Reverse Benzilic Acid Rearangements in Cyclopropenes

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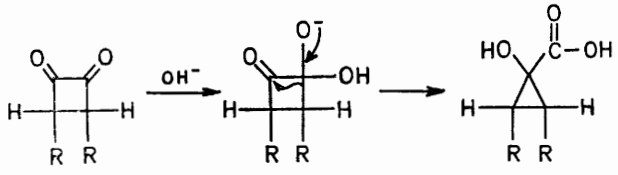
Summary The preparation of hitherto unreported 3-hydroxy-1,2-diphenylcyclopropene-3-carboxylates and their base-catalysed reverse benzilic acid rearrangement to diphenylcyclobutenedione are described.

ONE of the oldest molecular rearrangements known is the benzilic acid rearrangement. In cyclic systems the reaction has usually been observed in the preparation of five-membered rings from cyclohexane-1,2-diones.[1] There have been recent reports of the preparation of 1-hydroxycyclopropanecarboxylic acids from cyclobutanediones, equation (1).[2]

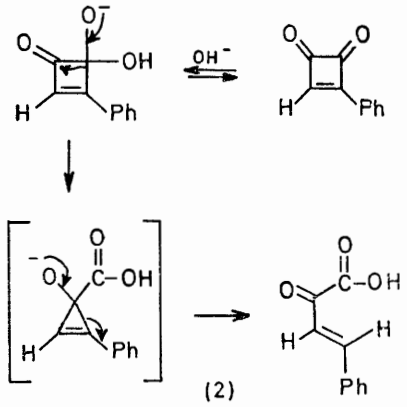


R = H or alkyl. (1)

The benzilic acid rearrangement has also been postulated as intermediate in the base-catalysed ring cleavage of 1-phenylcyclobutene-3,4-dione, equation (2).[3] In this case, however, the 3-hydroxycyclopropene intermediate has not been isolated, and others have postulated alternative mechanisms for the rearrangement which do not involve the unknown hydroxycyclopropenes.[4]

This work describes the preparation of a 3-hydroxycyclopropene derivative and its base-catalysed *reverse* benzilic acid rearrangement to 1,2-diphenylcyclobutenedione.

A cyclohexane solution of phenylchlorodiazirine[5]† (a neutral source of phenylchlorocarbene) and ethyl phenylpropiolate‡ was heated under reflux until nitrogen evolution ceased.[6] Concentrating and cooling the solution by evaporation precipitated a 47% yield (based on the phenylchlorodiazirine precursor, benzamidine hydrochloride) of ethyl 3-chloro-1,2-diphenylcyclopropene-3-carboxylate (**1**), m.p. 106—107° (benzene–hexane). Slow addition of 5% bicarbonate to a 10% solution of (**1**) in acetone precipitated a 90% crude yield of ethyl 3-hydroxy-1,2-diphenylcyclopropene-3-carboxylate (**2**), m.p. 118—119° (benzene–hexane). If ether was used instead of acetone, the two-phase hydrolysis gave only the dimeric ether (**3**), m.p. 160° (decomp.), equation (3).



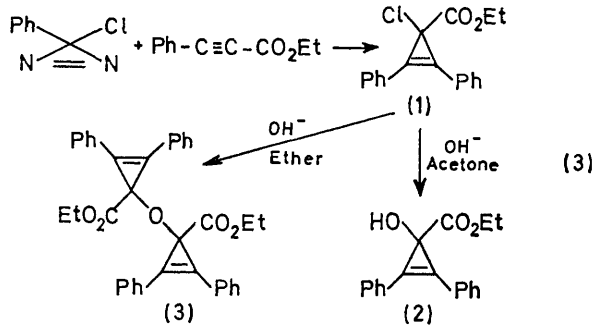
(2)

The assignment of structure (**1**) as the 1,2-diphenyl derivative rather than as the 2,3-diphenyl derivative (the formal product from addition of phenylchlorocarbene to ethyl phenylpropiolate) is complicated. Both compounds would be expected to show similar if not identical mass spectra, dominated by easy loss of chlorine. Perhaps the best evidence for structure (**1**) is found in the positions of the u.v. absorption maxima, which are nearly identical with

† In pure form, phenylchlorodiazirine is considerably more shock-sensitive than nitroglycerine. Diluted with cyclohexane or benzene, it is not shock-sensitive. All phenylchlorodiazirine used in this work was prepared in cyclohexane solution, purified by filtration through two inches of silica gel, and used without isolation.

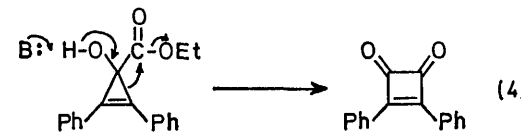
‡ Although only the ethyl ester is reported in the text, all of the reactions of (**2**) proceeded equally well with the methyl ester. Satisfactory elemental analyses and spectral data were obtained with all new compounds.

those of other 1,2-diphenylcyclopropenes.[7] Furthermore, the magnitude of the u.v. extinction coefficients allows the structure of (**1**) to be written as covalent.



When the hydroxycyclopropene (**2**) was treated with sodium methoxide in methanol or with a catalytic amount of 1,5-diazabicyclo[4,3,0]non-5-ene in chloroform or benzene, there was a rapid, quantitative reverse benzilic acid rearrangement to diphenylcyclobutenedione. Under these mild conditions the diphenylcyclobutenedione did not undergo ring cleavage.

Assuming 3-hydroxy-1-phenylcyclopropene-3-carboxylic acid also undergoes this rearrangement, Skattebøl and Roberts'[3] mechanism, equation (2), would require a rapid equilibrium between butenedione and hydroxycyclopropene with ring opening of the cyclopropene as the rate-determining step. Although this does not rule out equation (2), it adds a further constraint to the mechanism of cyclobutenedione ring cleavage.



Equation (4) provides a contrast to equation (1). Since the ring strain energy of a cyclopropene is thought to be *ca.* 20 kcal greater than that of a cyclopropane, while the strain energies of cyclobutanes and cyclobutenes are nearly equal,[8] simple strain arguments offer a possible explanation of the opposing direction of the two rearrangements.§

The best preparation of diphenylcyclobutenedione is by the Friedel–Crafts reaction of squaric acid dichloride on benzene,[9] but the rearrangement of hydroxycyclopropenes may provide a convenient route for the synthesis of cyclobutenediones not possible from Friedel–Crafts reactions. Also, reduction of (**1**) with dimethylamine–borane in dichloromethane offers an alternative synthesis of 1,2-diphenylcyclopropenecarboxylates to that in the literature.[10]

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§ A referee has pointed out that in equation (1) the product may be removed by salt formation. However, when R = Bu^t in equation (1) and the base is sodium methoxide, the product is the methyl ester and the reaction is not reversible. See ref. 2.

[1] D. Redmore and C. D. Butsche, *Adv. Alicyclic Chem.*, 1971, **3**, 70.
[2] H. D. Scharf, W. Droste, and R. Liebig, *Angew. Chem. Internat. Edn.*, 1968, **7**, 215; A. de Groot, D. Oudman, and H. Wynberg, *Tetrahedron Letters*, 1969, 1529; J. J. Bloomfield, J. R. S. Irelan, and A. P. Marchand, *ibid.*, 1968, 5647.
[3] L. Skattebøl and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 4085.
[4] A. T. Blomquist and E. A. LaLancette, *J. Amer. Chem. Soc.*, 1962, **84**, 220. See also ref. 2.
[5] W. H. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 4396.
[6] A. Padwa and D. Eastman, *J. Org. Chem.*, 1969, **34**, 2728.
[7] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, 1961, **83**, 2367.
[8] R. Breslow, J. Lockhart, and A. Small, *J. Amer. Chem. Soc.*, 1962, **84**, 2793.
[9] G. Maahs and P. Hegenberg, *Angew. Chem.*, 1966, **78**, 927.
[10] R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, 1959, **24**, 415.