Tetrahedron Letters No.29, pp. 2489-2492, 1969. Pergamon Press. Printed in Great Britain.

OXIDATION OF 1,2-BIS(2,6-DIKETO-4,4-DIMETHYLCYCLOHEXYL)ETHANE WITH OXYGEN OVER PALLADIUM

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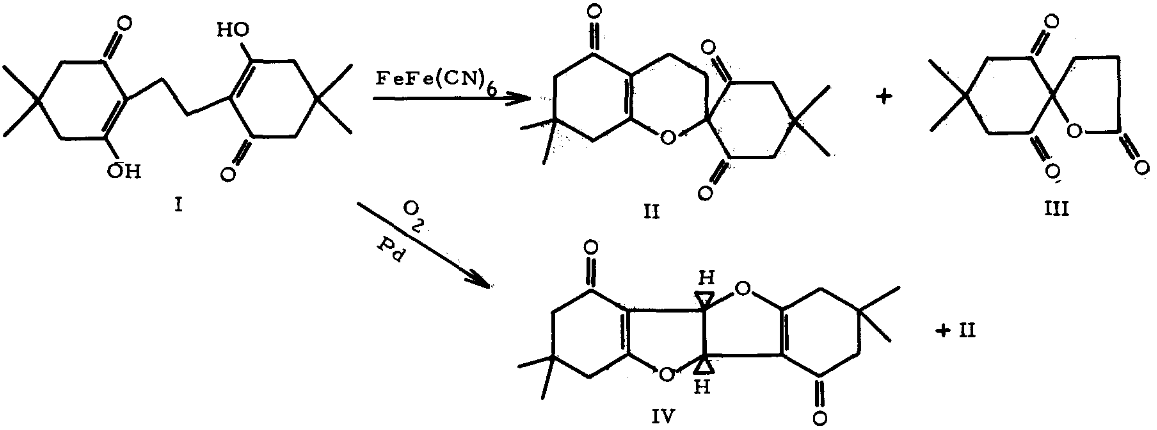
(Received in UK 6 February 1969; accepted for publication 23 May 1969)

A novel reagent for oxidative coupling of β-dicarbonyl compounds, oxygen (or hydrogen peroxide as in situ oxygen source) over palladium on barium sulphate, has been investigated using 1,2-bis(2,6-diketo-4,4-dimethylcyclohexyl)ethane (I) as model compound.

It has earlier been reported that highly reactive β-diketo derivatives such as 2-phenyl-1,3-indandione undergo intermolecular oxidative carbon-carbon dimerisation when treated with potassium hexacyanoferrate(III) (1) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2). The carbon-carbon or the carbon-oxygen dimers of e.g. acetylacetone and 2-methyldimedone have been obtained using lead tetraacetate as dehydrogenating agent (3,4). Attempts have been made to prepare dimers of several β-diketones by means of anodic oxidation in aqueous or aqueous-methanolic sodium hydroxide solutions (5,6,7).

Intramolecular carbon-carbon as well as carbon-oxygen oxidative coupling of a number of 1,3-cyclohexanedione derivatives has been accomplished in this laboratory using iron(III) hexacyanoferrate(III) as oxidation reagent (7,8,9,10). Thus, compound I when treated with a slight excess of the reagent gave several products. So far two products have been isolated in low yields, the carbon-oxygen coupling product, the spirane enol ether II, and the spirane γ-lactone III (9).

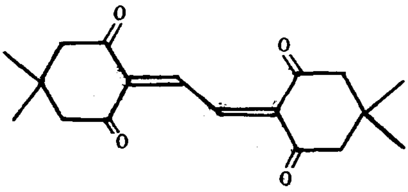
A different result was obtained when compound I was treated with oxygen over palladium on barium sulphate (11) in refluxing methanol for 3 h. Two products,



A and B were isolated in yields of up to 25 % and 20 %, respectively. Compound A was identified as the spirane enol ether II, mentioned above (9). Compound B has the empirical formula $C_{18}H_{22}O_4$, m.p. 237-238°. The IR spectrum of B shows strong bands at 1655, 1630 and 1225 cm^{-1} typical for dimedone enol ethers. There were no bands in the OH-region or in the carbonyl region above 1700 cm^{-1}. The UV spectrum has a maximum at 250 nm, the high molar extinction coefficient (ε 25 000) indicating the presence of two enol ether systems. From these spectral data and by model inspection compound B was formulated as the racemate IV.

The n.m.r. spectrum of B gives further evidence for structure IV. A singlet at δ1.11 (12H) is assigned to the gem-dimethyl protons. Two singlets at δ2.30 (4H) and δ2.40 (4H) are ascribed to the two types of methylene protons (12). The remaining two protons are equivalent (as confirmed by inspection of the model) and give rise to a singlet at δ6.20 (2H). The mass spectrum of B gives the pattern expected from IV with prominent fragments at m/e 302 (M^+, 53 %), 246 ($M-C_4H_8$, 29 %), 218 ($M-C_4H_8-CO$, 40 %), 134 (29 %) and 83 (100 %) (13).

Although evidence can be found in favour of the alternative structure V for compound B, this structure was rejected because V would be expected to give only one singlet in the n.m.r. spectrum for the methylene protons which in all probability are equivalent. Furthermore V would be predicted to give a UV maximum at a longer wavelength than that found for compound B and only a weak IR band at 1225 cm^{-1}, if any.



V

Noteworthy are the carbon-oxygen coupling involving the methylene group adjacent to the dimedone ring and the absence of the carbon-carbon coupling product. Russell and Lokensgard (14) have shown that the highest spin density of the enolate radical is found on the 2-carbon, which would strongly favour a carbon-carbon coupling. However, a model of the postulated carbon-carbon coupling derivative shows that it is highly crowded and steric hindrance seems to be the main reason why it is not formed.

Oxygen over platinum has recently been used for oxidative coupling of phenolic compounds (15).

The author is indebted to Dr. C.A. Wachtmeister for his interest. This work has been supported by Statens Naturvetenskapliga Forskningsråd.

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