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# SYNTHESIS AND SOME REACTIONS OF 1-ADAMANTYL TRIFLUOROMETHANESULFONATE

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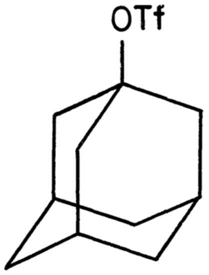
1-Adamantyl trifluoromethanesulfonate (1) has been prepared from 1-bromoadamantane and silver trifluoromethanesulfonate in 2,2-dimethylbutane. The trifluoromethanesulfonate (1) abstracts hydride from pentane or hexane to form adamantane, initiates ring-opening polymerization of tetrahydrofuran, and reacts with alkyllithiums to afford 1-alkyladamantanes.

Various alkyl, alkenyl, and aryl trifluoromethanesulfonates (triflates) have been reported and utilized as the substrates for solvolytic reactions, alkylating reagents, and the catalysts for the ring-opening polymerization of cyclic ethers. However, the tertiary triflates hitherto reported have been limited to relatively unreactive compounds, such as 1-methylcyclopropyl triflates[1)] and the bridgehead triflate esters of norbornane,[2)] nortricyclene,[2a,b,3)] noradamantane,[2b,3)] and tricyclo[2.2.2.0$^{2,6}$]octane[2a)] and their related compounds.[2,3)] Perfluoro-tert-butyl and hexafluorocumyl triflates have also been reported,[4)] but they are unusually unreactive because of the electron-withdrawing effect of the trifluoromethyl substituents.

In the course of our mechanistic studies of solvolysis[5)] we required 1-adamantyl triflate (1) which is expected to be so reactive as to solvolyze in acetic acid with a first-order rate constant of approximately 50 $s^{-1}$ ($t_{1/2}$ 0.014 s) at 25°C,[6)] being more reactive than the above-mentioned bridgehead triflate esters by a factor of at least $10^5$. A literature survey revealed that even 3-cyano-1-adamantyl triflate (2) had been reported to be too unstable for isolation.[7)] The only successful preparation of the triflate esters containing the 1-adamantyl skeleton has been reported for



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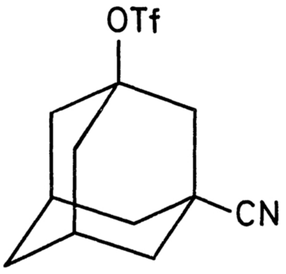

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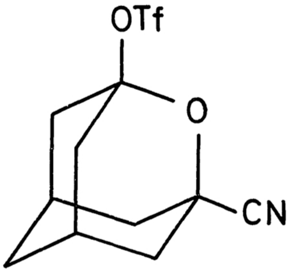

(3)

3-cyano-2-oxa-1-adamantyl triflate (3),[7] which is very stable owing to the negative inductive effect of the oxygen and the cyano substituent.

In this communication we wish to report a facile synthesis of 1-adamantyl triflate (1), along with its behaviors in aliphatic hydrocarbon solvents and tetrahydrofuran, and the reaction with butyllithium.

Synthesis and behavior in hydrocarbon solvents —— Anhydrous silver triflate (1.58 g, 6.14 mmol) and 1-bromoadamantane (1.26 g, 5.85 mmol) were stirred in dry 2,2-dimethylbutane (90 ml) in the dark under nitrogen at 0°C for 3 h. The organic layer was separated and the solvent evaporated at 3 Torr and 0°C to afford colorless crystals of 1 quantitatively: m.p. 25.0 - 25.6°C (uncorrected); $^1$H NMR ($CDCl_3$, 60 MHz) $\delta$ = 1.67 (6H, br.s) and 2.27 ppm (9H, br.s); $^{13}$C NMR ($CDCl_3$, 25 MHz) $\delta$ = 32.5 (d), 35.4 (t), 43.3 (t), 103.7 (s), and 118.3 ppm (q, J = 318 Hz). The use of dry pentane or hexane as solvent also afforded the solutions of 1. However, they turned yellow during evaporation of the solvent and eventually afforded impure 1 contaminated with adamantane. Presumably, 1-adamantyl carbocation generated by the catalysis of trace amounts of trifluoromethanesulfonic acid easily abstracts hydride from these solvents, forming adamantane, olefins, and trifluoromethanesulfonic acid. The acid thus formed appears to accelerate the ionization and hydride abstraction sequence. Possibly, 2,2-dimethylbutane resists the hydride abstraction for steric reasons. If pentane or hexane has to be used as solvent, extreme care should be taken in drying the solvents and the reagents.

Ring-opening polymerization of tetrahydrofuran —— The $S_N2$ type initiation of the ring-opening polymerization of tetrahydrofuran by ethyl triflate has been reported by Saegusa and his coworkers.[8] However, no clear-cut example of the $S_N1$ type initiation has been described in the literature to our knowledge. When a solution of 1 in anhydrous tetrahydrofuran (0.091 M) was heated under nitrogen at 50°C for 71 h, a viscous solution was obtained. Hydrolysis followed by usual workup of the solution afforded tough polymer films ($\bar{M} = 2.0 \times 10^5$ by gpc) in 51% yield. The yield is close to the equilibrium polymerization percent (55%) attained at 50°C.[9] The $^{13}$C NMR spectra of the polymers (in CDCl$_3$) revealed that the adamantyl group is attached as the terminal group.

Reaction with butyllithium —— The direct quarternization of 1-haloadamantanes with alkyl Grignard reagents,[10] trimethylaluminum,[11] trialkynylaluminum,[12] and allyltrimethylsilicon and related organosilicon reagents[13] have been reported. However, no successful reactions by the use of easily available alkyllithiums are found in the literature. We found that the triflate (1) reacts with butyllithium under mild conditions to afford 1-butyladamantane in a good yield. A solution of butyllithium (13.1 mmol) in hexane (8.8 ml) was added to a solution of 1 (0.746 g, 2.62 mmol) in 2,2-dimethylbutane (10 ml) at 0°C and the resulting solution stirred at the same temperature for 1 h. The reaction mixture was worked up in the usual manner to afford a mixture of 1-butyladamantane, adamantane, and 1-adamantanol, as identified by glc. Treatment of the mixture on column chromatography (silica gel) afforded 1-butyladamantane (0.356 g, 71%), adamantane (0.049 g, 14%), and 1-adamantanol (0.009 g, 2%). 1-Butyladamantane was further purified by bulb-to-bulb distillation at 4 Torr with the bath temperature of 80.0 - 83.5°C; $^{13}$C NMR (CDCl$_3$, 25 MHz) $\delta$ = 14.5 (q), 24.0 (t), 25.0 (t), and 44.8 ppm (t) for the butyl group, and 29.1 (d), 32.5 (s), 37.6 (t), and 42.8 ppm (t) for the adamantyl group.

We are now investigating the scopes of the above reactions, and exploring other reactions of 1, such as carboxylation with carbon monoxide, initiation of cationic polymerization, and the uses as a protecting group.

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