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Radical fluoroalkylation of [1.1.1]propellane

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Abstract

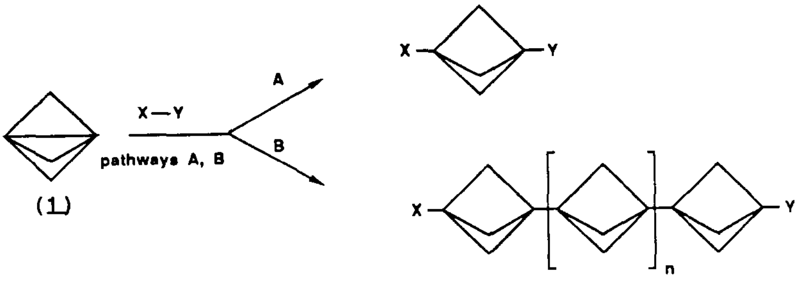
UV irradiation-initiated addition of CF_2Br_2 (**2**) and $BrCF_2CF_2Br$ (**3**) to propellane (**1**) has been found to occur giving 1,3-disubstituted bicyclo[1.1.1]pentanes (**4**) and (**6**), and 'staffanes' (**5**) and (**7**). In the case of reaction with $BrCF_2CF_2Br$, the product (**8**) was also isolated. The relative stability of fluorinated radicals and their influence on product formation are discussed.

Introduction

The generation of perfluoroalkyl radicals via the UV irradiation of iodo- or bromo-perfluoroalkanes is an extremely useful method for the incorporation of these fragments into olefinic, aromatic heteroaromatic compounds [1]. Recently, it was shown that [1.1.1]propellane (**1**) undergoes facile radical additions across the unusual central C–C bond to give 1,3-disubstituted bicyclopentanes (Scheme 1, pathway A) [2–6]. However, if the intermediate radicals is relatively unstable the formation of 'staffanes'' (Scheme 1, pathway B) [6, 7] was observed.

Experimental

Propellane (**1**) was obtained by the method of Semmler *et al.* [8].



Scheme 1.

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Reaction of propellane (1) with dibromodifluoromethane (2)

A solution of propellane (**1**) (1.32 g) and dibromodifluoromethane (**2**) (2.1 g) in pentane (150 ml) was irradiated for 1 h by UV light. The pentane was evaporated and the residue distilled to give compound **4**. The residue was also chromatographed on silica gel and eluted with hexane to yield compound **5**. Compound **4**: 2.24 g, 85% yield. ^{1}H NMR (CCl_4): δ 2.40 (s) ppm. ^{19}F NMR (CCl_4): δ -51.32 ppm. Analysis: Found: C, 26.3; H, 2.5%. $C_6H_6Br_2F_2$ requires: C, 26.1; H, 2.2%. Compound **5**: 0.33 g, 10% yield, m.p., 112 °C. ^{1}H NMR (CCl_4): δ 1.90 (s), 2.20 (s) ppm. ^{19}F NMR (CCl_4): δ -53.12 ppm. Analysis: Found: C, 39.0; H, 3.71%. $C_{11}H_{12}Br_2F_2$ requires: C, 38.6; H, 3.51%.

Reaction of propellane (1) with 1,2-dibromotetrafluoroethane (3)

A solution of propellane (**1**) (0.99 g) and 1,2-dibromotetrafluoroethane (**3**) (3.9 g) in pentane (100 ml) was irradiated for 2 h by UV light. The pentane was carefully evaporated and the residue distilled to give compound **6** with a b.p. 65 °C/14 mmHg and a mixture of compounds **5** and **6** with a b.p. 130 °C/14 mmHg. Their ratio (2:1) was determined by GLC methods. Compound **6**: 2.49 g, 40% yield. ^{1}H NMR (CCl_4): δ 2.50 (s) ppm. ^{19}F NMR (CCl_4): δ -111.42 ($C-CF_2-$), -64.45 ($-CF_2Br$) ppm. Analysis: Found: C, 25.2; H, 1.8%. $C_7H_6Br_2F_4$ requires: C, 25.7; H, 1.8%. Compound **7**: ^{1}H NMR ($CDCl_3$): δ 1.93 (s), 2.17 (s) ppm. ^{19}F NMR ($CDCl_3$): δ -113.83 ($C-CF_2$), -64.09 (CF_2Br) ppm. GCMS (70 eV) *m/z*: 313, 311 ($M-Br$), 272, 270 ($M-Br-C_3H_5$), 213, 211 ($M-CF_2CF_2Br$), 182 ($M-Br-CF_2Br$), 118, 91, 65. Compound **8**: ^{1}H NMR ($CDCl_3$): δ 2.43 (s) ppm. ^{19}F NMR ($CDCl_3$): δ -113.81 ppm. GCMS (70 eV) *m/z*: 232 ($M-2Br$), 212 ($M-2Br-HF$), 192 ($M-2Br-2HF$), 115 ($M-2Br-C_5H_6CF_2$), 39. Analysis of a mixture of compounds **7** and **8**: Found: C, 36.8; H, 3.1%. $C_{12}H_{12}Br_2F_4$ requires: C, 36.7; H, 3.1 %.

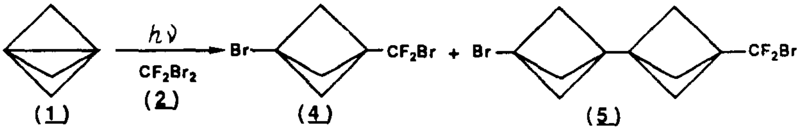
Results and discussion

In the course of our systematic studies of propellane (**1**) [9–13], we have studied its reaction with fluoroalkyl radicals to obtain the first examples of fluoroalkyl derivatives of bicyclo[1.1.1]pentane.

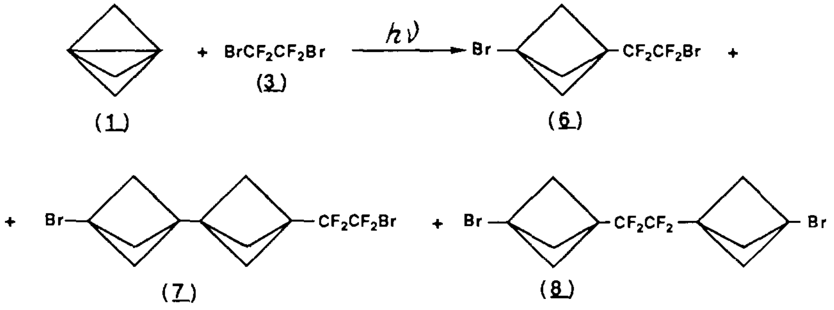
We have studied the photochemical reactions of propellane (**1**) with CF_2Br_2 (**2**) and CF_2BrCF_2Br (**3**). The processes were performed employing UV irradiation of pentane solutions of these reagents. In the case of bromide **2**, two compounds, viz. **4** and **5**, were obtained in the ratio 17:2 (total yield, 95%) (see Scheme 2).

Dibromide **3** reacted with propellane (**1**) to give three products, viz. **6**, **7** and **8**, in the ratio 11:2:1 (total yield 80%) (Scheme 3).

In this regard it is important to remember that the addition of CBr_4 to propellane (**1**) gave derivatives of bicyclo[1.1.1]pentane exclusively without the formation of staffane derivatives. A comparison with the present data shows that *a decrease* in the stability of the transient radical $\cdot CF_2Br$ versus



Scheme 2.



Scheme 3.

$\cdot CBr_3$ leads to the formation of the staffane **5**. A larger decrease in the relative stability to $\cdot CF_2BrCF_2$ leads to even larger content of staffane **7**. In general, the competition between the two pathways A and B (Scheme 1) should be dependent on (i) the stability of the terminating radical and (ii) the energy required for radical abstraction in the chain propagation step. This study experimentally supports the first statement.

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