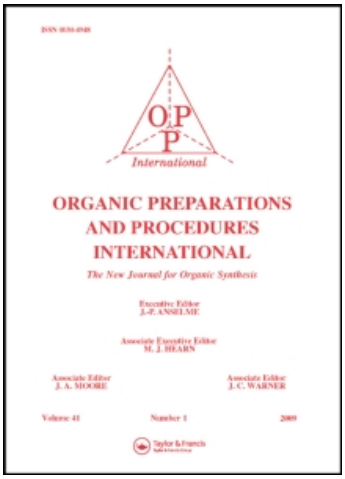

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THE PREPARATION AND CHARACTERIZATION OF *trans*-1-METHYLENECYCLOPROPANE-2, 3-di-t-BUTYL PERESTER

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THE PREPARATION AND CHARACTERIZATION OF trans-1-METHYLENECYCLOPROPANE-2,3-di-t-BUTYL PERESTER

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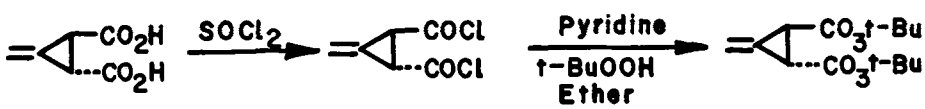
As part of a continuing interest in the synthesis and chemical reactivity of methylenecyclopropene,[1] it appeared of interest to synthesize and determine the chemistry of trans-1-methylenecyclopropane-2,3-di-t-butyl perester, 1,(Feist's Perester). The title compound was synthesized (70%) using the procedure of Bartlett,[2] as described for alicyclic t-butyl peresters. Since the addition of pyridine to 2 directly caused the formation of tarry, insoluble complexes, the acid chloride 2 was slowly added to a solution of pyridine and t-butyl hydroperoxide in ether at 0°. The acid chloride 2 was prepared as described previously from Feist's Acid, 3.[3,4]



3 2 1

The perester 1 was purified by column chromatography on Florisil using petroleum ether (bp 40-65°) as the eluting solvent. The pure material is a white solid, mp 33-34°, showing a single spot in several TLC solvent systems. Refluxing a solution of 1 in dry benzene for a period of 24 hours caused no detectable decomposition of the material. The perester is stable for indefinite periods of time in chloroform solution at 0°, or when stored neat at -20°.

There have been no reports in the chemical literature describing the mass spectral fragmentation patterns of any peresters. The mass spectrum of perester 1, was recorded on an Atlas MAT CH4 instrument at an inlet temperature of 100°. It is of interest that the mass spectral results are extremely temperature dependent. Consistent results were obtained only when the material was introduced into the mass spectrometer at a temperature low enough to prevent thermal decomposition or rearrangement. The mass spectrum of perester 1 at 70 e.V. is as follows: M/e (Rel. Int.); 286 (0.08); 271 (0.08); 230 (2.8); 197 (7.75); 153 (1.13); 125 (1.6); 97 (1.06); 73 (50); 57 (100). The most significant feature of the mass spectrum is the presence of a detectable molecular ion at M/e = 286. This, together with major fragmentation peaks found, may represent a new method for the characterization of peresters. Other t-butyl peresters have been studied under similar mass spectral conditions; however, these shall be described in greater detail in a later publication.

Experimental

trans-1-Methylenecyclopropane-2,3-di-t-butyl perester (Feist's Perester), 1. trans-1-Methylenecyclopropane-2,3-dicarbonyl chloride, 2, was prepared according to the procedure of Blomquist,[3,4] and was placed in an addition funnel as an ethereal solution (1.0 g, 0.0056 mol). This solution was added dropwise to an ice-cold, stirred solution of freshly distilled, dry pyridine (0.9 g, 0.0112 mol), and t-butyl hydroperoxide (1.0 g, 0.0112 mol) in 35 ml of dry ether. After completion of the addition (30 min), stirring was continued for approximately one hour at 0°, and an additional 30 min at room temperature. The ethereal solution was decanted from the precipitated pyridinium HCl. This solution was poured onto crushed ice, washed with 10% sulfuric acid, 10% sodium carbonate solution, and finally with water. After drying the solution over $MgSO_4$, the solution was concentrated and passed through a short column of Florisil (25 g) in petroleum ether. Removal

of all solvents on a rotary evaporator at 35° left an oil which, in the absence of any residual hydroperoxide, immediately solidified upon cooling at -20°. Any remaining t-butyl hydroperoxide could be easily removed by an additional column chromatography on Florisil. The solid was washed with cold petroleum ether or hexane to give an analytically pure material, mp 33-34°, showing a single spot in a number of TLC solvent systems (benzene, ethyl acetate, acetone, 1:1 methylene chloride:chloroform) (1.15 g, 70%).

trans-1-Methylenecyclopropane-2,3-di-t-butyl perester, 1,[5] had the following spectral properties, ir: $\nu_{cm^{-1}}^{CHCl_3}$ 3000, 2975, 2930, 1770 (perester carbonyl),[2] 1470, 1385, 1365, 1260, 1190, 1120, 1095, 1025, 910, and 842; nmr ($CDCl_3$): δ 5.72 (t, 2H); δ 3.0 (t, 2H); and δ 1.35 (s, 18H). Found: C, 58.82; H, 7.66. $C_{14}H_{22}O_6$ requires: C, 58.73; H, 7.75%.

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(5) The title compound might be more appropriately named according to Chemical Abstracts nomenclature as: trans-2,3-Di-t-butylperoxy-1-methylenecyclopropanoate.

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