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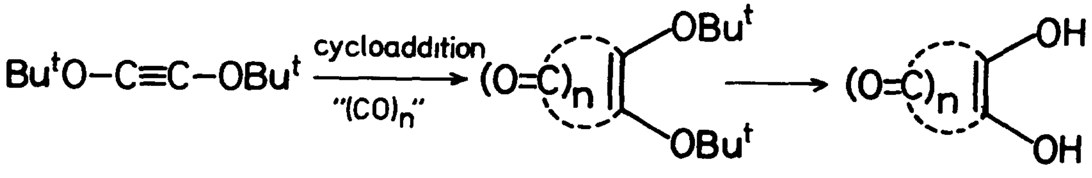
SYNTHETIC APPLICATIONS OF DI-TERT-BUTOXYETHYNE, II: NEW SYNTHESES OF SQUARIC, SEMISQUARIC AND CROCONIC ACIDS[1]

Anna Bou, Miquel A. Pericàs and Fèlix Serratosa

Departament de Química Orgànica. Facultat de Química. Universitat de Barcelona. Barcelona-28. Spain

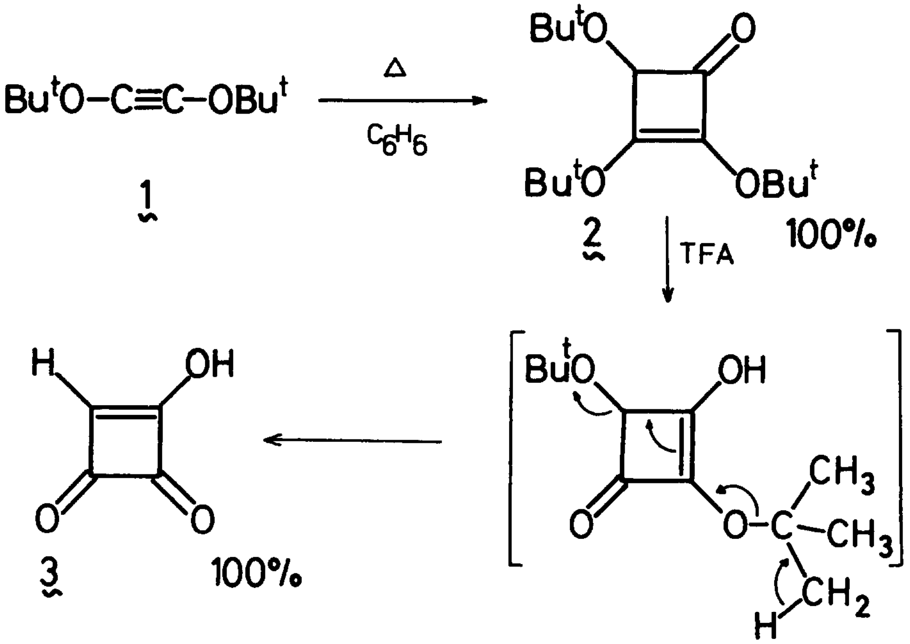
Summary.- New synthetic entries to: a) the semisquaric acid skeleton of the natural mycotoxin "moniliformin", b) the squaric acid system, and c) the croconic acid system, *via* (η-tetra-*tert*-butoxycyclopentadienone)(η-cyclopentadienyl)cobalt, starting from di-*tert*butoxyethyne are reported.

THE syntheses of deltic and squaric acids, as well as the formal syntheses of croconic and rhodizonic acids, starting from di-*tert*-butoxyethyne (**1**)[2] have already been reported [3,4]. The uniqueness of this readily accesible starting material[5] for oxocarbon synthesis, which allows the transfer, by pertinent cycloadditions, of the protected *enediol* fragment in such a way that at the end of the synthesis it can be actualized under mild acid conditions, prompted us to pursue our investigations on this field.

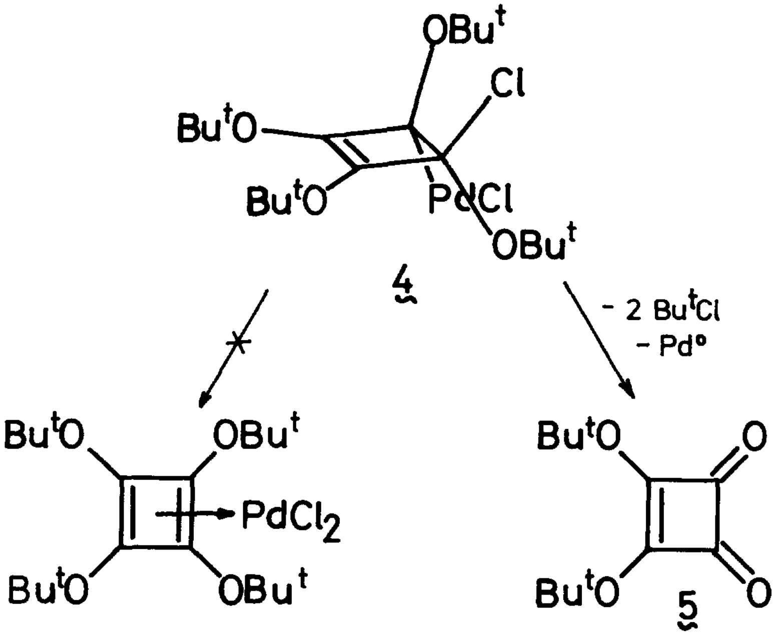


3-Hydroxycyclobutene-1,2-dione ("semisquaric acid"), 3, the parent compound of the natural mycotoxin "moniliformin"[6] has been synthesized from 2,3,4-tri-*tert*-butoxycyclobutenone (2), the thermal dimerization product of 1, which was used as an intermediate in our earlier synthesis of squaric acid[3]. In fact, both compounds, 2 and 3, have the same oxidation level, so that a single deprotection/elimination process on 2 was expected to lead to 3.

Such a transformation could be readily achieved by a one pot procedure: solvolysis of 2 with anh trifluoroacetic acid, in pentane soln for 18 h at 6° , afforded semisquaric acid (3) in quantitative yield, as white crystals m.p. 163°(dec) (reported[6] 163°dec)(Found. C, 49.01; H, 2.01%. Calc. for $C_4H_2O_3$ C, 48.97; H, 2.06%).

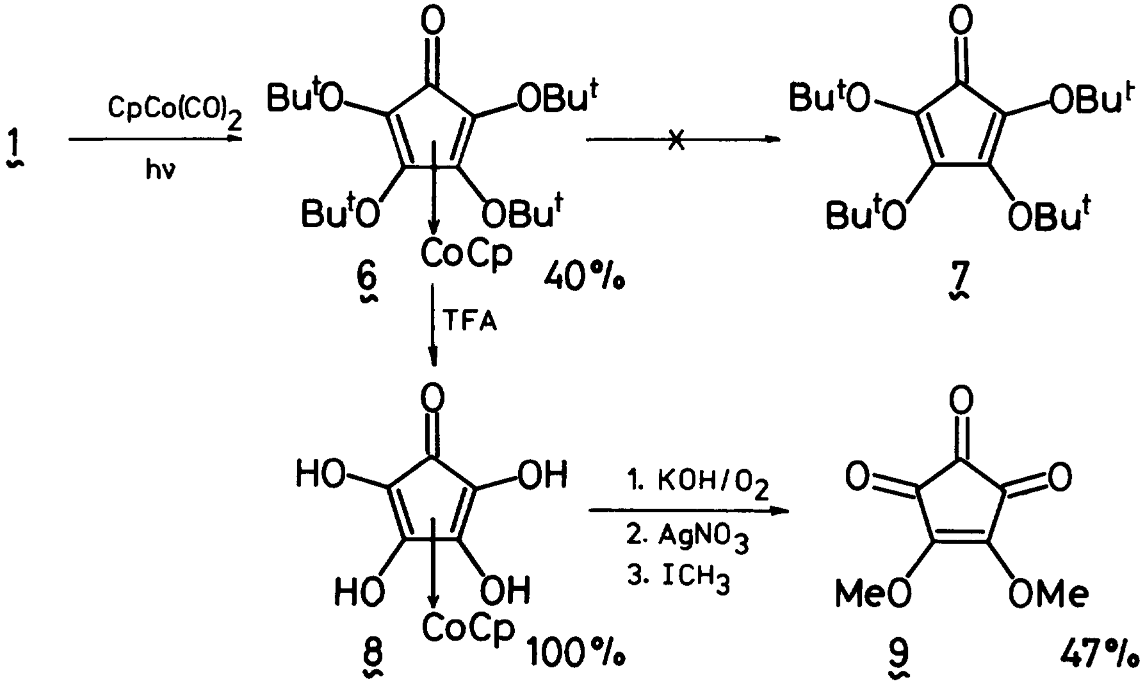


Dihydroxycyclobutenedione ("squaric acid") Analysis of Maitlis' mechanism[7] for palladium induced cyclodimerization of alkynes suggested that, in the case of di-*tert*-butoxyethyne, the possibility of an intramolecular Bu^{t}Cl elimination in intermediate 4, could deviate the ordinary course of the reaction in an oxidative way, as depicted in the following scheme, leading directly to di-*tert*-butyl squarate (5) rather than to the usual cyclobutadiene structure observed with other alkynes.



Consequently, a soln of di-*tert*-butoxyethyne in CH_2Cl_2 was treated with $PdCl_2.CH_3CN$, for 3 h under reflux, the formation of **5** being observed. However, probably due to slow Pd° elimination in the latter stage of the process, purification of **5** was rather difficult. This problem could finally be circumvented by treatment of crude **5** with trifluoroacetic acid under reflux, for 2 h, the free acid (dihydroxycyclobutenedione) being isolated in 52% overall yield from **1** (*Cf.* with 83% overall yield *via* intermediate **2**)[3].

Dimethoxycyclopentenetrione ("dimethyl croconate"), **9** One of the synthetic goals to which more efforts we have devoted in the last times is tetra-*tert*-butoxycyclopentadienone (**7**) that represents not only a direct entry to the croconic acid system from an acetylene diether, but also a suitable precursor for tetra-*tert*-butoxycyclobutadiene and tetra-*tert*-butoxytetrahedrane.[8] In fact, we have succeeded in preparing (η-tetra-*tert*-butoxycyclopentadienone)(η-cyclopentadienyl)cobalt (**6**), in 50% yield, by low temperature irradiation[9] of a mixture of **1** and (η-cyclopentadienyl)dicarbonylcobalt in pentane soln (orange crystals, m.p. 152-153°. NMR (CCl_4). δ 4.65 (s)(5H), 1.52 and 1.4 (2s, 36H). Found 492 2283; calc. for $C_{26}H_{41}O_5Co$: 492.2285). All the efforts we have made in order to liberate **7** from this complex by standard methods[10] have been up to the moment unsuccesful. However, treatment of **6** with trifluoroacetic acid, for 2 h at room temperature, afforded in quantitative yield (η-tetrahydroxycyclopentadienone)(η-cyclopentadienyl)cobalt (8) (IR: 3200b, 2920, 2880, 1670, 1570, 1475, 1320, 1200, 1150 and 975 cm^{-1}. Found: C, 44.91; H, 3.70. Calc. for $C_{10}H_9O_5Co$. C, 44 76; H, 3.38%). Finally, 8 could be converted into dimethyl croconate (9), in 47% overall yield, by oxygen oxidation in basic medium, precipitation of the silver salt of croconic acid and methylation with methyl iodide· orange-red crystals, m.p. 109-110°, λ_{max} 294 (in methanol)(reported: m.p. 114° from benzene[11], λ_{max} 292, in methanol[12]).



1. Taken, in part, from a communication presented at ESOC II, Stresa (Italy), June 1-5, 1981.
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