Tetrahedron Letters No. 50, pp 4437 - 4438, 1977. Pergamon Press. Printed in Great Britain.

SYNTHETIC APPLICATIONS OF DI-tert-BUTOXYETHYNE: SYNTHESIS OF DELTIC AND SQUARIC ACID[1]

M.A.Pericás and F.Serratosa*

Instituto de Química Orgánica Aplicada de Cataluña (C.S.I.C.), and Departamento de Química Orgánica, Universidad de Barcelona. Barcelona-14, Spain

(Received in UK 30 September 1977; accepted for publication 21 October 1977)

In the present communication we wish to report some synthetic applications of di-tert-butoxyethyne, a fairly stable acetylene diether that we have recently prepared in our laboratory[2].

From the chemistry of acetylene monoethers, it is well known that the derivatives having at least one hydrogen atom at the β position are thermally unstable and, when heated, eliminate alkene and form a ketene, by a concerted process involving an intramolecular hydrogen shift[3].

The intermediate ketene reacts then with the parent acetylene to afford a cyclobutenone as the final reaction product.

In a similar way, di-tert-butoxyethyne, in boiling benzene, gives 2,3,4-tri-tert-butoxycyclobut-3-en-1-one, via tert-butoxyketene, in quantitative yields[4]. Oxidation with NBS, in carbon tetrachloride, leads to di-tert-butyl squarate in 83% yield (m.p. 104-5º; 1800, 1681 cm^{-1}), from which squaric acid[5] could be liberated, in quantitative yield, by trifluoroacetic acid (Chart I).

Squaric acid is a member of the so-called "aromatic oxocarbons dianions"[6] ($C_nO_n^{=}$), the first member of which is deltic acid. Although deltic acid and its esters have been recently prepared by photochemical degradation of squaric acid esters[7], a total synthesis was still lacking. Chart II summarizes a-long-time-awaited-synthesis: di-tert-butoxyethyne reacts with dichlorocarbene -generated in the presence of TEBA, by phase-transfer catalysis[8]- to give directly di-tert-butyl deltate (m.p. 80-2º; 1885, 1650 cm^{-1}), in 13-35% yield. Treatment of this ester with trifluoroacetic acid at 6º, leads, in quantitative yields, to analytically pure deltic acid Cf.[7b]

CHART I:

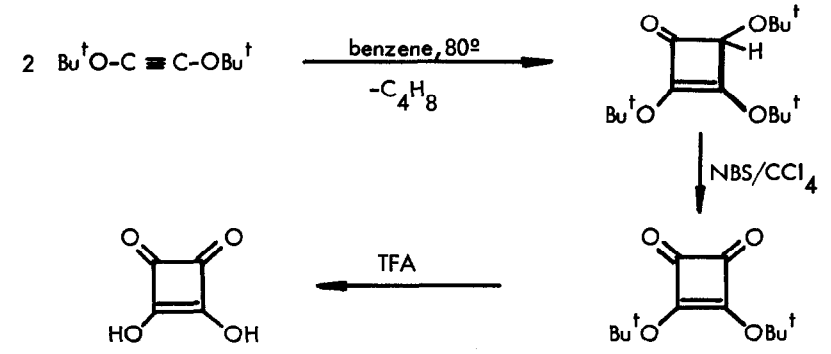
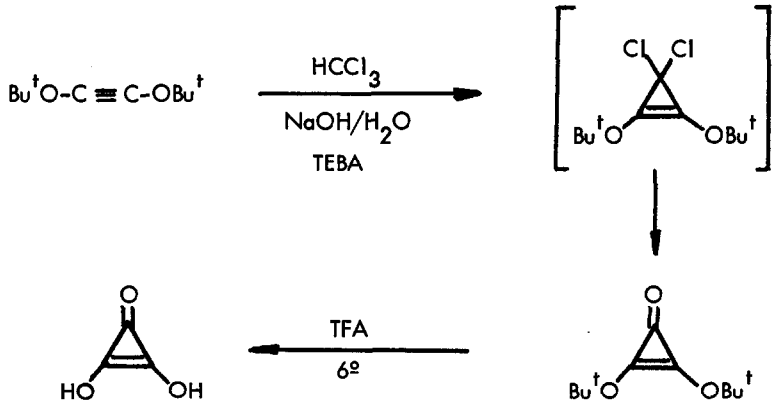


CHART II:



References and Notes

1. Taken, in part, from a communication presented at the Second International Symposium on Acetylenes, Allenes and Cumules, held in Nottingham, 5-8 September 1977, by The Chemical Society (London).

2. M.A. Pericás and F. Serratosa, see preceding communication.

3. L. Brandsma, H.J.T. Bos, and J.F. Arens, in "Chemistry of Acetylenes" (H.G. Viehe, Editor), pag. 808-9, Marcel Dekker, New York, 1969, and references cited therein.

4. All compounds gave satisfactory elemental analysis.

5. S. Cohen, J.R. Lacher, and J.D. Park, J. Am. Chem. Soc., 1959, 81, 3480; G. Maahs and P. Hegenberg, Angew. Chem. internat. Edit., 1966, 5, 888.

6. R. West, H.Y. Niu, D.L. Powell, and M.V. Evans, J. Am. Chem. Soc., 1960, 82, 6204.

7. a) E.V. Dehmlow, Tetrahedron Letters, 1972, 1271.
b) D. Eggerding and R. West, J. Am. Chem. Soc., 1976, 98, 3641.

8. E.V. Dehmlow and M. Lissel, Tetrahedron Letters, 1976, 1783.