Vinyl Cations; 11[1].
Improved Synthesis of Nonafluorobutanesulfonates (Nonaflates)

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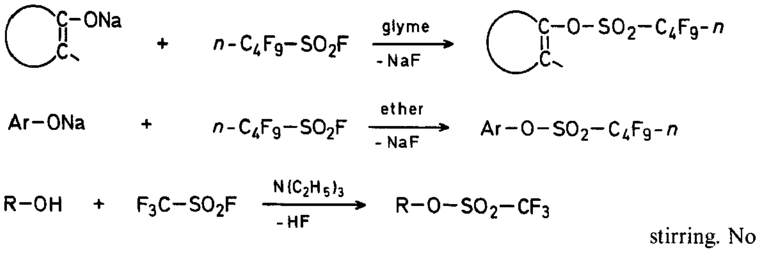
Our interest in vinyl cations led us to investigate the use of the nonafluorobutanesulfonate (Nonaflate) ion (n-C_4F_9—$SO_3^{\ominus}$) as a leaving group in solvolytic reactions[2]. The advantages of the new group, which is the fastest leaving group reported so far[2], in studying the kinetics and solvolysis of vinyl compounds have already been demonstrated[1,2,3]. Nonaflates are usually prepared via the known methods[4] with little or no variation[2,3] by reacting ketones, alcohols, or phenols with nonafluorobutanesulfonic acid anhydride. The crude reaction products are normally dark, partially polymerized mixtures, from which the required nonaflates are isolated in generally modest yields by column chromatography over silica gel[2].

During the course of our work on vinyl cations it became necessary to prepare various nonaflates from ketones which are prone to rearrangements under the conditions of the reaction with the anhydride. In the case of nopinone, for instance, it was not possible to prepare the required nonaflate (**5**, see Table) or the trifluoromethanesulfonate (triflate) (R—OSO_2—CF_3) using the corresponding anhydride; only rearranged products were obtained[5].

We wish to report here a new synthesis of nonaflates, which is superior to the known procedures in terms of manupulative simplicity and cleanness of the reaction. The convenience of this new process is that, instead of the nonafluorobutanesulfonic acid anhydride, the easily available nonafluorobutanesulfonyl fluoride (n-C_4F_9—SO_2F) can be used directly for the preparation of the nonaflates.



$$Ar{-}ONa \quad + \quad n\text{-}C_4F_9{-}SO_2F \xrightarrow[-\,NaF]{ether} Ar{-}O{-}SO_2{-}C_4F_9\text{-}n$$

$$R{-}OH \quad + \quad F_3C{-}SO_2F \xrightarrow[-\,HF]{N(C_2H_5)_3} R{-}O{-}SO_2{-}CF_3$$

The cyclic vinyl nonaflates (**1**–**5**, see Table) were prepared by treating the sodium enolates of the corresponding ketones with nonafluorobutanesulfonyl fluoride in dry glyme as solvent under a nitrogen atmosphere. Possible formation of unsaturated ethers and other side products if any, in analogy with the reaction of sulfonyl fluorides with sodium alcoholates as reported by Beyl et al.[6], were not investigated. The aryl nonaflates (**8**–**10**, Table) were made from the sodium phenoxides and nonafluorobutanesulfonyl fluoride in dry ether. The latter reaction parallels that described by Beyl et al.[6] and Hansen[7] for the preparation of phenyl perfluoroalkanesulfonates by treating the trimethylphenoxysilane or the phenols in the presence of triethylamine or sodium phenoxide, respectively, with the sulfonyl fluoride. Use of trifluoromethylsulfonyl fluoride in preparing the triflates from alcohols in the presence of triethylamine was already described by Hansen[8].

Enolates from ketones could also be used in general for the preparation of triflates, for instance by treating them with trifluoromethanesulfonic imidazolide according to the method of Effenberger and Mack[9]. As examples of this method, the cyclohexenyl and nopinyl triflates are given (**6**, **7**, Table).

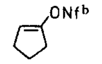
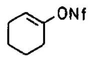
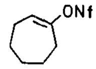
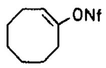
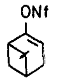
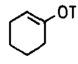
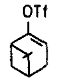
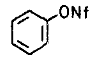
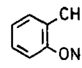
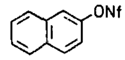
Preparation of Vinyl Nonaflates; General Procedure:

Sodium hydride (Fluka, 1.2 g, 27 mmol, as 55–60% dispersion in mineral oil) was washed three times with dry ether and rinsed once with dry glyme. Dry glyme (50 ml) was then added to the sodium hydride and a slow stream of dry nitrogen was maintained during the reaction. A solution of the ketone (20 mmol) in dry glyme (10 ml) was then added at room temperature. The reaction mixture was refluxed for 10 hr with magnetic stirring, cooled to 0°, and the nonafluorobutanesulfonyl fluoride (12 g, 40 mmol) was added. After stirring for 1 hr at 0° the reaction mixture was refluxed gently for 15 hr at 50–60°. The reaction mixture was then cooled in an ice bath, ice-cold water was added with caution, and the nonaflate formed extracted with ether. The combined ether solution was washed with water, dried with anhydrous sodium sulfate, and evaporated. The residue was chromatographed over silica gel; elution with petroleum ether (40–60°) gave the nonaflate, which was distilled (see Table).

Preparation of Aryl Nonaflates; General Procedure:

A solution of the phenol (20 mmol) in dry ether was added slowly to sodium hydride (Fluka, 1.2 g, 27 mmol, as 55–60% dispersion in mineral oil, washed with ether as described above) in dry ether (75 ml) at ice-bath temperature with magnetic stirring. Nonafluorobutanesulfonyl fluoride (12 g, 40 mmol) was then added to the sodium salt formed, care being taken that the reaction did not become too exothermic. The reaction mixture was then refluxed for 3 hr, cooled, and water was added with caution. The ether layer was separated and the aqueous layer extracted once with ether. The combined ether layers were washed with 5% sodium hydroxide solution, then with water, and dried with anhydrous sodium sulfate. The solvent was evaporated and the product distilled to give the pure nonaflate (see Table).

Table. Physical and Chemical properties of Nonaflates and Triflates[a]

	Products	Yield (%)	b.p./torr	I.R. ν[cm^{-1}]	^{1}H-N.M.R. δ[ppm]	References
1		15				2
2		55				2
3		45	105–110°/8[c]	1695 ($\nu_{C=C}$)	5.88 (t) (vinyl H)	
4		45				2
5		50	95–100°/8[c]	1670 ($\nu_{C=C}$)	5.55 (m) (vinyl H)	
6		55				4
7		55	60–65°/8[c]	1680 ($\nu_{C=C}$)	5.55 (m) (vinyl H)	
8		91	100–101°/15			2
9		84	110–111°/15	1150 1240 (—O—SO$_2$—) 1445	2.38 (s, CH$_3$) 7.25 (aromatic protons)	
10		88	128–129°/2	1150 1240 (—O—SO$_2$—) 1450	7.5 (m) aromatic Protons	

[a] All new compounds gave satisfactory microanalytical data.
[b] —ONf = —O—SO$_2$—C$_4$F$_9$.
[c] Bath temperature.
[d] —OTf = —O—SO$_2$—CF$_3$.

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