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Formation of 3-Methyl-1-adamantyl Trifluoromethanesulfonate in the Reaction of 3,7-Dimethylenebicyclo[3.3.1]nonane with Trifluoromethanesulfonic Acid. Dissociation and Carbocationic Rearrangements*

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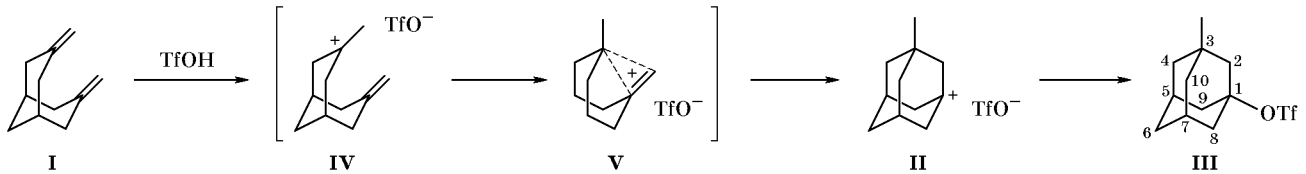
Abstract—According to the ^{1}H NMR data, the reaction of equimolar amounts of 3,7-dimethylenebicyclo-[3.3.1]nonane with trifluoromethanesulfonic acid in CD_2Cl_2 leads to formation of 3-methyl-1-adamantyl trifluoromethanesulfonate. Further addition of trifluoromethanesulfonic acid promotes partial dissociation of 3-methyl-1-adamantyl trifluoromethanesulfonate into 3-methyladamantyl cation and trifluoromethanesulfonate anion, and the cation undergoes fast pericyclic rearrangement involving migration of bridgehead hydrogen atoms to the cationic center.

3,7-Dimethylenebicyclo[3.3.1]nonane (**I**) is known to react with nucleophiles in the presence of acids, yielding addition products, 1-substituted 3-methyltricyclo[3.3.1.1^{3,7}]decanes (1-substituted 3-methyladamantanes) [1]. It is believed that these reactions involve formation of short-lived carbocationic intermediates. Probably, the stability of the latter can be enhanced using superacids as reaction medium and reducing the temperature. For this purpose, we have studied the behavior of diene **I** in trifluoromethanesulfonic acid.

According to the ^{1}H NMR spectra recorded in the temperature range from –90 to –10°C, the reaction of **I** with CF_3SO_3H in CD_2Cl_2–SO_2ClF at –70°C gives rise to an equilibrium mixture of 3-methyl-1-adamantyl cation (**II**) and 3-methyl-1-adamantyl trifluoromethanesulfonate (**III**) which are interconverted at a high rate (on the NMR time scale). The process is also accompanied by pericyclic rearrangement of cation **II**. We failed to detect formation of ion **IV** (or **V**) which should be primary protonation product of **I**. It should be noted that, in keeping with the results of MP2/6-31G* quantum-chemical calculations, minima on the potential energy surface do not correspond to structures **IV** and **V**.

The formation of an equilibrium mixture of cation **II** and ester **III** was confirmed by studying the behavior of the latter in trfluoromethanesulfonic acid.

Scheme 1.



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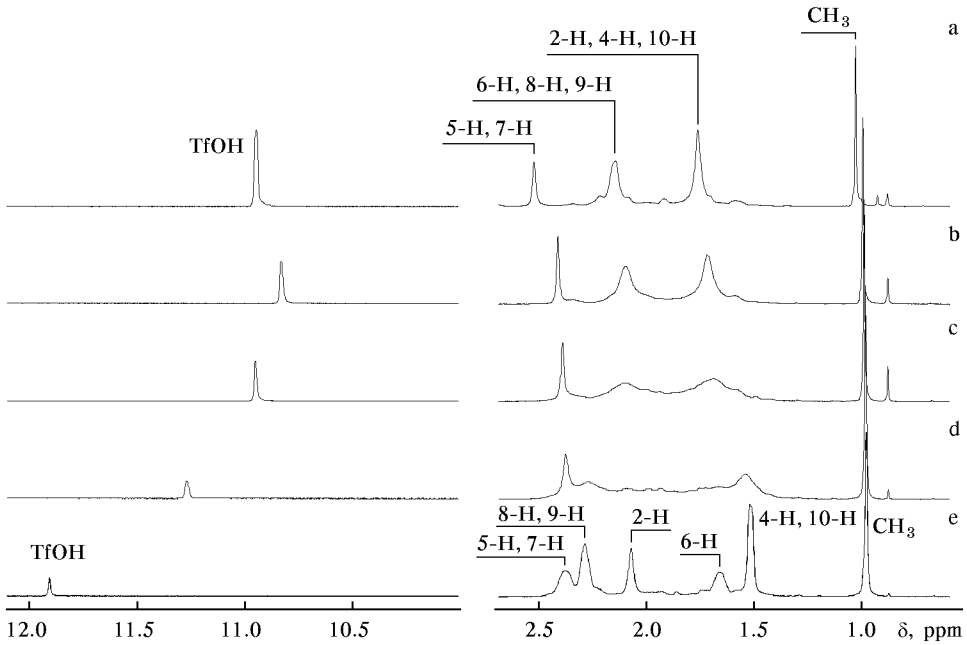


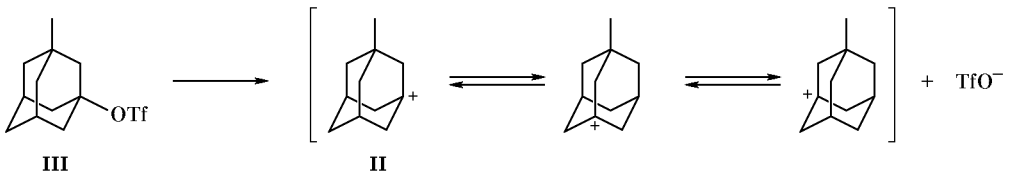
Fig. 1. ^{1}H NMR spectra of 3-methyl-1-adamantyl trifluoromethanesulfonate (**III**) (0.9 mmol in 0.3 ml of CD_2Cl_2) at 20°C after addition of (a) 2.5, (b) 1.1, (c) 0.8, (d) 0.5, and (e) 0.25 mmol of CF_3SO_3H.

We succeeded in preparing a solution of **III** in CD_2Cl_2 by carefully adding a solution of diene **I** in CD_2Cl_2 to a solution of an equimolar amount of trifluoromethanesulfonic acid in SO_2ClF at –95°C and subsequently removing SO_2ClF by distillation (Scheme 1). On adding trifluoromethanesulfonic acid to this solution we observed an exchange process by ^{1}H NMR spectroscopy: the signals from 2-H, 4-H (10-H) and from 6-H, 8-H (9-H) broadened and coalesced in pairs (Fig. 1). Analogous spectra were obtained for solutions of diene **I** in TfOH–SO_2ClF–CD_2Cl_2 and in TfOH containing a small amount of CD_2Cl_2. Presumably, the observed spectral pattern corresponds to an equilibrium mixture of trifluoromethanesulfonate **III** and cation **II** (probably as a mixture with the respective ion pair; cf. [2]) which are rapidly interconverted; also, triply degenerate rearrangement of cation **II** (Scheme 2) is superimposed.

This assumption is confirmed by the existence of linear correlations between the observed averaged chemical shifts of protons and mole fraction of cation **II** in the equilibrium mixture with ester **III** (Fig. 2). Increase in the mole fraction of the cation on raising the concentration of TfOH is likely to result from rise in the solvent polarity. The reverse effect is produced by increase in the ester concentration. These data are consistent with those obtained by Kessler and Feigel [2] while studying dissociation of compounds which are carbocation precursors.

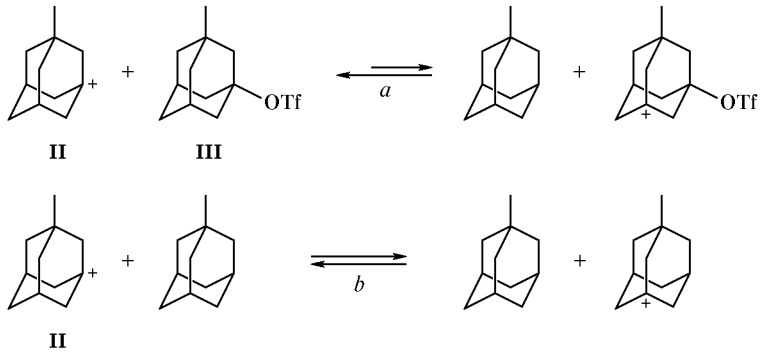
When an equilibrium mixture of trifluoromethanesulfonate **III** and cation **II** was obtained from diene **I** in TfOH–SO_2ClF–CD_2Cl_2 (systems nos. 1–3, see table), broadening of the averaged signals from 6-H, 8-H, 9-H and 2-H, 4-H, 10-H was observed as the temperature decreased. Obviously, this is the result of deceleration of the degenerate rearrangement of cation **II**. It should be noted that the ^{1}H NMR spectra of solutions containing equilibrium mixtures of ester **III** and cation **II** (for compositions of these solutions, see table) displayed signals from 6-H, 8-H, 9-H and 2-H, 4-H, 10-H which were characterized by similar chemical shifts and shapes, their halfwidth being

Scheme 2.



III **II**

Scheme 3.



about 45 Hz for different temperatures (at –75°C for system no. 1 and at –38°C for system no. 2). The fact that the rates of the rearrangement in solutions differing only by quantitative composition are approximately similar at considerably different temperatures indicates intermolecular mechanism of the process, for the rate of intramolecular carbocationic rearrangements is almost insensitive to variation of the medium [4]. The spectra shown in Fig. 1 rule out any mechanism involving proton of trifluoromethanesulfonic acid: The corresponding signal did not broaden throughout the examined range of rates of the rearrangement. The available data are consistent with the mechanisms illustrated by Scheme 3.* A mechanism related to *b* was proposed to interpret the transformation of 1-hydroxyadamantane into 2-hydroxy isomer in concentrated sulfuric acid [5]. It was presumed that hydride ion is abstracted from the adamantane methylene group. In our case, abstraction of hydride ion from methylene group of 1-methyladamantane is also possible. In some cases (systems nos. 1–3, see table), expected broadening of the 5-H (7-H) signal was observed with rise in temperature. Adams *et al.* [5] also presumed deprotonation of adamantyl cation which is accompanied by cleavage of the adamantane ring system. In our case, even if this process does occur, it is slow (otherwise, broadening of the TfOH signal would be observed; cf. Fig. 1).

The comparable thermodynamic stabilities of ester **III** (RX) and the system $\mathbf{II}^+$ TfO^- (R^+ X^-) in strongly polar media (cf. [2]) may be explained in terms of the unique nature of 1-adamantyl cations. Cation **II**, being an aliphatic carbocation which is not stabilized by π-system [6], is likely to be relatively unstable; therefore, the energy of the system R^+ X^- becomes comparable with the energy of RX even in strongly polar medium (TfOH) where the rate of dissociation of RX is high. However, cation **II** is characterized by a high kinetic stability (even at room temperature) which originates from the lack of low-barrier rearrangement pathways. The impossibility for its fast deprotonation (without ring opening) to give the

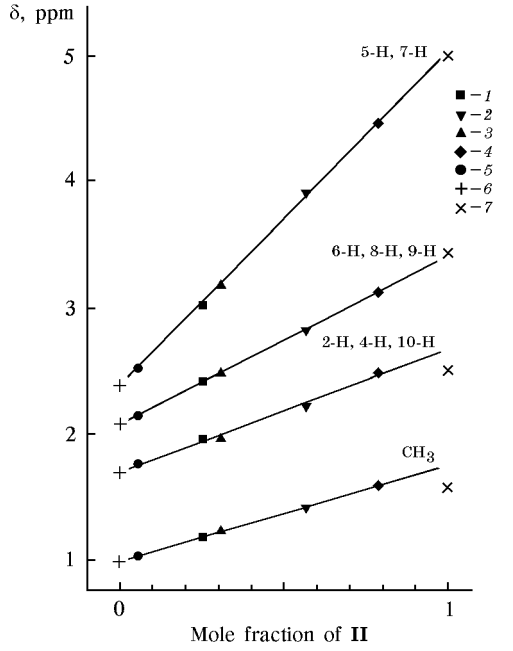


Fig. 2. Averaged chemical shifts of protons corresponding to equilibrium mixture of trifluoromethanesulfonate **III** and cation **II** (see table): (*1*) –28°C; (*2*) –38°C; (*3*) –38°C; (*4*) –28°C; (*5*) spectrum (a) from Fig. 1; (*6*) data for trifluoromethanesulfonate **III**; (*7*) data for cation **II** [3]. The mole fractions γ^i of cation **II** were calculated by the formula $\gamma^i = (\delta^i - \delta^i(\mathbf{III})/[\delta^i(\mathbf{II}) - \delta^i(\mathbf{III})]$, where δ^i is the exchange-averaged chemical shift of the *i*th proton of equilibrium mixture **III**/**II**, and $\delta^i(\mathbf{III})$ and $\delta^i(\mathbf{II})$ are chemical shifts of the corresponding protons in the spectra of ester **III** and cation **II**. $\delta^{6,8,9}(\mathbf{III}) = [2\,\delta^{8,9}(\mathbf{III}) + \delta^6(\mathbf{III})]/3$; likewise, $\delta^{2,4,10}(\mathbf{III})$, $\delta^{6,8,9}(\mathbf{II})$, and $\delta^{2,4,10}(\mathbf{II})$ were determined. The mole fractions given on the *x* axis are averaged values of γ^i, where *i* refers to 6-H, 8-H, 9-H and 5-H, 7-H.

* 1-Methyladamantane, which is necessary for mechanism *b* (Scheme 3), is usually present as an impurity in initial diene **I**.

^{1}H NMR spectra of equilibrium mixtures of cation **II** and ester **III**

System no.	Composition	Temperature, °C	Chemical shifts δ (ppm) and halfwidths[a] (Hz)			
			5-H, 7-H	6-H, 8-H, 9-H	2-H, 4-H, 10-H	CH_3
1	30 mg (0.2 mmol) of **I**,	–93	3.241 (10)	Very broad signals		1.210 (7)
	0.15 ml (1.7 mmol) of TfOH,	–84	3.210 (9)	Very broad signals		1.204 (5)
	0.09 ml of CD_2Cl_2,	–75	3.173 (11)	2.45 (47)	1.95 (43)	1.199 (6)
	0.23 ml of SO_2ClF	–61	3.131 (14)	2.46 (35)	1.97 (29)	1.197 (5)
		–47	3.10 (22)	2.45 (30)	1.97 (23)	1.193 (9)
		–28	3.02 (29)	2.42 (28)	1.957 (17)	1.182 (10)
2	15 mg (0.1 mmol) of **I**,	–75	4.097 (5)	Very broad signals		1.430 (3)
	0.19 ml (2.1 mmol) of TfOH,	–66	4.070 (5)	Very broad signals		1.431 (3)
	0.1 ml of CD_2Cl_2,	–56	4.046 (5)	Very broad signals		1.431 (3)
	0.2 ml of SO_2ClF	–47	4.010 (5)	Very broad signals		1.429 (3)
		–38	3.968 (6)	2.86 (65)	2.22 (50)	1.424 (3)
		–28	3.916 (14)	2.82 (55)	2.22 (45)	1.414 (7)
		–19	3.836 (17)	2.76 (45)	2.20 (35)	1.389 (11)
3	15 mg (0.1 mmol) of **I**,	–93	3.836 (7)	Very broad signals		1.380 (4)
	0.19 ml (2.1 mmol) of TfOH,	–84	3.736 (5)	Very broad signals		1.354 (3)
	0.1 ml of CD_2Cl_2,	–75	3.650 (8)	Very broad signals		1.336 (4)
	0.7 ml of SO_2ClF	–66	3.590 (8)	Very broad signals		1.323 (4)
		–56	3.487 (6)	Very broad signals		1.300 (3)
		–47	3.334 (6)	2.56 (70)	2.04 (65)	1.268 (3)
		–38	3.269 (8)	2.49 (45)	2.01 (45)	1.249 (4)
		–28	3.180 (10)	2.48 (45)	1.96 (32)	1.226 (6)
		–19	3.07 (20)	2.41 (45)	1.95 (30)	1.182 (11)
4	15 mg (0.1 mmol)of **I**,	–38	4.470 (13)	3.12 (20)	2.477 (9)	1.578 (5)
	0.36 ml (4.1 mmol) of TfOH,	–28	4.468 (13)	3.12 (20)	2.484 (9)	1.588 (5)
	0.1 ml of CD_2Cl_2	–19	4.459 (14)	3.11 (19)	2.481 (7)	1.589 (5)

[a] In parentheses.

corresponding olefin excludes its polymerization under the conditions which would ensure comparable stabilities of ions (R^+, X^-) and neutral molecules (RX, olefins).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer using CD_2Cl_2 as solvent and reference (δ 5.33 ppm, δ_C 53.6 ppm). The following reagents and solvents were used: trifluoromethanesulfonic acid of pure grade (from Fluka); SO_2ClF was prepared by the procedure described in [7] and was purified by passing through concentrated sulfuric acid; CD_2Cl_2 (99.5 at % of D) was dried over 4-Å molecular sieves. 3,7-Dimethylenebicyclo[3.3.1]-nonane (**I**) was synthesized by reaction of zinc with 1-bromo-3-bromomethyladamantane in anhydrous dimethylformamide [8] (cf. [9]). All solutions were prepared under dry argon.

Quantum-chemical calculations were performed with the aid of GAMESS program [10].

Solution of 3-methyl-1-adamantyl trifluoromethanesulfonate (III) in CD_2Cl_2. A solution of 0.12 g (0.87 mmol) of diene **I** in 0.3 ml of CD_2Cl_2 was added at –95°C under vigorous stirring to a solution of 0.13 g (0.87 mmol) of trifluoromethanesulfonic acid in 1 ml of SO_2ClF in such a way that drops of the former solution fall directly into the acid solution (to prevent diene polymerization). A light violet solution was thus obtained, which became colorless at –60°C. To remove SO_2ClF, the mixture was stirred at room temperature under a stream of argon until its volume no longer decreased (about 0.5 h). The residue was filtered from a small amount of polymeric products into an NMR ampule and was stored at 0°C. ^{1}H NMR spectrum, δ, ppm (cf. [11]): 0.98 s (3H, 3-CH_3), 1.52 m (4H, 4-H, 10-H), 1.66 m (2H, 6-H), 2.07 s (2H, 2-H), 2.29 m (4H, 8-H, 9-H), 2.38 m (2H, 5-H, 7-H). ^{13}C NMR spectrum, δ_C, ppm (cf. [11]):

30.0 q or d, 33.2 d or q, 35.1 t, 42.9 t, 43.0 t, 50.2 t, 104.7 s, 119.0 q (J_{CF} = 319 Hz).

Equilibrium mixture of cation II and ester III. *a*. Trifluoromethanesulfonic acid was added in portions at –15°C to a solution of ester **III** prepared as described above. After addition of each portion, the mixture was stirred, and its ^{1}H NMR spectra were recorded at room temperature (Fig. 1). Before recording the spectrum next time, the mixture was stored at –15°C. The amount of TfOH (see legend to Fig. 1) was determined from the ^{1}H signal intensity.

b. A solution of diene **I** in CD_2Cl_2 was added in one portion to a solution of TfOH in SO_2ClF at –95°C or to neat TfOH at –50°C, and the mixture was stirred and filtered from polymeric products (10–15%) into an NMR ampule. The amount of diene **I** in the sample was determined from the intensities of signals of cation **II** and ester **III** with respect to the TfOH signal. The amounts of the reactants and the ^{1}H NMR spectra are given in table.

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