

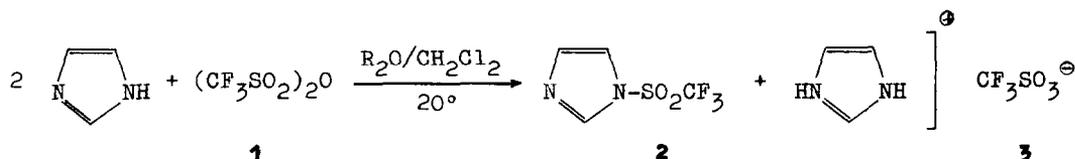
TRIFLUORMETHANESULFONIC IMIDAZOLIDE
A CONVENIENT REAGENT FOR INTRODUCING THE TRIFLATE GROUP *

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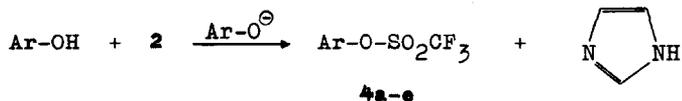
In all investigations of solvolysis reactions, the trifluoromethanesulfonate (triflate) anion has proven the best leaving group. (1-3) While a series of alkyl and alkenyl triflates have already been synthesized, little is known about aryl triflates the solvolysis of which we are investigating. So far, only phenyl and p-methoxy-phenyl trifluoromethanesulfonate have been reported on in the literature. (3) No experimental data are given, though, for the synthesis following the thallium salt method. 2-Naphthyl triflate has been synthesized from β-naphthol with trifluoromethanesulfonic acid anhydride, 1. (4) The instability of the anhydride, however, limits the general applicability of this reaction. We have modified the imidazolide procedure developed by STAAB et al. (5) to afford smooth introduction of the triflate group.



Upon reaction of imidazole with 1 **, trifluoromethanesulfonic imidazolide, 2, is formed in good yield; the acid liberated in the course of the reaction is removed as the imidazolium salt 3.

Fractional distillation affords the imidazolide 2, a liquid of pleasant odour and rather low boiling point (b.p.₁₁ 46°), in pure form; in a closed vessel, it may be stored indefinitely.

With phenols, **2** reacts to give aryl triflates **4**. The yields of pure **4** are given below. Since all preparations were carried out on a small scale, higher yields are to be expected for laboratory scale experiments. Addition of catalytic amounts of phenolate results in improved yields within shorter reaction times.



Ar	yield		
4a phenyl	68 %	b.p. ₆₀	99-100°
4b p-cresyl	76 %	b.p. ₅₀	115°
4c p-chloro-phenyl	71 %	b.p. ₄₅	117°
4d p-nitro-phenyl	73 %	m.p.	53°
4e β-naphthyl	70 %	m.p.	31-32°

Trifluoromethanesulfonic imidazolide, **2**: 33.9 g of **1** in 30 ml abs. ether are added dropwise to a solution of 21.7 g imidazole in 300 ml abs. CH₂Cl₂ (30 min, 20°). The reaction mixture is kept at -20° for 12 hours, the imidazolium salt which precipitates is filtered off, and the filtrate fractionated: 20.4 g **2** (85 %); b.p.₁₁ 46°, m.p. 22°; n_D²⁵ 1.4148.

Phenyl trifluoromethanesulfonate, **4a**: 2.0 g **2**, 0.94 g phenol and 0.03 g phenolate are heated for 2 hours to 80 - 90°. Imidazole which immediately precipitates upon addition of 5 ml abs. ether to the cooled reaction mixture is filtered off, the ethereal solution is washed with 5 ml 2 N NaOH, dried over MgSO₄ and fractionated: 1.54 g **4a** (68 %); b.p.₆₀ 99-100°.

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