addition, Sanderson and Mosher⁵ have concluded that the deoxidation of optically active neopentyl-1-*d* alcohol does not involve a free neopentyl cation, since methyl migration was found to take place with inversion of configuration at C-1 highly stereoselectively.

A sensitive method for detecting the formation of carbonium ions from ionization of appropriate carboxylic⁶ or sulfonic⁷ esters is the use of specifically ¹⁸O-labeled substrates and analysis for rearrangement of the label in reactant recovered after partial solvolysis. In such an experiment scrambling of the label is clear evidence for an intermediate carbonium ion, although non-scrambling does not lead to a unique interpretation.

We have used this approach in an attempt to demonstrate the possible intermediacy of neopentyl cation in the acetolysis of neopentyl tosylate. The mechanistic possibilities, starting with sulfonyl-labeled neopentyl tosylate **1a**, are outlined in Scheme I. Evidence for the formation of neopentyl cation would be the conversion of **1a** to **1b**, *i.e.*, the incorporation of label into the etheral oxygen position.

p-Toluenesulfonyl chloride enriched with ¹⁸O to the extent of *ca.* 6% was prepared by the method of Oae and co-workers⁸ from *p*-toluenethiol, labeled water, and chlorine. Reaction with neopentyl alcohol in pyridine gave tosylate **1a**, which was shown by mass spectrometry⁹ to contain 4.1 (+0.1)% total ¹⁸O *i.e.*, 3.9% above natural isotopic abundance,¹⁰ corresponding to 5.8% excess ¹⁸O in the sulfonyl oxygens. (Oxygen scrambling has been found not to occur during the preparation of an arenesulfonate more reactive than the present one.)^{7c} Tosylate **1a** was solvolysed in boiling buffered acetic acid¹¹ (118°) to 67% completion and the unreacted substrate was recovered and cleaved at the chain O-S linkage by reaction

(2) W. Kirmse and K. Horn, *Tetrahedron Letters*, 1827 (1967).

(3) J. R. Owen and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **88**, 5809 (1966).

(4) R. L. Heidke and W. H. Saunders, Jr., *ibid.*, **88**, 5816 (1966).

(5) W. A. Sanderson and H. S. Mosher, *ibid.*, **88**, 4185 (1966).

(6) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964), and references therein.

(7) (a) H. L. Goering and R. W. Thies, 152nd National Meeting of the American Chemical Society, Sept 1966, p S38; (b) D. B. Denney and E. J. Kupchik, *J. Am. Chem. Soc.*, **82**, 859 (1960); (c) D. B. Denney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

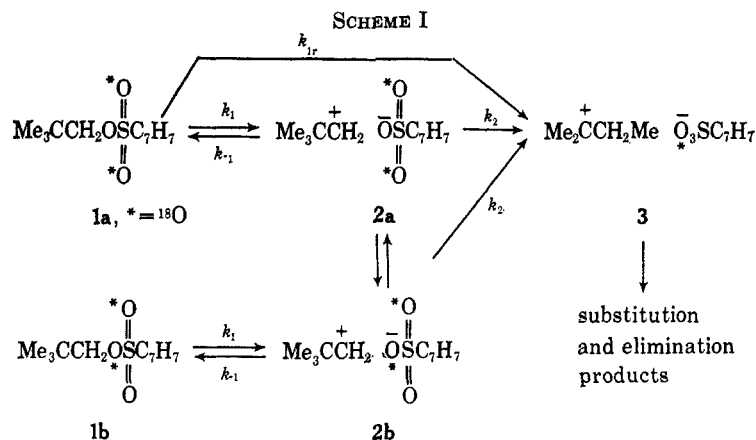
(8) S. Oae, T. Kitao, and Y. Kitaoka, *Tetrahedron*, 827 (1963).

(9) The mass spectra were measured by Morgan-Schaffer Corp., Montreal 26, Quebec, Canada.

(10) The natural abundance of ¹⁸O is 0.20%. K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., p 60.

(11) Ion-pair return phenomena are particularly prominent in this medium. See S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(1) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966).



with sodium naphthalene in tetrahydrofuran.¹² Mass spectrometric analysis⁹ of the neopentyl alcohol thus obtained showed negligible enrichment in ¹⁸O (<0.1% over natural abundance).¹⁰

Thus, evidence for intermediate neopentyl cation was not found in this experiment. Three alternative explanations of the results may be considered. First, ionization and rearrangement could proceed together to give *t*-amyl cation **3** directly, *i.e.*, $k_{1r} \gg k_1$. This interpretation would be inconsistent, however, with the comparative solvolysis results obtained for the 1-adamantylcarbinyl and neopentyl systems,¹ cited above. Second, neopentyl cation could be formed and participate in ion pair return, but without appreciable equilibration among the oxygens in the tosylate anion. This process would be significant if the return rate and methyl migration rate were comparable to each other and substantially greater than the rate of tosylate reorientation in the ion-pair. While not detectable in the present system, preferential ion-pair return on the originally bonded oxygen atom has been observed in Wagner-Meerwein isomerizations of two arenesulfonates during acetoysis.^{7a,c} In another case, involving a more stable carbonium ion, oxygen equilibration was complete before return.^{7c}

As a third limiting possibility, neopentyl-tosylate ion pairs could be initially formed but undergo rearrangement to *t*-amyl cation much faster than return. Within such an explanation the data may be treated to obtain a lower limit for k_2/k_{-1} as follows,¹³ taking 0.1% as the upper limit for per cent excess ¹⁸O in recovered neopentyl alcohol.

$$\begin{aligned} \text{fraction of ROTs} &= \frac{\text{fraction converted to products}}{\text{fraction converted to products} + \text{fraction ionized and returned}} \\ &= \frac{\text{fraction to products}}{\text{fraction to products} + \left(1 - \frac{\text{fraction to products}}{\text{fraction to products}}\right)} \times \\ &\quad \left(\frac{\% \text{ excess } ^{18}\text{O in recovered alcohol}}{\% \text{ excess } ^{18}\text{O at S=O in original reactant}}\right) \times \\ &\quad \left(\frac{3}{2}\right) \left(\frac{1}{\text{fraction of oxygen equilibration in } ^-\text{OTs prior to return}}\right) \\ &= 0.67 + 0.33 \left(\frac{0.1}{5.8}\right) \left(\frac{3}{2}\right) \\ &= 0.68 \end{aligned}$$

assuming for simplicity's sake that the tosylate oxygens become fully equivalent before return. Now

(12) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966).

(13) See C. C. Lee and L. Noszko, *Can. J. Chem.*, **44**, 2481 (1966), for a similar analysis in a different system and further references.

$$\frac{\text{fraction of ROTs converted to products}}{\text{fraction of ROTs ionized}} = \frac{k_2}{k_{-1} + k_2}$$

so

$$\frac{0.67}{0.68} = \frac{1}{1 + \frac{k_{-1}}{k_2}}$$

and

$$k_2/k_{-1} = 67$$

as a lower limit.

The results show incidentally that, as presumed, no oxygen scrambling takes place during either preparation of the tosylate or its degradation by sodium naphthalene.¹²

Experimental Section

***p*-Toluenesulfonyl-¹⁸O Chloride.**⁸—In a 100-ml, three-necked, round-bottomed flask, equipped with an overhead stirrer and gas inlet and outlet tubes, was placed 1.0 ml of water containing 42.2 atom % ¹⁸O (Yeda Research and Development Co., Ltd., Rehovoth, Israel), 5.0 ml of ordinary distilled water (0.33 mole of total water), and 10.0 g (0.0806 mole) of freshly sublimed *p*-toluenethiol (Eastman). Dry chlorine gas was bubbled into the stirred mixture, which was kept below 5° throughout the reaction by means of an ice-methanol bath. After 6.0 hr the red-orange suspension was filtered with suction and the collected solid was dissolved in 75 ml of hexane and dried over anhydrous magnesium sulfate. The solution was concentrated to 25 ml and cooled to 0°. The solid which formed was recrystallized from hexane in like manner, yielding 2.42 g (0.013 mole, 16.2%) of labeled tosyl chloride, mp 68.5–70.0° (lit.⁸ mp 69–70°). Neither in this nor in three preliminary runs with unlabeled water could yields be obtained which approached the 70% value reported by Oae, *et al.*⁸ The isotopic composition of the product was determined by analysis of the 15-ev mass spectral peaks⁹ at *m/e* 155, 157, and 159, corresponding to M – Cl; the total ¹⁸O was 6.5 ± 0.1%.

Neopentyl Tosylate-sulfonyl-¹⁸O (1a).—Reaction between 680 mg (7.5 mmoles) of neopentyl alcohol and 1.31 g (6.9 mmoles) of labeled *p*-toluenesulfonyl chloride in 10 ml of dry pyridine was carried out and worked up in the usual manner.¹⁴ The tosylate, recrystallized first from ethanol and then from hexane to ensure the removal of neopentyl alcohol, weighed 1.041 g (4.3 mmoles, 62%) and had mp 45.5–47.5° (lit. mp 48–49°, ¹⁵ 46.0–46.5°¹⁶). Mass spectral isotopic analysis⁹ was carried out using the peak intensities of the molecular ions, *m/e* 242, 244, 246 (70 ev), and also those of the ions at *m/e* 187, 189, 191 (14 ev) formed by rearrangement together with loss of C₄H₇.¹⁷ Total ¹⁸O content was found to be 4.1 ± 0.1%.

(14) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(15) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

(16) F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

(17) W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, Jr., *J. Phys. Chem.*, **69**, 1742 (1965).

Partial Acetolysis of Labeled Neopentyl Tosylate and Degradation and Analysis of Recovered Reactant.—A mixture of 998 mg (4.12 mmoles) of the labeled neopentyl tosylate and 40 ml of acetic acid, 1% in acetic anhydride, containing 4.80 mmoles of sodium acetate (0.120 M) was heated to reflux (ca. 118°) (drying tube to the atmosphere) and the progress of the reaction was followed by titrating, with standard perchloric acid in glacial acetic acid, aliquots withdrawn from a simultaneous reaction conducted with unlabeled tosylate but otherwise identical. After 67 ± 1% reaction (ca. 16.5 hr) the mixture was cooled in ice water, added to 400 ml of water, and extracted with three 150-ml portions of ether. The combined ether solution was washed with water, 10% sodium bicarbonate solution, and water, and was dried over anhydrous magnesium sulfate. After filtration the ether and *t*-amyl acetate were removed on a rotary evaporator with mild warming (<45°). The solid residue was crystallized from hexane with cooling to -50°, yielding 332 mg (1.37 mmoles) of crude recovered neopentyl tosylate. This material, dissolved in 5 ml of dry tetrahydrofuran, was added to a stirred solution of sodium naphthalene prepared by reaction between 0.16 g (0.0070 mole) of sodium chips and 0.90 g (0.0070 mole) of naphthalene in 15 ml of dry tetrahydrofuran for 3 hr under a dry nitrogen atmosphere.¹² After 15 min, during which the color of the solution changed from dark green to dark greenish brown, 3 ml of water was added cautiously and the mixture was then added to 150 ml of ether and 200 ml of water in a separatory funnel and thoroughly shaken. The ether layer was separated, washed several more times with water until the aqueous layer was no longer strongly basic, and dried over anhydrous magnesium sulfate. Most of the ether was removed by rotary evaporation and from a portion of the residual solution 6 mg of neopentyl alcohol was isolated by preparative gas chromatography. Comparison of the mass spectrum⁹ (51 ev) of the recovered neopentyl alcohol with that of a sample of pure unlabeled material in the *m/e* 73-75 region (M-CH₃) showed ¹⁸O enrichment of the former to be no greater than 0.1% and probably considerably less.

Registry No.—1a, 14128-46-2; neopentyl cation, 14128-47-3.

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The Polar Addition of Molecular Fluorine to Acetylenes^{1,2}

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The addition of halogen to the carbon-carbon triple bond is an old and established process³ studied by many workers. Direct low-temperature fluorine-olefin addition reactions have been examined extensively⁴⁻⁶ in this laboratory and molecular complexes as well as β -fluorocarbenium ions were postulated^{2,6} as intermediates for this process. It seemed of interest to complete the halogen-acetylene series for the case of fluorine as well as to provide more information on fluorine addition processes in general.

(1) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021 AMC-11536 (Z).

(2) Part IV of the Low-Temperature Fluorination Process: R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).

(3) M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966), and references therein.

(4) R. F. Merritt and T. E. Stevens, *ibid.*, **88**, 1822 (1966).

(5) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

(6) R. F. Merritt, *ibid.*, 3871 (1966).

The additions were conducted at -78° and the acetylenes diluted with either Freon 11⁷ or methanol. No difference in absorption (addition) rates was observed for these two solvents even though they are of widely differing polarity.

The use of CCl₃F precluded solvent intervention and the major fluorine-containing product was the tetrafluoride (I). Less than stoichiometric amounts of fluorine did not favor difluoro olefin information and only tetrafluoride and unreacted acetylene were found. However, the use of methanolic solutions of the substrate led to the formation of *gem*-fluoro ethers (II) and dimethyl ketals (III) as well as tetrafluorides. Table I below lists the product distribution for the three acetylenes studied.

TABLE I
PRODUCT DISTRIBUTION FOR FLUOROMETHANOLYSIS

$$\text{C}_6\text{H}_5\text{C}\equiv\text{CR} + 2\text{F}_2\text{-CH}_3\text{OH} \longrightarrow$$

	$\text{C}_6\text{H}_5\text{CF}_2\text{CF}_2\text{R}$	$\text{C}_6\text{H}_5\text{CF}(\text{OCH}_3)\text{CF}_2\text{R}$	$\text{C}_6\text{H}_5\text{C}(\text{OCH}_3)_2\text{CF}_2\text{R}$
	I	II	III
	-----% composition-----		
	I	II	III
R = C ₆ H ₅	23	57	20
R = CH ₃	19	50	31
R = H	13	35	52

The product mixtures were analyzed by vapor phase chromatography (vpc) where appropriate and in every case by integration of the fluorine nuclear magnetic resonance (nmr) spectra. The relative position of the ether groups was easily ascertained by their nmr spectra (F¹⁹ and H¹) as well as acidic hydrolysis to the corresponding α,α -difluoro ketone.

The nature of the products found (*i.e.*, II and III) as well as the placement of the oxygen is a strong indication of the polar character of the fluorinating reagent. The formation of ketals and fluoro ethers may be envisioned as arising *via* path A or B (Scheme I).

To be of significance the methanolysis reaction (path B) would have to proceed exclusively to the enol ether (VI) and not continue to the unreactive (to fluorine) dimethyl ketal. It is expected that formation of the ketal under these conditions would be greatly favored over partial methanolysis to the enol ether.

The acetylenes seem to fluorinate completely (in inert solvents) to tetrafluoride which implies that difluoro-olefin is more reactive to fluorine than is the parent acetylene. In methanol, no products could be found that would correspond to the intermediate olefins shown in Scheme I as IV, V, or VI. This would be consistent with the general view that olefins and enol ethers are much more receptive to electrophilic addition than are acetylenes.

The relative ratios of products are not of great significance as the magnitude of the influence of path B cannot be ascertained. Bases strong enough to scrub out all the HF are also reactive to fluorine and cannot be incorporated in the fluorination solution. The only trend which is apparent is that as the substituent becomes more bulky the amount of tetrafluoride (I) and

(7) Trademark of E. I. du Pont de Nemours and Co., Wilmington, Del., for CCl₃F.