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1,2-CYCLOBUTANEDIONES I. THE SYNTHESIS AND REACTIONS OF TRICYCLO[4.4.2.0^{1,6}]-DODECA-3,8-DIENE-11,12-DIONE. [4.4.2]PROPELLA-3,8-DIENE-11,12-DIONE.

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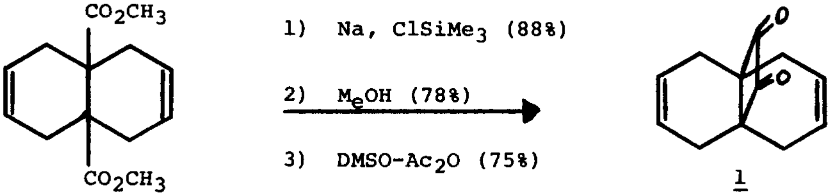
We have been interested in the chemistry of 1,2-cyclobutanediones because of their potential utility as intermediates in synthesis and to compare their chemistry with the extensively studied ketene dimers, 1,3-cyclobutanediones.[1] A simple technique for the conversion of diethyl succinate and a variety of α,β-substituted succinates to the corresponding 1,2-bis[trimethylsiloxy] cyclobutenes followed by methanolysis[2] and then by dimethylsulfoxide-acetic anhydride oxidation[3,4] now permits ready examination of the behavior of 1,2-cyclobutanediones.[5]

Thus, the title diketone, 1, a pink solid, mp. 119.6-120.8°, was prepared from 9,10-dimethyl-$\Delta^{2,6}$-hexalin dicarboxylate in overall yield of 52%.[6,7]



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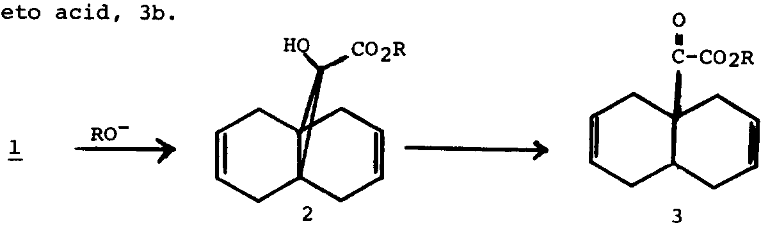
Treatment of 1 with slightly basic methanol or with aqueous base brings about a benzilic acid-type rearrangement to give the hydroxycyclopropane carboxylic acid derivative, 2 in 90-100% yield.[8] Strong aqueous base converts 2 to the α-keto acid, 3b.



2 3

a, R = CH3; b, R = H

Compound 2a, mp. 74.4-75.7° showed an infrared spectrum (KBr disc) with -OH absorption at 3480 cm^{-1} and >C = O at 1720 cm^{-1}. The nmr spectrum (CCl_4, internal tetramethylsilane) showed the vinyl protons as a pair of multiplets at δ5.38-5.46 and δ5.51-5.64; the $OC\underline{H}_3$ appeared at δ3.56(s); the O$\underline{H}$ appeared as a broad, temperature variable signal (erased by addition of D_2O) at about δ3.12 while the allylic protons appeared as an AB multiplet further split by vinyl hydrogens, δ1.85-2.90. The acid, 2b had mp. 145-147.5° (it could be converted to 2a with diazomethane). ν_{max} KBr >C = O 1690 cm^{-1}. The nmr spectrum in $CDCl_3$ showed the following characteristics: δ6.4-7.0(s) - OH and $CO_2\underline{H}$ (disappear on addition of D_2O); δ5.55 and δ5.68(t) (J = 1Hz), CH = CH and complex multiplet δ1.95-2.9 - CH_2 -.

Compound 3a was obtained by treating 1 or 2 with excess potassium hydroxide under reflux, followed by acidification and treatment of the crude carboxylic acid with diazomethane. The ester (60% yield) was purified by washing through a Florisil column and then by distilling (bulb-to-bulb), 0.1 mm/89-95°, n_D^{25} 1.5026, ν_{max} (smear) 1735 and 1715 cm^{-1}.

It is interesting to note that prolonged reflux (in the dark) of a neutral methanol solution of 1 produced a mixture of 2 (58%) and 3 (8%). In a slightly acid solution, under otherwise similar conditions, 2 was produced in 59% yield along with about 7% of a new compound that showed a 1780 cm^{-1} carbonyl absorption and $-OC\underline{H}_3$ at δ3.43. The quantity obtained precluded further structure determination.

Simply melting 1 together with an equimolar amount of o-phenylenediamine produced the expected quinoxaline in good yield, mp. 139.5-140.9°.

Heating of the α-diketone at about 160° caused gas evolution (CO) with the production of isotetralin. We hoped that a different reaction might occur on photolysis. However, exposure of solutions of 1 in methanol, carbon tetrachloride, pentane or benzene to pyrex filtered sunlight showed only carbon monoxide evolution with formation of isotetralin.[10] The mass spectrum showed no peaks above 132 m/e.[15]

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b) See also, K. Ruhlmann, H. Seefluth and H. Becker, Chem. Ber., 100, 3820 (1967).

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(4) The oxidation of linear acyloins by the DMSO-Ac_2O procedure has been recently reported, M. Van Dyke and N. D. Pritchard, J. Org. Chem., 32, 3204 (1967).

(5) Until now 3-phenyl-1,2-cyclobutanedione was the only known member of this class. However, this compound exists in the enolic form and is actually 2-hydroxy-3-phenyl-2-cyclobutenone. E. F. Silversmith and J. D. Roberts, J. Am. Chem. Soc., 80, 4083 (1958).

(6) Satisfactory analyses have been obtained for all new compounds described.

(7) The dihydro- and tetrahydro- derivatives of 1, pink, mp. 46.7-48.3° and yellow, mp. 42.5-43.4° respectively were obtained in similar overall yield from the appropriate diester. Their reactions parallel those of 1.

(8) This represents only the second example of an hydroxycyclopropane carboxylic acid derivative. The parent has recently been described[9a] and the intermediacy of such a compound in the base catalyzed rearrangement of 2-hydroxy-3-phenyl-2-cyclobutenone has been suggested.[9b]

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(10) This behavior should be contrasted with that of tetramethyl-1,3-cyclobutanedione[11] which produces a cyclopropanone; of benzocyclobutenedione which opens to a diketene[12]; and of camphorquinone which is reported to be relatively unreactive and does not eliminate CO.[13] Other questions relative to photodecarbonylation have been discussed.[14]

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