Novel Reaction of 2-Aryl-3,3-dimethylbicyclo[2.2.1]heptan-2-yl Cations; *X*-Ray Crystal and Molecular Structure of 11-Fluorosulphonyl-7,8,12-trimethyltetracyclo[7.4.0.0.^{2,7}.0^{4,8}]-trideca-1(9),10,12-triene

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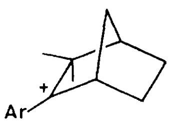
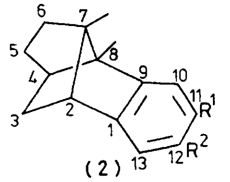
Summary The 2-*p*-tolyl-3,3-dimethylbicyclo[2.2.1]heptan-2-yl cation has been shown to reorganise in fluorosulphonic acid to 11-fluorosulphonyl-7,8,12-trimethyltetracyclo[7.4.0.0^{2,7}.0^{4,8}]trideca-1(9),10,12-triene (**2**) the *X*-ray structure of which is reported; in perchloric acid 2-aryl-3,3-dimethylbicyclo[2.2.1]heptan-2-ols give substituted 7,8-dimethyltetracyclo[7.4.0.0^{2,7}.0^{4,8}]trideca-1(9),10,12-trienes which on reaction with fluorosulphonic acid are converted into fluorosulphonyl derivatives.

During our investigations[1] of bicyclic carbocations we prepared several 2-aryl-3,3-dimethylbicyclo[2.2.1]heptan-2-yl cations (**1**) by reaction of 2-aryl-3,3-dimethylbicyclo-[2.2.1]heptan-2-ols with fluorosulphonic acid. The stability of the cations was dependent on the aryl group; the phenyl cation (**1a**) was stable below *ca.* −15 °C while the *p*-tolyl cation (**1b**) was stable below +10 °C. Above these temperatures we observed an unexpected molecular reorganisation to give neutral species which were isolated. The *p*-tolyl cation (**1b**) gave in near quantitative yield a single product (m.p. 95—96 °C) identified as (**2b**) from its mass spectrum, n.m.r. spectra, and analytical data; the structure was confirmed by *X*-ray analysis.



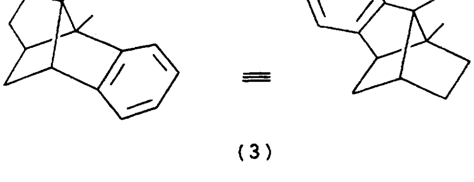
(1)

a; Ar = Ph
b; Ar = *p*-MeC$_6$H$_4$
c; Ar = *m*-ClC$_6$H$_4$



(2)

a; R^1,R^2= H,SO$_2$F
b; R^1 = SO$_2$F, R^2=Me
c; R^1 = Cl,R^2= SO$_2$F



(3)

Crystal data: $C_{16}H_{19}FO_2S$, monoclinic, space group $P2_1/c$, $a = 6{\cdot}875(6)$, $b = 19{\cdot}948(3)$, $c = 11{\cdot}861(9)$ Å, $\beta = 151{\cdot}7(1)°$, $U = 1432$ Å^3, $Z = 4$, $D_m = 1{\cdot}36$, $D_c = 1{\cdot}37$ g cm^{-3}. Intensity data ($0° \leqslant \theta \leqslant 24°$) were recorded on a Hilger-Watts four-circle automatic diffractometer using Zr-filtered Mo-K_α *X*-radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 2{\cdot}37$ cm^{-1}. The structure was solved by direct methods using 1119 unique intensities [$I \geqslant 3{\cdot}0\sigma(I)$]. Least-squares refinements for all non-hydrogen atoms converged with an R value of 0·087 (F, O, and S atoms anisotropic; C atoms isotropic).

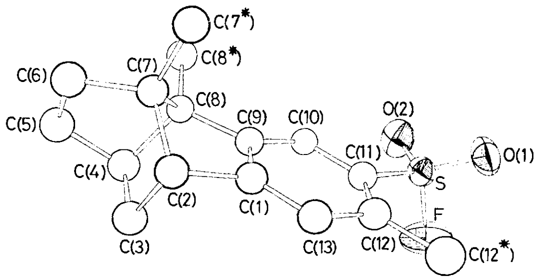


Figure. The molecular structure of (**2b**).

The bond lengths do not deviate significantly from the expected values; for the fluorosulphonyl group C(11)–S = 1·76(1) Å, S–O = 1·399(9) and 1·412(8) Å, S–F = 1·533(7) Å.

The C(2)–C(7)–C(8) angle is 94·2(8)° and the C(4)–C(8)–C(7) angle is 92·8(7)°.† The structure is shown in the Figure.

Analogous tetracyclic compounds were obtained from other 2-aryl-3,3-dimethylbicyclo[2.2.1]heptan-2-yl cations. The cation (**1a**) gave a mixture of two isomers which differ in the position of substitution of the fluorosulphonyl group in the aromatic ring, while (**1c**) afforded predominantly (**2c**).

The novel geometric features of these tetracyclic compounds[2] (**2**) which may be regarded as a norbornyl framework superimposed on a benzonorbornyl framework prompted us to prepare compound (**3**) by reaction of 2-phenyl-3,3-dimethylbicyclo[2.2.1]heptan-2-ol with concentrated perchloric acid at room temperature. Reaction of 2-*p*-tolyl-3,3-dimethylbicyclo[2.2.1]heptan-2-ol under similar conditions gave (**4**) which on reaction with fluorosulphonic acid was converted into (**2b**). We envisage that reorganisation of the *p*-tolyl cation (**1b**) occurs as shown in the Scheme with fluorosulphonation occurring at the less hindered but activated C(11) carbon atom.

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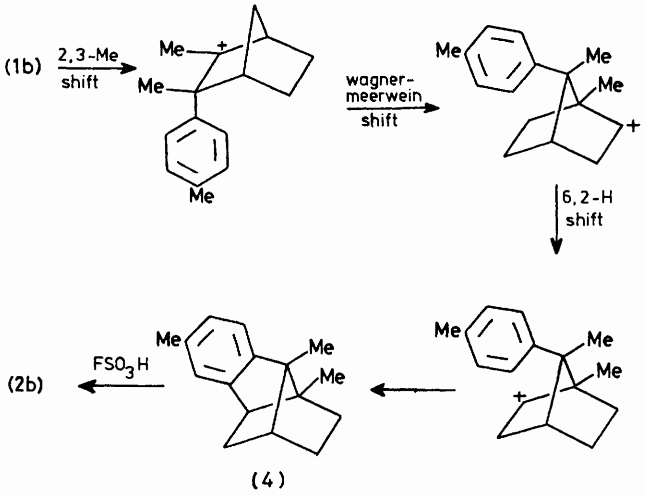

SCHEME

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] J. M. Coxon, A. J. Jones, C. P. Beeman, M. U. Hasan, and I. D. Rae, *Tetrahedron Letters*, 1975, 577; J. M. Coxon, P. J. Steel, J. M. Coddingron, I. D. Rae, and A. J. Jones, *Austral. J. Chem.*, 1977, in the press.
[2] R. E. Leone and P. von R. Schleyer, *Angew. Chem. Internat. Edn.*, 1970, **9**, 860.