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THE PENTACYCLOPROPYLETHYL CARBOCATION

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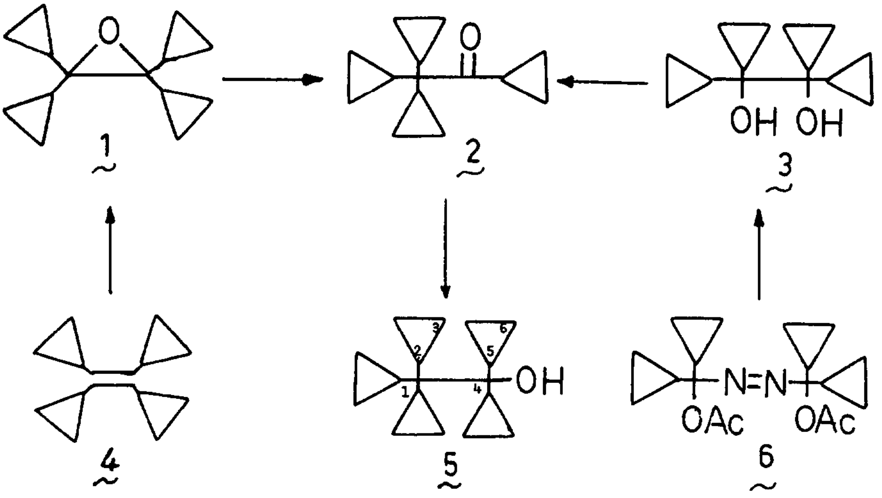
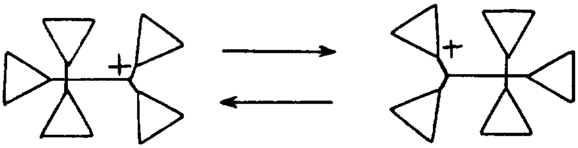
Abstract: The synthesis of pentacyclopropylethanol and the nmr of the corresponding cation is described.

In the course of our studies on cyclopropyl substituted systems we have successfully prepared pentacyclopropylethanol (PCPE, 5) from which we have generated the corresponding carbocation. The synthetic sequence is described below:



The synthesis of 1,1,2,2-tetracyclopropylethylene glycol (3) and tetracyclopropylethylene (4) have been previously reported.[1] However, the improved method using $TiCl_4$-Mg(Hg)[2] gave more workable quantities; for example at 0°C for 4h in THF and chromatography on silica gel gave 24% of 3 and 19% of 4. Oxidation of 1,1,2,2-tetracyclopropylethylene with m-chloroperbenzoic acid in CH_2Cl_2 with suspended sodium bicarbonate for 10h at 25°C gave epoxide 1 in 42% yield; ^{1}H nmr ($CDCl_3$) δ 0.80-1.45(m,4H), 0.25-0.70(m,16H). The acid catalyzed Wagner-Meerwein rearrangement of epoxide 1 or diol 3 in 100% formic acid (0°,4h) gave cyclopropyl pinacolone 2 in 60% yield: ^{1}H nmr ($CDCl_3$) δ 2.22-2.65 (m,1H), 0.75-.97(m,4H), 0.60-0.75(m,3H) and 0.20-0.60(m, 12H); ir(neat) 3085 and 1695 cm^{-1}. The final addition of cyclopropyl lithium gave 28% of pentacyclopropylethanol (5) after distillation (bp 136-140°/1mm) and recrystallization from pentane (mp 33-34°C): ^{1}H nmr ($CDCl_3$) δ 1.89 (s,1H), 1.21-1.53 (n,20H); ^{13}C nmr ($CDCl_3$) δ 0.0 (C-3), 1.5 (C-6), 10.5 (C-2), 15.0 (C-5), 43.0 (C-1), and 77.1 (C-4).

The ^{1}H nmr of the 2,3,3-trimethyl-2-butyl[3] and the related pentaphenylethyl[4] carbocations have been examined by Olah and co-workers and, at low temperature, they display five equivalent methyl and phenyl groups respectively. Both were regarded as being classical in nature with rapid 1,2 alkyl and aryl shifts accounting for the substituent equivalency. More recently the total ^{13}C chemical shift difference between cation and corresponding hydrocarbon has been used by Schleyer, Lenoir and Olah[5] to substantiate this classical nature. We find a similar situation for the pentacyclopropylethyl cation. For example, the ^{13}C nmr of PCPE in FSO_3H-SbF_5/FSO_2Cl (1:1) at -85°C (proton decoupled) shows three signals at δ 125.6, 81.7 and 13.1 ppm thus indicating that each of the quaternary, tertiary and secondary carbon atoms are equivalent. Likewise the ^{1}H nmr shows all α-protons as a broad absorption at δ 3.4 and all β-protons at 0.3 ppm. We were not able to compare the total chemical shift difference between hydrocarbon and cation as the attempted reduction of PCPE gave mostly ring opened products. However, the cation - PCPE difference of 601 ppm can be corrected to ~650 ± 2.0 ppm using a number of values reported by Stothers for alcohol-hydrocarbon differences.[6] This falls well within the range for classical ions and would on this basis alone favor rapidly equilibrating classical ions.



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