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REARRANGEMENT REACTIONS OF 1,2-DIMETHYL- AND 1,3-DIMETHYL-1-CYCLOBUTYL CATIONS

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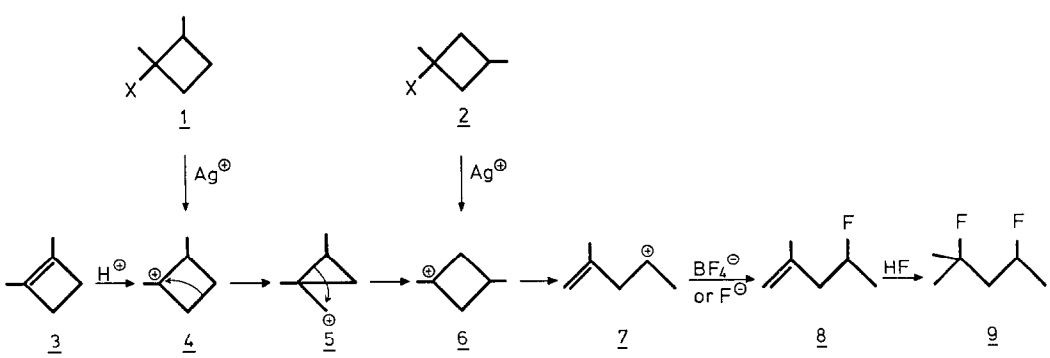
Abstract: Reactions of $AgBF_4$ with 1-bromo (1a)- and 1-chloro-1,2-dimethylcyclobutane (1b) as well as 1-bromo (2a)- and 1-chloro-1,3-dimethylcyclobutane (2b) gave 4-fluoro-2-methyl-1-pentene (8) as the major product. Reaction of 1,2-dimethyl-1-cyclobutene (3) with excess HF yielded 2,4-difluoro-2-methylpentane (9).

In connection with a study of ^1H- and ^{13}C-NMR-spectra of a series of methyl substituted halocyclobutanes (1) we needed samples of the stereoisomers of 1c and 2c. In line with a method which we have recently found (2), we have tried to prepare these by reactions of $AgBF_4$ with 1a or 1b and 2a or 2b, respectively. As expected, addition of 0.15 mmol of $AgBF_4$ to a stirred solution of 0.10 mmol of the respective substrate in 1 ml of ether at 0°C resulted in the spontaneous precipitation of silver halide. G.l.c.-analyses of the reaction mixtures (glass column, 0.3 x 300 cm, 5 % Carbowax 20 M on Chromosorb G; 60°C) showed, however, in each case only the peaks of 8 (85-90 %) and of 9 (10-15 %). An attempt at synthesizing 1c by the addition of HF to 3 was also unsuccessful: 6.5 g of a 7:3-mixture of HF-pyridine was added to a stirred solution of 0.8 g (9.8 mmol) of 3 in 5 ml of trichloromethane at 0°C. After 6 h the mixture was poured into ice water, the organic layer was washed with aqueous sodium bicarbonate and water and dried over sodium sulfate. ^1H-NMR-analysis showed 9 as the only detectable product. By contrast, free radical reduction of 180 mg of trans-1-bromo-2-fluoro-1,2-dimethylcyclobutane (2) with 508 mg of tributyltin hydride at room temperature afforded 40 mg of a mixture of cis- and trans-1c (ratio 2:1, respectively).



a : X = Br ; b : X = Cl ; c : X = F

It is obvious from the above results, that the initial cyclobutyl cations 4 and 6 are not trapped by fluoride ions to give 1c and 2c, respectively. Instead, they undergo rearrangements to form the acyclic cation 7, from which both 8 and 9 are derived. While the conversion of 6 into 7 is readily rationalized by cleavage of the 2,3-bond, the conversion of 4 into 7 requires formally a 1,2-methyl shift. This could be achieved by ring contraction of 4 to 5 and subsequent ring expansion of 5 to 6. It is noteworthy, that the reaction of $AgBF_4$ with 1,2-dibromo-1,2-dimethylcyclobutane also resulted in partial ring contraction, albeit by rupture of the ring in a different position (2,3). By contrast, both the reaction of $AgBF_4$ with 1,3-dibromo-1,3-dimethylcyclobutane and the addition of HBr or of HCl to 3 occurred without ring cleavage and afforded 1,3-difluoro-1,3-dimethylcyclobutane and 1,2-dimethyl-1-halocyclobutanes, respectively. These findings show, that, as previously reported for other substituted cyclobutyl cations (4), 1,2- and 1,3-dimethylcyclobutyl cations can react via several paths which may be determined by subtle differences in the nature and position of substituents and/or in the reaction medium.

Compounds 8 and 9 have been isolated by preparative g.l.c. (glass column, 0.7 x 350 cm, 10 % Carbowax 20 M on Chromosorb G; 60°C) and the mixture of cis- and trans-1c by distillation at room temperature and 20 Torr. They were colorless liquids, each, and have been characterized by the following data: 1c: ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ 0.97 (broad d, 7.0 Hz; 3H), 1.31 (dd, 22.9 and 0.9 Hz; 3H) for cis-1c and δ 1.10 (dd, 7.1 and 1.6 Hz; 3H), 1.41 (dd, 22.2 and 0.7 Hz; 3H) for trans-1c. - ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ -120.1 (cis-1c) and -147.9 (trans-1c; m, each). - GC/MS (column and conditions as above): m/e = 102 M^+, 87 $(M - CH_3)^+$, 74 $(M - C_2H_4)^+$, 67 $(M - CH_4F)^+$, 60 $(M - C_3H_6)^+$, 42 $(M - C_3H_5F)^+$ for either cis- or trans-1c.- t_R = 3.0 min (cis-1c), 2.8 min (trans-1c). 8: ^{1}H-NMR (60 MHz, C_6D_6, TMS) δ 1.06 (dd, 23.2 and 6.1 Hz; 3H), 1.58 (broad s; 3H), 2.02 (dd, 25.2 and 5.6 Hz; 1H), 2.21 (dd, 18.3 and 7.1 Hz; 1H), 4.55 (dm, 48.5 Hz; 1H), 4.76 (broad s; 2H). - ^{13}C-NMR (broad band decoupled, $CDCl_3$, TMS) δ 20.8 (d, 22.9 Hz), 22.7 (s), 45.2 (d, 21.1 Hz), 89.4 (d, 167.0 Hz), 113.2 (s) 141.7 (d, 4.6 Hz). - ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ -170.1 (dd pent., 48.0, 24.0 and 18.3 Hz). - IR ($CDCl_3$) C=C at 1650 cm^{-1}. - MS: m/e = 102 (74 %) M^+, 87 (48 %) $(M - CH_3)^+$, 82 (10 %) $(M - HF)^+$, 56 (100 %) $(C_4H_8)^+$, 55 (93 %) $(C_4H_7)^+$. 9: ^{1}H-NMR (300 MHz, $CDCl_3$, TMS) δ 1.36 (dd, 23.8 and 6.3 Hz; 3H), 1.40 (d, 21.7 Hz; 3H), 1.43 (d, 21.7 Hz; 3H), 1.74 - 2.10 (m; 2H), 4.92 (dm, 49.2 Hz; 1H). - ^{13}C-NMR (broad band decoupled, $CDCl_3$, TMS) δ 22.0 (dd, 22.9 and 0.9 Hz), 25.9 (dd, 24.8 and 2.3 Hz), 28.3 (dd, 22.9 and 1.8 Hz), 48.1 (dd, 22.9 and 20.2 Hz), 87.3 (dd, 165.2 and 6.4 Hz), 94.3 (dd, 166.1 and 0.9 Hz). In the coupled spectrum the following ^{1}J(CH)-couplings were observed: δ 22.0, 25.9, 28.3 (q, 127 Hz, each), 48.1 (t, 125 Hz), 87.3 (d, 150 Hz). - ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ -136.7 (m), -171.3 (m). - MS: m/e = 122 (2 %) M^+, 107 (4 %) $(M - CH_3)^+$, 102 (5 %) $(M - HF)^+$, 87 (38 %) $(M - CH_4F)^+$, 61 (100 %) $M/2^+$.

References

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(3) In this case, products having a cyclopropane structure could be isolated.

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