Notes A department for short papers of immediate interest.

Reduction of Conjugated 1,4-Diketones with Tin Amalgam

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A kinetic study of the oxidation of 1,4-diketones in which we are currently engaged has necessitated the synthesis of a series of these compounds. Since the unsaturated 1,4-diketones are readily available, reduction of the olefinic linkage offers a convenient route to these substances.

The usual reducing agent for effecting this conversion is zinc in acetic acid; however, this reduction is often accompanied by serious side reactions which make it useless as a synthetic tool. In studies on the reduction of 1,4-diphenyl-2-butene-1,4-dione (I) Lutz[1,2] has reported the isolation of five different bimolecular reduction products along with the desired saturated diketone. In an effort to develop a reliable system for converting 1,4-enediones to 1,4-diones a more specific reducing agent was sought.

We have found that amalgamated tin and acid will rapidly reduce unsaturated 1,4-diketones to the saturated derivative in high yield without any detectable side reactions in the cases studied. Reduction of I with tin amalgam and hydrochloric acid in ethanol gave 1,4-diphenylbutane-1,4-dione (II) in 90% yield. 1,4-*p*-Chlorophenyl-2-butene-1,4-dione (III) reacted in an analogous manner to give similar results.

Utilizing the same procedure β-norcholest-4-ene-3,6-dione (IV) was quantitatively reduced to β-norcoprostane-3,6-dione[3] and quinone (V) to hydroquinone. Substitution of acetic acid for hydrochloric acid was attempted in the cases I and V and also worked well, although reaction times were considerably longer and the reaction mixtures were usually lightly colored. Typical experimental procedures are illustrated below.

EXPERIMENTAL

Tin amalgam. To a flask containing 15 g. of mercuric chloride and 100 ml. of water was added 100 g. of 30-mesh tin metal. The flask was stoppered and shaken for a few minutes until all of the tin appeared to have a shiny coating of mercury on the surface. The tin amalgam was then washed repeatedly with water until the washings were clear, and stored under distilled water.

Reduction of 1,4-diphenyl-2-butene-1,4-dione. To 5.0 g. of 1,4-diphenyl-2-butene-1,4-dione and 10 g. of tin amalgam was added 150 ml. of ethanol. The solution was heated to reflux and 20 ml. of concd. hydrochloric acid was added cautiously. After 5 min. the solution was colorless. The solution was filtered and cooled to give 4.5 g. (90%) of crystalline product, m.p. 142–143°.

Reduction of quinone. To 5.7 g. of quinone was added 10 g. of tin amalgam and 50 ml. of glacial acetic acid. The mixture was heated on a steam bath and after 3 min. lustrous green crystals separated (quinhydrone). The crystals soon dissolved to give a light yellow solution. After 0.5 hr. the solution was filtered and the solvent removed *in vacuo.* Recrystallization of the hydroquinone from benzene-acetone gave 5.0 g. (88%) of product, m.p. 169–170°.

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[1] R. E. Lutz, *J. Am. Chem. Soc.*, **51**, 3008 (1929).

[2] R. E. Lutz and F. S. Palmer, *J. Am. Chem. Soc.*, **57**, 1947 (1935).

[3] W. G. Dauben and W. Templeton, private communication.

The Stereochemistry of Some Hydrophenanthrones[1]

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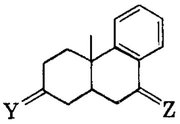
The recent synthesis of hydrophenanthrones Ia by three new routes[2] has made available compounds which can serve as the backbone for tricarbocyclic diterpenes. A partial use of Ia for the synthesis of the latter has been illustrated already,[3] while further work in this connection is continuing. Since any rational synthesis of the natural products was dependent, among other things, on the stereochemistry of the two isomers of Ia every effort had to be made to determine their configuration. Thus, a correlation of *cis-* and *trans-*Ia with substances of known constitution was sought, even though a large body of stereochemical evidence had been accumulated already.[2,3]



I

a, Y = O, Z = H_2
b, Y = Z = H_2
c, Y = H_2, Z = O

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[2] (a) and (b) E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 2318, 5627 (1956); (c) E. Wenkert and R. D. Youssefyeh, unpublished data, *cf.* Ph.D. dissertation of R. D. Youssefyeh, Iowa State University, June 1959.

[3] E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, 81, 5601 (1959).