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HEXAMETHOXYCYCLOPROPANE

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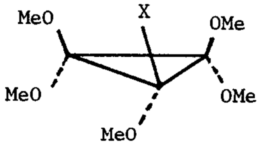
Summary. Hexamethoxycyclopropane, obtained by reaction of lithiopentamethoxycyclopropane with dimethyl peroxide, decomposes at 200°C to dimethoxycarbene and tetramethoxyethylene.

The efficient thermolytic cycloreversion of hexafluorocyclopropane to difluorocarbene and tetrafluoroethylene[1-3] led us to inquire whether the analogously persubstituted hexamethoxycyclopropane (1) would extrude dimethoxycarbene upon pyrolysis. We now describe the first preparation of cyclopropane 1, the tris ketal of cyclopropane trione, as well as pyrolysis experiments which support retrocarbene addition as its principal mode of thermal decomposition.



1, X = OMe 2, X = Cl 3, X = Li
4, X = H 5, X = OH

Addition of methoxychlorocarbene,[4] generated thermally (25°C/16 h) from methoxychlorodiazirine,[5] to tetramethoxyethylene,[6] afforded 24% of chloropentamethoxycyclopropane 2.[7] The latter (6 mmol in 20 ml of ether) was added to 24 mmol of t-butyllithium in 50 ml of ether at <-55°C to generate lithiopentamethoxycyclopropane 3,[8] which was quenched after 15 min by addition of 40 mmol of dimethyl peroxide[9] in 20 ml of ether (-60°C), followed by stirring at ambient temperature for 16 h. Crude product was isolated by filtration, evaporation of ether, and Kugelrohr distillation

(50°C/0.1 mm-Hg), whence gas chromatography (10% SE-30, 140°C) afforded 31% of pentamethoxycyclopropane 4, accompanied by 7% of the desired hexamethoxy derivative 1.

The yield of 1 is low, but we note that the reaction of 3 with methyl *t*-butyl peroxide failed to afford any 1.[8] Similarly, treatment of 3 with oxygen, followed by hydrolysis, did not give hemiketal 5.[8] Interestingly, the pentamethoxycyclopropane 4, which is the major product of the reaction that produces 1, can be recycled. It is itself converted to 3 upon exposure to *t*-butyllithium, whereupon a dimethyl peroxide quench returns 47% of 4 accompanied by 16% of 1.

Hexamethoxycyclopropane 1[10] has mp 115-116°C (from isooctane); ^{1}H n.m.r. $\delta(CDCl_3)$ 3.47, $\delta(CCl_4)$ 3.33; ^{13}C n.m.r. $\delta(CDCl_3)$ 54.6 ($\underline{CH_3}O$), 92.7 (ring $\underline{C}$). The simple i.r. spectrum (KBr, cm^{-1}) presents bands at 3000-2864, 1458, 1442, 1213 and 1138 (C-O-C), 1011 (cyclopropane), 839, and 646.

Mass spectra of 1 provide information about available fragmentation pathways and serve as an introduction to the molecule's pyrolytic chemistry. A parent ion at *m/e* 222.2 (0.2%) is visible in the chemical ionization (C.I.) m.s. of 1, but not in the 70 eV electron impact (E.I.) spectrum, where the heaviest observed ion is (M^+-CH_3) at 207.1 (4.9%). C.I. affords a base peak at *m/e* 191 (M^+-OCH_3), whereas this pathway is largely eschewed (2.6%) in E.I. Here, elimination of "$(MeO)_2C$" affords an ion corresponding to tetramethoxyethylene at *m/e* 148 (17.5%), from which the base peak arises by loss of CH_3 (*m/e* 133). Indeed, from *m/e* 148 and lower, the E.I. m.s. of (1) is very similar to that of tetramethoxyethylene.[11]

The pyrolytic chemistry of 1 resembles its E.I. fragmentation. Pyrolysis of 1 in decane (200°C, 16 h, sealed tube) afforded mainly trimethylorthoformate 6, 30%, dimethyl oxalate 7, 51%, and methyl pyruvate dimethyl ketal 8,[12] 14%. Product identities were established by capillary gas chromatographic (50 m, SE-30, 80-120°C) and mass

$HC(OMe)_3$

6

$MeO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OMe$

7

$MeC(OMe)_2COOMe$

8

spectroscopic comparisons to authentic materials. Yields were determined by calibrated electronic integration of the gas chromatography product signals relative to that of an anisole standard.

These products are supportive of efficient cycloreversion of 1 to dimethoxycarbene and tetramethoxyethylene. Thus, 7 and 8 are known thermolysis products of tetramethoxyethylene,[13,14] whereas 6, which is not formed from the alkene, is most reasonably attributed to capture by coproduct methanol of the dimethoxycarbene fragment extruded from 1.[1,15] The origin of the methanol is unclear.[15]

Efforts to transfer $(MeO)_2C$ from 1 to alkenes such as styrene or dimethyl fumarate have thus far been thwarted by the high temperature required for efficient decomposition of 1, and the concomitant instability of the substrates. At present, therefore, norbornadienone ketals[16] remain more appropriate precursors for dimethoxycarbene.

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