Homo-1,4-elimination

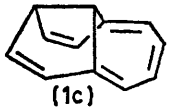
By TERUKIYO HANAFUSA,* SHINOBU IMAI, KATSUO OHKATA, HITOMI SUZUKI, and YOSHIKO SUZUKI
(*Chemistry Department, Faculty of Science, Hiroshima University, Higashi-senda-cho, Hiroshima* 730, *Japan*)

Summary 1,4-Dienes were prepared by the homo-1,4-elimination of αα′-dihydroxy derivatives of cyclopropanes with diphosphorus tetraiodide in the presence of pyridine.

THE unsaturated hydrocarbons (**1a**—**c**) and their analogues are of interest in a study of homoconjugation.[1] Cyclopropane derivatives of type (**2**) might be useful in the synthesis of such compounds, *via* reductive elimination.

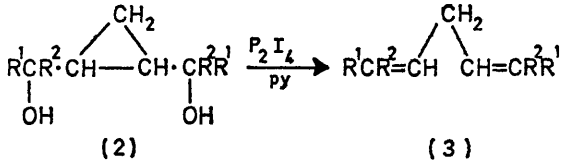

(1a)


(1b)


(1c)

Birladeanu *et al.*[2] reported an example of a similar elimination of a dichloride by lithium amalgam in the synthesis of tetramethylhomotropylidene. Here, we report a novel homo-1,4-elimination of 1,2-di-(α-hydroxybenzyl)cyclopropane and its analogue by the use of Kuhn–Winterstein reagent[3] to afford 1,4-dienes (**3**) (Scheme).

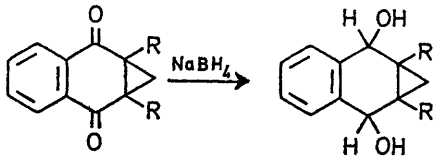
The cyclopropane (**2a**) has been prepared by $NaBH_4$ reduction of *trans*-1,2-dibenzoylcyclopropane starting from 1,3-dibenzoylpropane.[4] In the diol (**2a**), three diastereomers should be formed on reduction. The reduction product showed multiplets for the cyclopropyl protons and the α-protons in its n.m.r. spectra. Since neither a carbonyl stretching absorption band nor n.m.r. signals of the diketone were observed, the product was employed without further purification.



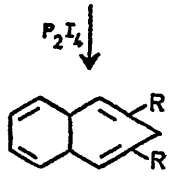
(2) (3)

SCHEME. a; R^1 = Ph, R^2 = H; b; R^1 = *p*-tolyl, R^2 = H; c; R^1 = *p*-anisyl, R^2 = H; d; R^1 = *p*-chlorophenyl, R^2 = H; e; R^1 = *p*-tolyl, R^2 = D.

To a solution of diphosphorus tetraiodide[5] in benzene was added a solution of the diol (**2a**) in pyridine at room temperature, then the mixture was heated under reflux for 1 h. Usual work-up gave an oil (54%) which was purified



(4) R=H
(5) R=Me



(6) R=H
(7) R=Me

by column chromatography. This oil was assigned as the *trans, trans*- diene (**3a**) from its mass, i.r., and n.m.r. spectral data. Substituted derivatives (**2b**—**d**) were similarly prepared and transformed by the same reaction into olefins (**3b**—**d**) in reasonable yields.

trans-1,2-Ditoluoylcyclopropane was reduced with $NaBD_4$ to give the dideuteriated diol (**2e**). Reduction as before gave the dideuteriated olefin (**3e**), m.p., 84—87°. The structure was characterized by its n.m.r. spectrum in CCl_4.

The analogous cyclic dihydroxy-compounds [(**4**) and (**5**)] were prepared by reduction of the corresponding homonaphthoquinones.[6] These diols were also stereoisomeric mixtures but underwent homo-1,4-elimination as before. The purified products were characterized as the 3,4-benzotropylidenes[7] (**6**) (**7**) from mass, i.r., and n.m.r. spectral data. In (**6**) 1,2-benzotropylidene contained *ca.* 20% of the 3,4-benzo-derivative which would have rearranged to the former under the reaction conditions.

It was also found that (**2a**) underwent similar elimination by another reductive reagents such as stannous chloride in acid. This elimination product, however, was a complex mixture including (**3a**) probably due to the high sensitivity of both the cyclopropane derivative and the product to the acid.

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[1] S. Winstein, *Quart. Rev.*, 1969, **23**, 141; P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 1425; L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, 1972, **94**, 4739.
[2] L. Birladeanu, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, 1970, **92**, 6387.
[3] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1928, **11**, 87.
[4] G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, 1963, **85**, 1001; I. Colon, G. W. Griffin, and E. J. O'Connell, *Org. Synth.*, 1972, **52**, 33.
[5] 'Gmelins Handbuch der anorganischen Chemie,' Verlag Chemie, 8 Aufl., 1965, 16, Phosphor Tl. C, S. 518.
[6] G. L. Buchanan and J. K. Sutherland, *J. Chem. Soc.*, 1956, 2620.
[7] G. Wittig, H. Eggers, and P. Duffner, *Annalen*, 1958, **619**, 10.