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A NOVEL CARBONIUM ION REARRANGEMENT DURING CERIC ION OXIDATION OF A STRAINED POLYCYCLIC SYSTEM

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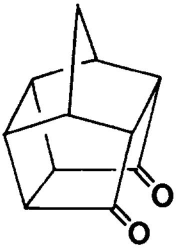
Several examples of oxidation of carbonyl compounds with ceric ion have been recorded in literature[1]. In an earlier communication, we had described a few cases[2] of efficient Baeyer-Villiger oxidation of strained polycyclic ketones with ceric ion. Therein, we had reported that Ce^{+4} oxidation of the pentacyclic dione 1 furnished a keto-lactone in high yield to which structure 2 was assigned on the basis of limited spectroscopic data available at that time. However, a recheck on the structure of 2 with the aid of ^{13}C nmr spectroscopy, in the light of our recent delineation of a new[3] rearrangement sequence from 1, compels us to reformulate the Ce^{+4} oxidation product of 1 as a novel tetracarbocycle 3.

1



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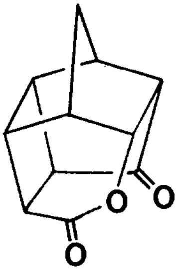
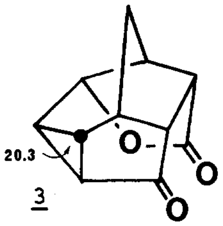


The ^{13}C nmr spectrum[4] of 3 exhibited signals due to 11 carbons at 211.2 (s), 175.2 (s), 76.1 (d), 49.8 (d), 47.1 (d), 44.2 (d), 36.6 (d), 34.6 (d), 32.1 (d), 31.6 (t) and 20.3 ppm (d). The highly shielded carbon signal at 20.3 ppm appeared characteristic of a cyclopropyl carbon (marked in 3) and this contention was strengthened by the presence of a similarly shielded carbon of the cyclopropane



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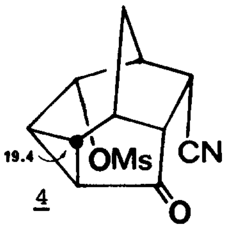
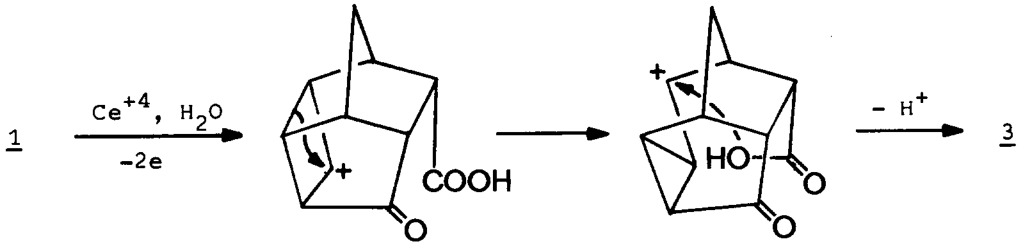


4

in the ^{13}C nmr spectrum of 4 at 19.4 ppm (d)[3]. The presence of the cyclopropane was also indicated by the signals of four shielded protons (1.81 - 2.06 ppm, m, methylene and cyclopropane CH′s) in the 90 MHz ^1H nmr spectrum of 3. The UV spectrum of 3 (λ_{max}^{MeCN} = 199 nm, ε = 3064; cf. 4: λ_{max}^{EtOH} = 201 nm, ε = 3240) further revealed the presence of a cyclopropane ring in conjugation with a carbonyl group. Finally, the ir bands at 1725 cm^{-1} (cyclopropyl conjugated 5-membered carbonyl) and 1780 cm^{-1} (strained δ-lactone) were fully compatible with 3.

The formation of the novel lactone 3 from 1 involves a cyclobutyl ⟶ cyclopropylcarbinyl-type carbonium ion rearrangement as depicted below:



References and Notes:

1. T.L. Ho, Synthesis,347 (1973).
2. G. Mehta, P.N. Pandey and T.L. Ho, J. Org. Chem., 41, 531 (1976).
3. G. Mehta, P. Ghosh, B. Chaudhury, V.K. Singh, R. Usha, K.I. Varughese and K. Venkatesan, Tetrahedron Lett., 4109 (1977).
4. The ^{13}C nmr spectra of 3 and 4 were recorded in $CDCl_3$ and DMSO-d_6, respectively, using a Bruker WH-90 spectrometer operating at 22.64 MHz. Chemical shifts are reported with respect to internal TMS and off-resonance multiplicities are indicated in parentheses.

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