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CYCLOBUTANE-1,2-DIONE. RING CONTRACTION BY WATER.

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It is known that the acyloin condensation in the presence of Me_3SiCl, occuring via isolable trimethylsilyl ether, improves the yield of cyclic product and is very useful in the preparation of cyclobutane rings (1). It has been pointed out that bromine oxydation of trimethylsilyl ether is a better pathway to diones (3,4) that acyloin DMSO-Ac_2O oxidation (2).

Cyclobutane-1,2-dione (4) itself, although invoked as intermediate in some reactions (e.g. 5), is still unknown. We wish to report that 4 is readily available quantitatively from bromination of bis-[trimethylsiloxy]-cyclobutene (1).

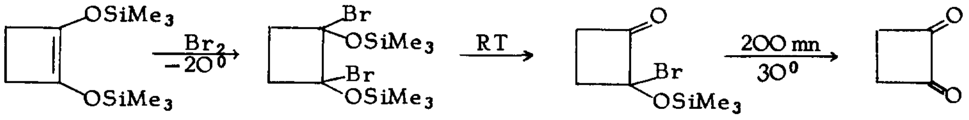
Bromine (1 mole) in CCl_4 is added to a solution of 1 (1 mole) in the same solvent at -20^0C. The IR and NMR examination of the solution clearly shows that the dibromoadduct formed 2 is quickly converted to the monoketone 3 : $\nu_{C=O}$ 1804 cm^{-1} ; $\delta(CH_2)_2$ 2.65 ppm (ABCD system), $\delta Si(CH_3)_3$ 0.60 ppm (s). The subsequent formation of dione 4 is easily observed in IR by the appearance of a second carbonyl band and the progressive shifting of the first one. The total conversion $2 \longrightarrow 4$ is obtained after some hours at 30^0C.

Cyclobutane-1,2-dione (4) is isolable by vacuum distillation of CCl_4 and washing of the residue with petroleum ether ; a pure sample (sublimation) shows : mp 56^0 (yellow cristals) ; $\nu_{C=O}$ 1778 and 1810 cm^{-1} (CCl_4) ; λ_{max} (hexane) (nm) : 407 (4), 423 (8), 436 (10.5), 453 (19), 463 (17), 489 (42), 500.5 (28) ; $\delta(CH_2)_2$ 2.98 ppm (s) (CCl_4). Mass spectrum : parent peak M^+84 and two main peaks : m/e 56.025 [calculated for $(CH_2)_2CO$: 56.026] (100%) and m/e 42 (keten peak) (79%). Dione 4 can be stored in the dark for a few weeks in sealed tube.

The formation of monohydrate 5a occurs when 4 is dissolved in water ; then NMR (TMS ext.ref.) shows an A_2B_2 system at $\delta 3.09$ ppm besides the singlet of 4 at 2.44 ppm. After 15 mn, 28% of 4 is still present, but a new product (9%) gives rise to a signal at $\delta 1.74$ ppm (AA'BB' system), which remains alone after two days. It can be isolated by vacuum distillation of water and is recognized as 1-hydroxy-cyclopropanecarboxylic acid 6a ; mp 108^0C (litt (5) : $106\text{-}107^0$).

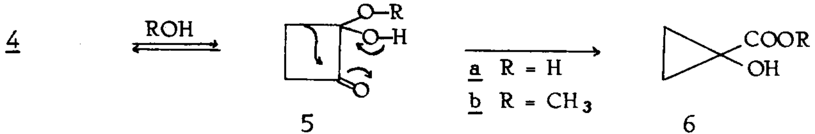
The same experiment conducted in deuterium oxide leads to 1-hydroxy-cyclopropanecarboxylic acid, in which no deuterium incorporation into the C_3 ring can be detected (NMR, MS). Such a result implies that no enolisation of dione 4 occurs in these conditions.

Another experiment conducted in CCl_4 / CH_3OH shows an immediate decoloration and the practically total conversion of 4 to hemi-ketal 5b : $\delta(CH_2)_2$ 2.50 ppm (ABCD system) and δCH_3 4.00 ppm (s)(TMS int.ref.) ; λ_{max} 321 nm (21). It is followed by the rearrangement of 5b to 1-hydroxy-cyclopropanecarboxylic ester (6b) : $\delta(CH_2)_2$ 1.10 ppm (AA'BB' system). The ring contraction 4 → 6b is slower than 4 → 6a and never complete ; its examination is complicated by the formation of ketal and possibly bis-ketal derivatives (NMR). See (2a).



1 2 3 4

Two related ring contraction of cyclobutane-1,2-diones, in basic or acidic conditions, have recently been noted (5)(2a). The reaction 4 → 6a is the first true benzilic acid rearrangement obtained with water alone (an analogous result to the reaction 4 → 6b can be found in (2a)). Such a result is clearly related to the quasi-Favorsky rearrangement undergone by halocyclobutanones, which is well known as occuring in water or alcohols (7 → 8) by a semi-benzilic process (6). Details of other more or less related ring contractions or enlargements which have recently been elucidated in our laboratory will be published elsewhere.



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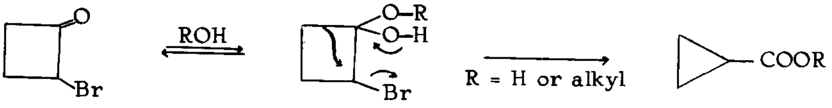

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