COMMUNICATIONS TO THE EDITOR

REDUCTION OF KETONES WITH DIPHENYLTIN DIHYDRIDE. A NEW TYPE OF HYDRIDE REDUCTION

Sir:

Recently van der Kerk, Luijten and Noltes have reported that organotin hydrides of the type R_3SnH (R = phenyl, n-propyl, *n*-butyl) add readily at 70–90°, via an apparently non-radical mechanism, to olefins substituted with groups such as alkyl, aryl, cyano, carbomethoxy, carboxamido, and aryloxy.[1] We attempted to bring about a similar reaction between diphenyltin dihydride and methyl vinyl ketone, reaction (1). However, in wet ether at room temperature in 15 hours, reaction (2) occurred instead.

$$(C_6H_5)_2SnH_2 + CH_2{=}CHCOCH_3$$

$$\longrightarrow (C_6H_5)_2Sn(CH_2CH_2COCH_3)_2 \qquad (1)$$

$$\longrightarrow (C_6H_5)_2Sn + CH_2{=}CHCHOHCH_3 \qquad (2)$$

The products were separated easily by virtue of the fact that the yellow diphenyltin which was formed is insoluble in ether. A 59% yield of pure methyl vinyl carbinol was isolated.

In the usual reductions of carbonyl compounds by metal hydrides a metal salt of the alcohol is formed by the addition $M - H + R_2C{=}O \rightarrow R_2CHOM$. A hydrolysis step is thus necessary in the isolation of the alcohol. The distinctive characteristic of the present reaction is that *two hydrogens* undergo uncatalyzed[2] transfer from tin to the carbonyl group leading directly to the alcohol—no hydrolysis step is required.

Diphenyltin dihydride selectively reduces the carbonyl group of α,β-unsaturated aldehydes and ketones as suggested by the above and the following examples. In each case the α,β-unsaturated alcohol was the only product isolated. The yield of pure product is indicated in parentheses: cinnamaldehyde (75%), mesityl oxide (60%), chalcone (75%), and crotonaldehyde (59%).

Simple carbonyl compounds which have been reduced include cyclohexanone (82%), benzophenone (59%), and benzaldehyde (62%). Camphor and 2-acetylcyclohexanone, on the other hand, are unaffected by diphenyltin dihydride under the same conditions in two days.

A substantial degree of stereoselectivity in this reduction is revealed by the following results: benzil yields 84% of pure *meso*-hydrobenzoin; *d*-carvone, 83% of carveols containing 97% *d-cis*-carveol (based on optical rotation); 4-*t*-butylcyclohexanone, 85% of 4-*t*-butylcyclohexanols containing about 90% *trans* isomer; 2-methylcyclohexanone, 83% of 2-methylcyclohexanols containing 78% *trans* isomer.

Further details on this and other reductions by organotin hydrides will be submitted later.

Acknowledgments.—We wish to express our appreciation to the Office of Ordnance Research for support of this research and to the Metal and Thermit Corporation for generous supplies of organotin compounds.

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Received June 10, 1958

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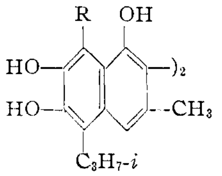
[1] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Applied Chem.*, **7**, 356 (1957).

[2] Uncatalyzed in the sense that a solid hydrogenation catalyst is not needed.

TOTAL SYNTHESIS OF GOSSYPOL

Sir:

Reaction of freshly prepared apogossypol[1,2] (I), 2,2′ - bi - 1,6,7 - trihydroxy - 5 - isopropyl - 3-methylnaphthyl, the very unstable degradation product of gossypol[2] (II), with N,N′-diphenylformamidine[3,4] ($C_6H_5NHCH{=}NC_6H_5$) gave a compound identical with dianilinogossypol[2,5] (III) prepared from gossypol by the action of aniline, m.p. and mixed m.p. 302° (dec.); infrared spectra (KBr) identical. Hydrolysis[6,7,8] of dianilinogossypol yields gossypol. Apogossypol hexamethyl ether has now been demethylated to apogossypol by the use of boron bromide.[9] Identification was established by infrared ($CHCl_3$) comparison and acetylation of the demethylated product. The latter was identical (infrared and mixed m.p.) with apogossypol hexacetate.[1] Since (a) reaction of N,N′-diphenylformamidine with phenols is reported always to introduce the entering group ($C_6H_5N{=}CH-$) ortho to a hydroxyl group[3] and (b) the structure of apogossypol and its hexamethyl ether[10] has been established by an unambiguous synthesis, the results described comprise a total synthesis of gossypol. The structure of gossypol (II), 2,2′-bi-8-formyl-1,6,7-trihydroxy-5-isopropyl-3-methylnaphthyl, formulated by Adams[2] as a



I, R = H
II, R = CHO
III, R = $C_6H_5N{=}C-$

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[5] Kindly supplied by Drs. A. M. Altschul and V. L. Frampton, Southern Regional Laboratory, U. S. D. A.

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[10] J. D. Edwards, Jr., and J. L. Cashaw, *ibid.*, **79**, 2283 (1957).