

SHORT
COMMUNICATIONS

Reaction of [Fluoro(trifluoromethylsulfonyloxy)iodo]benzene
with Dimethyl *exo*-3,4-Epoxytricyclo[4.2.2.0^{2,5}]deca-7,9-diene-
9,10-dicarboxylate

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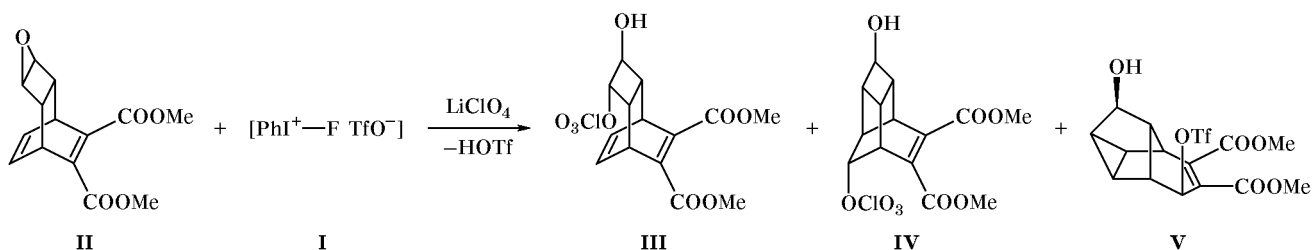
We previously showed that hypervalent iodine compounds, specifically [fluoro(trifluoromethylsulfonyloxy)iodo]benzene (**I**), react with alkenes to give bis-sulfonates and fluorosulfonates [1–3]. In continuation of our studies on reactions of compound **I** with polycyclic hydrocarbons [3] we intended to examine its reaction with polycyclic epoxy derivatives. As substrate we selected dimethyl *exo*-3,4-epoxytricyclo[4.2.2.0^{2,5}]deca-7,9-diene-9,10-dicarboxylate (**II**). We have found that polycyclic epoxide **II** reacts with compound **I** in the presence of lithium perchlorate at a molar ratio of 1:2:8 to afford a mixture of products. By column chromatography on silica gel we isolated three main products **III–V** at a ratio of ~1:2.5:4 in an overall yield of 40% (Scheme 1). According to the TLC data, the mixture also contained a number of by-products, including perchlorates and trifluoromethanesulfonates which we failed to isolate in the pure state.

The structure of compounds **III–V** was established on the basis of the ¹H NMR spectra which were in full

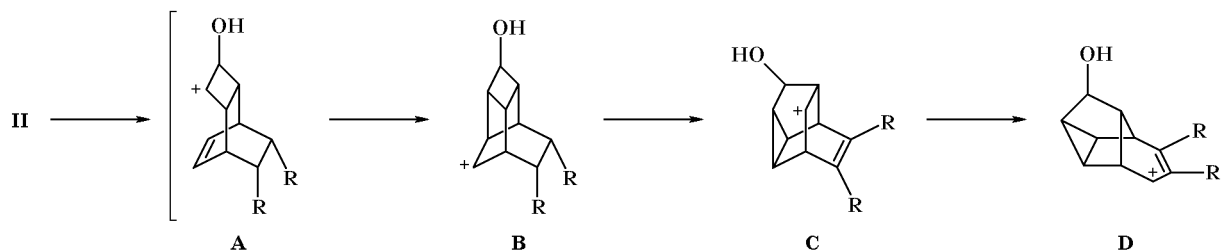
agreement with the spectral data of previously synthesized structurally related compounds [4, 5]. The structure of **III–V** suggests initial formation of cation **A** which reacts with perchlorate ion to give compound **III**. Cationoid rearrangement of cation **A** to **B** with subsequent addition of ClO₄⁻ ion leads to cross-structure **IV**. Compound **V** is formed as a result of more profound intramolecular rearrangements. The formation of cation **D** is preceded by transannular cyclization to cation **C** and two successive 1,2-shifts. The appearance of compound **V** seems surprising, for it contains a cyclopropane ring and hence should be more strained. However, as shown previously, compound **V** is much less strained than, e.g., cross-structure **IV** [4]. Apparently, this factor may be regarded as driving force of intramolecular rearrangements preceding formation of **V**.

Thus the formation of covalent perchlorates and trifluoromethanesulfonates indicates that nucleofugic perchlorate and trifluoromethylsulfonate ions exhibit nucleophilic properties in one more type of reactions,

Scheme 1.



Scheme 2.



namely reactions of epoxy derivatives with electrophilic hypervalent iodine compounds.

Dimethyl *trans-exo*-3-hydroxy-*endo*-4-perchloryloxytricyclo[4.2.2.0^{2,5}]deca-7,9-diene-9,10-dicarboxylate (III). Oily substance, R_f 0.23 (ethyl acetate–hexane, 1:2). IR spectrum (CCl_4), ν , cm^{-1} : 3380 (OH); 1740 (C=O); 1650, 1260, 1230 (OCIO_3). ^1H NMR spectrum (CDCl_3), δ , ppm: 6.00 m and 5.64 m (2H, CH=CH), 4.24 m (2H, 1-H, 6-H), 3.84 s and 3.80 s (6H, $2\text{CO}_2\text{CH}_3$), 3.60 m (2H, 3-H, 4-H), 2.60 m (2H, 2-H, 5-H), 2.10 s (1H, OH).

Dimethyl *exo*-9-hydroxy-*endo*-6-perchloryloxy-tetracyclo[6.1.1.0^{2,7}.0^{5,10}]dec-3-ene-3,4-dicarboxylate (IV). mp 92–94°C (decomp.; from methylene chloride–hexane, 1:1). R_f 0.50 (ethyl acetate–hexane, 1:2). IR spectrum (CCl_4), ν , cm^{-1} : 3400 (OH); 1745 (C=O); 1640, 1260, 1235 (OCIO_3). ^1H NMR spectrum (CDCl_3), δ , ppm: 4.95 d (1H, CHOCIO_3 , $J = 6$ Hz), 4.10 s (1H, CHOH), 3.85 s and 3.76 s (6H, $2\text{CO}_2\text{CH}_3$), 3.46–2.40 m (6H, H_{ring}), 2.30 s (1H, OH).

Dimethyl 9-hydroxy-4-trifluoromethylsulfonyloxytetracyclo[5.3.0.0^{2,10}.0^{3,8}]dec-5-ene-5,6-dicarboxylate (V). Oily substance, R_f 0.12 (ethyl acetate–hexane, 1:2). IR spectrum (CCl_4), ν , cm^{-1} : 3400

(OH); 1665, 1610 (C=C). ^1H NMR spectrum (CDCl_3), δ , ppm: 5.74 m (1H, 10-H), 4.84 m (1H, 5-H), 3.81 s and 3.74 s (6H, $2\text{CO}_2\text{CH}_3$), 2.66 m (2H, H_{ring}), 2.02 s (1H, H_{ring}), 1.80–1.20 m (3H, H_{ring}). Found, %: C 43.17; H 3.31. $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_8\text{S}$. Calculated, %: C 43.69; H 3.64.

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