[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Synthesis of Alkyl and Substituted Alkyl Fluorides from *p*-Toluenesulfonic Acid Esters. The Preparation of *p*-Toluenesulfonic Acid Esters of Lower Alcohols[1]

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A number of alkyl and substituted alkyl fluorides has been prepared from the corresponding *p*-toluenesulfonic acid esters (tosylates) by reaction with potassium fluoride. Isomerization, extensive elimination and doubling of chain length, the common disadvantages of the reaction between alkyl halides and transition metal fluorides, were not encountered. The method constitutes a convenient and dependable laboratory synthesis of primary and secondary alkyl fluorides, and substituted alkyl fluorides. The preparation of methyl tosylate from methanol and *p*-toluenesulfonyl chloride in the presence of pyridine at −40° has been found to give a yield of 96.8% of the ester on the basis of methanol. *p*-Toluenesulfonic acid esters which react rapidly with pyridine at 0° may be prepared conveniently and in high yields at lower temperatures. The role of the base in the reaction is discussed. The work was carried out with the purpose of developing a general laboratory synthesis of alkyl and substituted alkyl fluorides which could be adopted for the synthesis of similar isotopically substituted compounds for spectroscopic studies.

Introduction

The work described in this paper was originated by the need of obtaining several alkyl and substituted alkyl fluorides for the study of their infrared, Raman and microwave spectra. It was required that the synthesis would be sufficiently general to allow the preparation of substituted alkyl fluorides of widely varying physical and chemical properties especially those containing isotopic atoms.

Alkyl fluorides and substituted alkyl fluorides have been prepared by a number of methods.[2–11] The reaction of alkyl chlorides, bromides and iodides with transition metal fluorides, that of alkylene chlorides and bromides with potassium fluoride, of potassium alkyl sulfates and dialkyl sulfates with potassium fluoride, and alkyl amines with alkali metal nitrates and hydrofluoric acid have led to the desired products. The reaction of sulfonic acid esters with inorganic salts[12] has been extended on two occasions to the preparation of several alkyl fluorides.[10,11]

The reaction of sulfonic acid esters with potassium fluoride appeared to be most suitable for our purpose if it could be developed into a convenient laboratory synthesis, not requiring pressure equipment. Since most of the esters of *p*-toluenesulfonic acid are easily accessible from alcohols, and the synthesis of a number of isotopically substituted alcohols has been described in the literature, it was decided to study the reaction of alkyl tosylates with potassium fluoride in some detail.

Numerous methods are available for the preparation of alkyl tosylates.[13–20] The method developed by Patterson and Frew,[14] employing alcohols, *p*-toluenesulfonyl chloride and pyridine, has been used extensively. It suffers from the disadvantage that the tosylates of lower alcohols, and of benzyl alcohol, form alkylpyridinium salts with great ease,[15,18,21,22] effectively reducing the yield. To circumvent this difficulty Tipson[18] has recommended a reaction temperature slightly below 0° and stopping the reaction when the ester formation is estimated to have approached the maximum. Klamann and Drahowzal[23] have found it advantageous to prepare methyl tosylate in a polar solvent. Two other side reactions, the formation of alkyl chlorides[24,25] and alkyl esters,[26] have been shown to be negligible under the conditions of the Patterson–Frew method. The above methods require modification to become suitable for the preparation of alkyl tosylates from alcohols containing isotopic atoms. The problem is to obtain high conversion of the alcohol.

The Preparation of Tosyl Esters.—It seemed desirable to study methods of preparing methyl tosylate since we were interested mainly in tosylates of the lower alcohols. The procedure of Roos, Gilman and Beaber,[27] which involves the treatment of methanol and *p*-toluenesulfonyl chloride with aqueous potassium hydroxide, could be adapted to the problem. Yields as high as 89% were obtained when methanol was treated with equimolar amounts (or slight excesses) of *p*-toluenesulfonyl chloride. Any excess or unreacted *p*-toluene-

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(1) Presented before the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

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(3) Gy. Olah and A. Pavlath, *Acta Chim. Acad. Sci. Hung.*, **3**, 191 (1953).

(4) F. Swarts, *Bull. soc. chim. Belg.*, **30**, 302 (1921).

(5) O. Scherer, *Angew. Chem.*, **52**, 457 (1939); German Patent 600,706.

(6) W. H. Bennett, THIS JOURNAL, **51**, 377 (1929).

(7) K. P. Yates and H. H. Nielsen, *Phys. Rev.*, **71**, 349 (1947).

(8) E. Gryszkiewicz-Trochimowski, A. Sporzynski and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947).

(9) F. W. Hoffmann, *J. Org. Chem.*, **15**, 425 (1950).

(10) B. Helferich and A. Gnüchtel, German Patent 710,129 (1936).

(11) V. V. Razumovskii and A. E. Fridenberg, *J. Gen. Chem. (USSR)*, **19**, 92 (1949).

(12) This subject recently has been reviewed briefly by F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 970 (1950), in one of a series of papers dealing with the chemistry of toluenesulfonic acid derivatives.

(13) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley & Sons, Inc., New York, N. Y., 1944, pp. 507–508, 514–515.

(14) T. S. Patterson and J. Frew, *J. Chem. Soc.*, **89**, 332 (1906).

(15) J. Ferns and A. Lapworth, *ibid.*, **101**, 273 (1912).

(16) S. S. Rossander and C. S. Marvel, THIS JOURNAL, **50**, 1491 (1928).

(17) V. C. Sekera and C. S. Marvel, *ibid.*, **55**, 345 (1933).

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

(19) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 452 (1951).

(20) *Ibid.*, **82**, 460 (1951).

(21) Z. Foldi, *Ber.*, **55**, 1535 (1922).

(22) C. S. Marvel, E. W. Scott and K. L. Amstutz, THIS JOURNAL, **31**, 3638 (1929).

(23) D. Klamann and F. Drahowzal, *Monatsh.*, **83**, 154 (1952).

(24) A. Praetorius, *Sitzber. Akad. Wiss. Wien. Math.-naturw. Klasse*, Abt. IIb, **113**, 941 (1904).

(25) D. Klamann, *Monatsh.*, **83**, 1399 (1952).

(26) J. H. Kastle and P. Murrill, *Am. Chem. J.*, **17**, 290 (1895).

(27) A. T. Roos, H. Gilman and N. J. Beaber, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.

sulfonyl chloride was neutralized with pyridine and hydrolyzed, which proved to be a disadvantage.

A series of experiments were performed in which methanol was added to a slight excess of *p*-toluenesulfonyl chloride in pyridine at −6° and the reaction quenched after a suitable time. The results are given in Fig. 1. The decrease in yield when the reaction proceeded longer than 30 minutes is caused by the formation of methylpyridinium *p*-toluenesulfonate. Similar observations were made by Tipson[11] on the preparation of ethyl tosylate. A consideration of the possible modes of the reaction suggested that higher yields might be obtained in 2,6-lutidine solution. The results of several experiments of this kind at 8° also are given in Fig. 1 and give information regarding the mechanism of the reaction. It has been suggested by Hückel[28] that the first step in the formation of tosylates involves the formation of *p*-toluenesulfonylpyridinium chloride followed by a nucleophilic attack of the alcohol on the sulfonyl group of the complex. Except for this suggestion, it has been assumed generally that the role of the pyridine is as an acceptor for the hydrogen chloride formed in the reaction.[18,29,30] Reliable evidence for the formation of sulfonylpyridinium salts has been presented recently.[31,32]

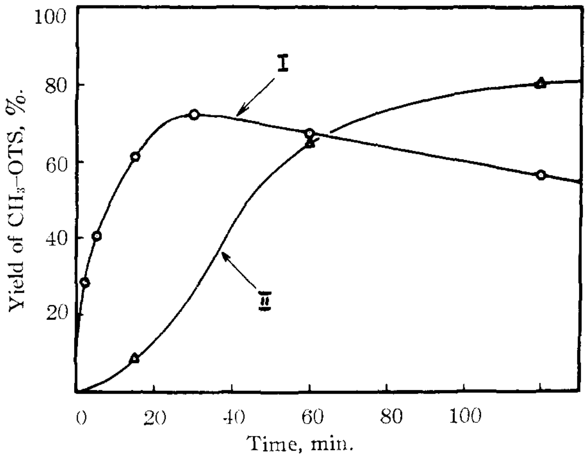
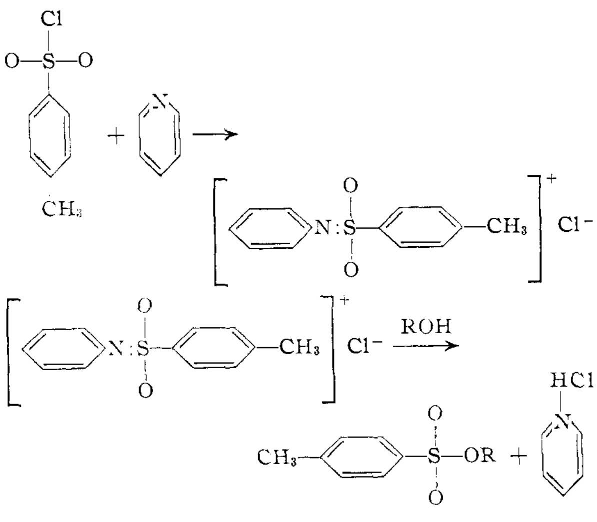


Fig. 1.—The yield of methyl tosylate as a function of time: I, pyridine solution at −6°; II, 2,6-lutidine solution at +8°.

The slopes in Fig. 1 may be considered as a measure of the rate of formation of methylpyridinium *p*-toluenesulfonate and methyl-2,6-lutidinium *p*-toluenesulfonate superimposed on the rate of formation of methyl tosylate. It is obvious that the rate of formation of methyl-2,6-lutidinium *p*-toluenesulfonate is much slower than the rate of formation of the corresponding pyridine complex. Another significant difference is the slower rate of formation of methyl tosylate in 2,6-lutidine solution. Since the solvent characteristics of the two bases are very similar and the base strengths toward protonic acids do not differ greatly, it is concluded that the esterification of *p*-toluenesulfonyl chloride in a tertiary base solution involves the formation of the complex between tosyl chloride and the base as the first step of the reaction.



Approach of the alcohol to the reaction center and nucleophilic substitution of the base is highly hindered in *p*-toluenesulfonyl-2,6-lutidinium chloride. From the comparison of the experimental results with rate expressions for the two reactions leading to the tosylate formation it may be concluded that the pseudo first-order initial step is rate-determining in pyridine solution. In 2,6-lutidine solution the two reactions proceed at a comparable rate. Thus the second reaction is slowed much more than the first one by the presence of the methyl groups of 2,6-lutidine.

These results suggested that the optimum conditions involved the addition of pyridinium to methanol and tosyl chloride at low temperatures. When the pyridine was added over a period of two hours at −44 to −32° and the reaction allowed to proceed for an additional hour, a yield of 96.8%, based upon the alcohol, was obtained. A number of alkyl and substituted alkyl tosylates was prepared by the same method except for a reaction temperature of 0° and the use of a smaller amount of pyridine. This is possible since the formation of alkylpyridinium tosylate proceeds much slower with the higher alkyl tosylates. In the preparation of secondary alkyl tosylates longer reaction times may be used for the same reason. The reaction conditions and results are listed in Table I.

Conversion of Tosyl Esters to Fluorides.—A number of alkyl fluorides and substituted alkyl fluorides was prepared from the corresponding *p*-toluenesulfonic acid esters with potassium fluoride. The method was used for the preparation of primary and secondary alkyl fluorides, halogen-substituted alkyl fluorides and alkylene fluorides. The first two members of the 1,1-dihydroperfluoroalkane series also were prepared, although in low yields. Cyclohexyl tosylate yielded only cyclohexene, and phenyl tosylate did not react.[33] With methyl and ethyl tosylate higher yields of the corre-

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[28] W. Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. 1, 6th edition, Akademische Verlagsgesellschaft, Leipzig, 1949, p. 573.

[29] K. H. Slotta and L. Lorenz, *Ber.*, **58**, 1320 (1925).

[30] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 508.

[31] L. Field, THIS JOURNAL, **74**, 394 (1952).

[32] L. Field and P. H. Settlage, *ibid.*, **76**, 1222 (1954).

[33] D. Klamann, *Monatsh.*, **83**, 1398 (1952).

TABLE I

PREPARATION OF ALKYL AND SUBSTITUTED ALKYL TOSYLATES

R	ROH, mole	$CH_3C_6H_4$-SO_2Cl, moles	C_5H_5N moles	t_A,[a] hr.	t_R,[b] hr.	F.p., or (m.p.), °C.	Yield %
CH_3	0.40	0.44	5.00	2	3	24.13	96.8
iso-C_3H_7	1.00	1.10	2.00	2.25	11.25	19.87[c]	94.4
cyclo-C_6H_{11}	1.00	1.10	2.06	3.25	9.25	(43.3–43.8)[d]	50.5[e]
CH_2FCH_2	1.00	1.10	2.00	2	4	20.52[f]	91.2
CH_2ClCH_2	1.00	1.20	2.52	2	4	22.10[g]	97.0
CH_2BrCH_2	0.75	0.90	1.50	1	3	11.88[h]	94.1
CH_2CH_2	.50	1.10	4.00	2	5	(126.0–127.0)[i]	85.1
CF_3CH_2	.784	1.00	1.86	4	9.2	(41.0)[j]	90.1
$C_2F_5CH_2$	.575	0.690	1.65	0.5	6.5	(52.2–53.0)	[k]

[a] Time required for addition of pyridine. [b] Total reaction time. [c] The cooling curves were analyzed by the simplified method developed by K. L. Nelson (Ph.D. Thesis, Purdue University, 1952). The calculated freezing point of pure isopropyl *p*-toluenesulfonate 19.90°, and the calculated purity of the sample 99.94 mole %; F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 452 (1951), have reported m.p. 20°. [d] S. Winstein, *et al.*, THIS JOURNAL, **70**, 816 (1948), have reported m.p. 43.5–44.0°. [e] The yield was low due to an attempt to recrystallize the product from a saturated solution in 90–100° petroleum ether at its boiling point where partial decomposition took place. Recrystallization from 60–70° petroleum ether caused no decomposition. [f] Calculated f.p. of pure 2-fluoroethyl *p*-toluenesulfonate 21.19°, calculated purity of the sample 98.8 ± 0.6 mole %. [g] Calculated f.p. of pure 2-chloroethyl *p*-toluenesulfonate 22.44°, calculated purity of the sample 99.4 ± 0.3 mole %; F. Drahowzal and D. Klamann, ref. *c*, have reported m.p. 22.5°. [h] Calculated f.p. of pure 2-bromoethyl *p*-toluenesulfonate 12.66°, calculated purity of the sample 98.8 ± 0.6 mole %. [i] Ethylene *p*-toluenesulfonate was recrystallized from benzene; F. Drahowzal and D. Klamann, ref. *c*, have reported m.p. 128°. [j] G. V. D. Tiers, H. A. Brown and T. S. Reid, THIS JOURNAL, **75**, 5978 (1953), have reported m.p. 41°. [k] Only a small amount of quite impure alcohol was available as starting material. Purification was carried out after the reaction by recrystallizing the tosylate from 60–70° petroleum ether and hence no value can be given for the conversion.

TABLE II

ALKYL AND SUBSTITUTED ALKYL FLUORIDES, PREPARED FROM *p*-TOLUENESULFONIC ACID ESTERS WITH POTASSIUM FLUORIDE

R	R–OTS, mole	KF, moles	β,β', grams	Time, hr.	Temp., °C.	P, mm.	Yield, % RF	Yield, % Olefin	Identification B.p. °C.	Identification B.p. Mm.	$n^{20}D$
CH_3	0.256	0.540		8	160–250	160	89.4				IR[a]
CH_3	.507	2.62	152	9	70–95	500	59.7				IR[a]
C_2H_5	.238	1.03		9	190–250	500	85.6	Traces			IR[b]
C_2H_5	.202	0.601	100	3.2	80	500	64.0				IR[b]
n-C_3H_7	.112	0.520	30	8.5	90–100	500	63.3		− 2.3	768[c]	
iso-C_3H_7	.411	2.00	116	8	100	500	50.7	11.3[d]	−10.0	760[e]	
n-C_7H_{15}	.700	3.50	350	3.5	100	760	24.7[f]	3.2			1.3863
n-C_7H_{15}	.727	3.50	203	3	150-180	40–50	55.1[g]	1.2	119.2	750	1.3860
CH_2FCH_2	.500	2.50	145	5	180–210	50	89.1	1			[h]
CH_2ClCH_2	.700	3.50	203	5	160	20–50	64.4	Traces[i]	53.2[j]		1.3752
CH_2BrCH_2	.500	2.50	726	8.5	100-130	20–30	61.6	1.8[k]	69.0	758[l]	1.4259
CH_2CH_2	.300	3.00	489	7.5	140–180	20-50	78.9	0.4	30.7	760[m]	
CF_3CH_2	.103	0.361	150	8	210–240	500	35.3		−26.2	736[n]	
$C_2F_5CH_2$	.200	1.00	290	8	210	10–100	13.8		1.2	760[o]	

[a] Infrared frequencies of the product agree with those listed for methyl fluoride in G. Herzberg "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Inc., New York, N. Y., 1951, p. 315. [b] Reference spectrum obtained from American Petroleum Institute Research Project 44, "Infrared Spectral Data," Carnegie Institute of Technology, Dept. of Chemistry, Pittsburgh, Penna., 1953, serial number 1302. [c] A. V. Grosse, R. C. Wacker and C. B. Linn, *J. Phys. Chem.*, **44**, 275 (1940), report b.p. −2.5° (755 mm). [d] B.p. of propylene −47.5° (760 mm.). G. B. Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 876 (1935), have reported b.p. −47.91°. [e] A. V. Grosse, R. C. Wackner and C. B. Linn, ref. *c*, have reported b.p. −9.4° (760 mm.). [f] The product was not removed during the reaction. Some *n*-heptyl tosylate remained unreacted. [g] F.p. −75.58°. Calculated freezing point of pure *n*-heptyl fluoride −75.56°, calculated purity of the sample 99.92 ± 0.04 mole %. F. Swarts, *Bull. soc. chim. Belg.*, **30**, 302 (1921), has reported m.p. −73°, b.p. 119.7–119.9° $n^{21.5}D$ 1.3855. [h] The infrared spectrum of ethylene fluoride, prepared from 2-fluoroethyl *p*-toluenesulfonate, identical with the spectrum of the same compound prepared from ethylene *p*-toluenesulfonate. [i] Contains traces of vinyl chloride and ethylene fluoride. [j] F. W. Hoffmann, *J. Org. Chem.*, **15**, 425 (1950), has reported b.p. 53.2°, $n^{25}D$ 1.3727. [k] Side products 1.8% vinyl bromide and 4.6% ethylene fluoride. [l] A. L. Henne and M. W. Renoll, THIS JOURNAL, **58**, 889 (1936), have reported b.p. 71.5–71.8° (760 mm.), $n^{25}D$ 1.42261. [m] Molecular weight calcd. 66.05, found 65.90. A. L. Henne and M. W. Renoll, THIS JOURNAL, **58**, 889 (1936), have reported b.p. 10–11° (760 mm.). Ethylene fluorides were stored without noticeable decomposition as a gas. The liquid decomposed slowly in closed glass vessels. On one occasion an explosion decomposition took place after standing for ten days. [n] Molecular weight of CF_3CH_2F 101.0, calcd. 102.03. *Anal.* Calcd. for $C_2H_2F_4$: C, 23.54; H, 1.98; F, 74.48. Found: C, 23.62; H, 2.05; F, 74.7. Analyses by Huffman microanalytical laboratories. [o] Molecular weight of $C_2F_5CH_2F$, calcd. 152.04, found 152.3.

sponding fluorides were obtained in the absence of a solvent. Due to the higher reaction temperatures required in the absence of solvent, this variation of the general method could not be profitably extended to the preparation of higher alkyl fluorides because of the decomposition of the tosylates. β,β'-Dihydroxyethyl ether proved to be a satisfactory solvent in these cases. The experimental conditions and results are reported in Table II.

In most of the experiments which were carried out in β,β'-dihydroxyethyl ether solution, five moles of potassium fluoride were used per mole of tosylate.

In many experiments equal weights of potassium fluoride and β,β'-dihydroxyethyl ether were used. When the reactions were carried out at lower pressures, the initial rate of evolution of the fluorides was rapid, requiring the control of the pressure in the reaction flask by means of the inlet-stopcock of the trap to avoid frothing. The major portion of the product is formed during the first two hours. In all reactions some 1,4-dioxane is formed due to the hydration of the solvent. Dioxane is separated easily by distillation, or with higher boiling fluorides by washing the product with water. In cases where infrared spectra of compounds prepared in this study were available the identification was accomplished by comparison of the spectra. 1,1,1,2-Tetrafluoroethane,[34] whose preparation has not been reported previously, was identified by determining its molecular weight from the gas density, and by comparison of its infrared spectrum with available spectra of compounds containing the CF_3CH_2 group. This identification was confirmed by the results of elemental microanalysis. In view of the reliability of the gas densitometric and spectrometric identification of CF_3CH_2F only these methods were used for the identification of $CF_3CF_2CH_2F$, which also has not been reported previously. 1,2-Difluoroethane (Caution! see note *m* in Table II), where a large discrepancy existed with the reported boiling point, was identified by determining its molecular weight by the gas density method, by using two different starting materials (2-fluoroethyl *p*-toluenesulfonate and ethylene *p*-toluenesulfonate), and by comparison of its infrared spectrum with the spectra for 1-chloro-2-fluoroethane and 1-bromo-2-fluoroethane.

The small amounts of low-boiling impurities (vinyl fluoride, vinyl chloride and vinyl bromide) were identified by means of their infrared spectra, and the amounts present were calculated from the average molecular weights of the low boiling fractions. The boiling points of compounds below room temperature were determined by rectification through a Podbielniak Hydrobot column.

Secondary alkyl fluoride led to some olefin as byproduct. Small amounts of olefin also are formed from 2-haloethyl *p*-toluenesulfonates. The two experiments on *n*-heptyl fluoride demonstrate the desirability of removing the fluoride from the reaction mixture during the reaction to prevent it from undergoing further reaction. In general higher reaction temperatures are required for tosylates with stronger C–O bonds. The lowest yields were obtained from 1,1-dihydroperfluoroalkyl tosylates where some decomposition also took place. Isomerization, extensive elimination and chain doubling, the common disadvantages of the reactions between alkyl halides and transition metal fluorides, were not encountered in this method. The main side reaction, which was not investigated, is believed to be the reaction of the tosylates with the solvent, leading to ether formation.[26]

Presently we are extending our work to the preparation of isotopically substituted alkyl fluorides.

Acknowledgment.—The authors express their gratitude to the Atomic Energy Commission and Purdue Research Foundation for the financial support of this work.

Experimental

Preparation of Methyl *p*-Toluenesulfonate in Pyridine.—To 12.8 g. (0.40 mole) of methanol and 83.9 g. (0.44 mole) of *p*-toluenesulfonyl chloride at −44° were added 395.5 g. (5.00 moles) of pyridine at a constant rate with rapid stirring over a period of two hours. The reaction was allowed to proceed for an additional hour and then was quenched by pouring the reaction mixture into 600 ml. of ice-water. The tosyl chloride was hydrolyzed by shaking the resulting suspension for five minutes. The suspension was extracted with approximately 300 ml. of ethyl ether and dilute sulfuric acid, containing finely crushed ice, was added to neutralize the excess of pyridine. The aqueous layer was removed and the ether solution was washed with ice-cold dilute sulfuric acid, ice-water, ice-cold dilute potassium hydroxide, and again with ice-water. The ether solution of methyl tosylate was dried over anhydrous sodium carbonate and the ether was removed by distillation; yield 96.8% based on the methanol.

The melting curve of the methyl tosylate was analyzed giving m.p. 24.13°; calculated m.p. of pure methyl tosylate 28.16°, and purity 95.0 ± 2.5 mole %. (Drahowzal and D. Klamann, *Monatsh.*, **82**, 452 (1951), have reported m.p. 28°.)

Preparation of Alkyl and Substituted Alkyl Tosylates.—A number of other tosylates were prepared by essentially the above procedure except for a reaction temperature of 0°. The details and results are collected in Table I.

Preparation of Methyl Fluoride in Absence of Solvent.—Into a flask were transferred 97.6 g. (0.524 mole) of methyl *p*-toluenesulfonate and 62.7 g. (1.08 moles) of potassium fluoride and the pressure of the system reduced to approximately 500 mm. The temperature was raised to 250° in two hours and maintained for five hours. The product was collected in a liquid nitrogen trap; yield 7.8 g. (89%). It was identified by its infrared spectrum.[35]

Methyl Fluoride, Prepared in β,β'-Dihydroxyethyl Ether.—Into a flask were transferred 94.5 g. (0.507 mole) of methyl tosylate, 152.2 g. (2.62 moles) of potassium fluoride and 152 g. of β,β'-dihydroxyethyl ether and the pressure in the system reduced to 160 mm. Heating was started while the reaction mixture was stirred constantly. Slow evolution of gas began at 70°. After the initial rapid reaction, which lasted for two hours, the temperature was raised to 95°, and maintained for 7.5 hours. The yield was 10.3 g. (59.7%).

Preparation of Alkyl and Substituted Alkyl Fluorides.—A number of fluorides were prepared by the above methods. The details and results are collected in Table II.

NOTE ADDED IN PROOF.—J. Cuculo and L. Bigelow, THIS JOURNAL, **74**, 710 (1952), report that they have prepared an azeotropic mixture of the tetrafluoroethanes citing the b. p. of CF_3CH_2F from a private communication of Dr. S. R. Dietrich (the du Pont Co., Wilmington, Del.). Also F. L. M. Pattison, *Nature*, **174**, 737 (1954), mentions that he has prepared monofluorides from alkyl sulfonates.

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[34] The infrared and Raman spectrum of CF_3CH_2F has been studied by Walter F. Edgell and Charlotte B. Ward and will be reported elsewhere.

[35] G. Herzberg, "Molecular Spectra and Molecular Structure. II. The Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Inc., New York, N. Y., 1951, p. 315.