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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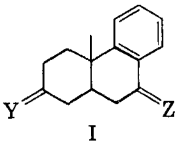
The recent synthesis of hydrophenanthrones Ia by three new routes[2] has made available compounds which can serve as the backbone for tricarbocyclic diterpenes. A partial use of Ia for the synthesis of the latter has been illustrated already,[3] while further work in this connection is continuing. Since 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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[1] This work was aided by research grant NSF-G6226. The authors are grateful to the National Science Foundation for this support.

[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).

A few years ago the stereoisomeric hydrocarbons Ib were converted *via* their ketones Ic to dibasic acids of known configuration.[4] As a consequence the saturated ketones Ia were transformed into their aromatic counterparts Ic by Wolff-Kishner reduction followed by chromic acid oxidation and the 2,4-dinitrophenylhydrazones of the latter compared with authentic samples.[5] These experiments were in full accord with the previous stereochemical assignment[2,3] of the isomers of Ia.

EXPERIMENTAL

Hydrocarbons Ib. A mixture of 350 mg. of *cis*-Ia and 0.7 ml. of hydrazine hydrate in 12 ml. of diethylene glycol was heated at 190° for 1 hr. After cooling to 70°, a solution of 700 mg. of sodium in 10 ml. of diethylene glycol was added and the mixture heated at 215–220° for 6 hr. Thereupon the mixture was cooled, poured into 100 ml. of saturated brine solution, and extracted with benzene. The extract was washed with water, dried, and its solvent removed, leaving 265 mg. of an oil. Chromatography of the latter on 25 g. of alumina and elution with petroleum ether (b.p. 30–60°) gave 204 mg. of colorless oil, which was used directly in the chromic acid oxidation.

A similar operation on 150 mg. of *trans*-Ia yielded 105 mg. of crude product which on chromatography on 9 g. of alumina led to 88 mg. of colorless hydrocarbon. The latter also was used for oxidation without further purification.

Ketones Ic. A solution of 50 mg. of chromic oxide in 0.1 ml. of water and 0.4 ml. of glacial acetic acid was added dropwise with stirring to a solution of 52 mg. of *cis*-Ib in 0.5 ml. of glacial acetic acid. The mixture was allowed to stand at room temperature for 6.5 hr. and then was diluted with 15 ml. of saturated brine solution and extracted with chloroform. The extract was washed three times with 10% sodium hydroxide solution and once with saturated brine solution, dried over anhydrous sodium sulfate, and evaporated. The resulting 30 mg. of residual neutral oil was chromatographed on 5 g. of alumina, yielding 9 mg. of colorless liquid ketone, infrared spectrum (chloroform): $C{=}O$ 5.88(s)μ, $C{=}C$ 6.26 (m)μ, by 9:1 petroleum ether–ether elution.

A similar operation on 126 mg. of *trans*-Ib, however for 11 hr. reaction time,[6] led to 105 mg. of neutral oil which on chromatography on 10 g. of alumina and 9:1 petroleum ether–ether elution gave 31 mg. of colorless liquid ketone, infrared spectrum (chloroform): $C{=}O$ 5.88(s)μ, $C{=}C$ 6.26(m)μ.

2,4-Dinitrophenylhydrazones. The derivative of *cis*-Ic melted at 182–183°, m.m.p. 179–183° with authentic sample[4] (m.p. 182.5–184°), identical infrared spectrum with that of an authentic sample.

The derivative of *trans*-Ic melted at 208–210.5°, m.m.p. 207°–210° with an authentic specimen[4] (m.p. 209.5–210.5°), identical infrared spectrum with that of an authentic specimen.

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[4] R. A. Barnes and M. T. Beacham, *J. Am. Chem. Soc.*, **77**, 5388 (1955) and preceding papers.

[5] The authors wish to express their gratitude to Professor Barnes for his gift of comparison samples.

[6] The *trans* hydrocarbon is over-oxidized more slowly than its *cis* isomer [*cf.* E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, **80**, 211 (1958)].

A Reinvestigation of the Action of Formaldehyde on 1,2- and 1,3-Hydroxyamines in the Pyrrolidine and Piperidine Series

RICHARD K. HILL AND LARRY J. LOEFFLER

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In 1913, Hess reported[1] a remarkable synthesis of the coca alkaloid hygrine (V) by heating the amino alcohol I with formaldehyde in acidic solution. Although direct comparison of his product with the natural base was not made at the time, the empirical formula and the close correspondence of the physical and chemical properties of the base and its derivatives[2] all supported his conclusion that a disproportionation reaction had occurred which resulted in simultaneous methylation of the nitrogen and oxidation of the secondary hydroxyl. Continued investigation showed that the reaction was apparently a general one for 1,2- and 1,3-hydroxyamines, and over a dozen examples were reported.[4,5]

It must be noted that except in two cases (those which gave hygrine and the isomeric ketone VI, both of which were reported to yield oximes) no experimental evidence was offered for the presence of either the *N*-methyl or the carbonyl group in the products. The structures were proposed solely on the empirical formulas of their picrates and the analogy to the initial reaction which had afforded hygrine. The only chemical behavior reported was first, that many of the reaction products gave a positive silver mirror test, and second, that with the exception of the two cases already mentioned, every effort to prepare carbonyl derivatives yielded only the corresponding derivative of formaldehyde plus the original hydroxyamine.

It is not surprising, in the face of this tenuous evidence, that it soon became apparent that some of Hess' products were incorrectly formulated. It was pointed out by both Kohn[6] and Rolfes[7] that the products from the reactions of aldehydes with diacetone alcohol amine were more likely tetrahydro 1,3-oxazines. In two other cases,[8,9]

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[1] K. Hess, *Ber.*, **46**, 4104 (1913).

[2] The picrate of the synthetic base was first reported to melt at 174°, although hygrine picrate melts at 149–150°; Hess regarded this discrepancy as due to differences in purity of the two samples. Some years later,[3] he reported that the original sample of the synthetic picrate now melted at 149–150°, and did not depress the melting point of authentic hygrine picrate.

[3] K. Hess and H. Fink, *Ber.*, **53**, 781 (1920).

[4] K. Hess, F. Merck, and C. Uibrig, *Ber.*, **48**, 1886 (1915).

[5] K. Hess and C. Uibrig, *Ber.*, **48**, 1974 (1915).

[6] M. Kohn, *Ber.*, **49**, 250 (1916).

[7] H. Rolfes, *Ber.*, **53**, 2203 (1920).

[8] K. Hess and A. Eichel, *Ber.*, **50**, 1407 (1917).

[9] K. Hess and W. Corleis, *Ber.*, **54**, 3010 (1921).