

the precipitate with plenty of water). (+)Co(*l*-pn)<sub>3</sub>(laurylsulphate)<sub>3</sub> was prepared following in principle the method for fractional crystallisation given by Dwyer, Garwan and Shulman,<sup>11</sup> but the purity was found to be even better than for the isomer prepared using chromatography if (-)Co(*l*-pn)<sub>3</sub>(laurylsulphate)<sub>3</sub> was removed by successive addition of sodium laurylsulphate. The solution remaining from the last precipitation thus gave a CD considerably higher than that reported by Mason<sup>7</sup> for the Sargeson sample.

The preparation of an oriented film has been described elsewhere.<sup>1</sup> The CD measurements were made as before.<sup>1,12</sup>

*Acknowledgement.* I would like to thank the Faculty of Science of the University of Lund and The Royal Physiographic Society in Lund for grants which made it possible to buy equipment and chemicals necessary for the syntheses. The Knut och Alice Wallenberg Stiftelse is also acknowledged for their gift, the CD instrument.

1. Larsson, R. and Nordén, B. *Acta Chem. Scand.* **24** (1970) 2681.
2. Mason, S. F. and Norman, B. J. *Proc. Chem. Soc.* **1964** 339.
3. Corey, E. J. and Bailar, J. C. *J. Am. Chem. Soc.* **81** (1959) 2620.
4. Nakatsu, K. *Bull. Chem. Soc. Japan* **35** (1962) 832.
5. Nakatsu, S., Saito, Y. and Kuroya, H. *Bull. Chem. Soc. Japan* **33** (1960) 98.
6. Iwasaki, H. and Saito, Y. *Bull. Chem. Soc. Japan* **39** (1966) 92.
7. Mason, S. F. and Norman, B. J. *J. Chem. Soc. A* **1966** 307.
8. Nordén, B. *Acta Chem. Scand. In press.*
9. Nordén, B. *Acta Chem. Scand. To be published.*
10. Nordén, B. *Acta Chem. Scand.* **23** (1969) 2925.
11. Dwyer, F. P., Garwan, F. L. and Shulman, A. *J. Am. Chem. Soc.* **81** (1959) 290.
12. MacCaffery, A. J., Mason, S. F. and Ballard, R. E. *J. Chem. Soc.* **1965** 2883.
13. Evans, M. G. and Nancollas, G. H. *Trans. Faraday Soc.* **49** (1953) 363.
14. Ogino, K. *Bull. Chem. Soc. Japan* **42** (1969) 447.
15. Larsson, R. *Acta Chem. Scand.* **16** (1962) 2460.
16. Cannon, C. G. *Spectrochim. Acta* **10** (1958) 341.
17. Dwyer, F. P., MacDermott, T. E. and Sargeson, A. M. *J. Am. Chem. Soc.* **85** (1963) 2913.

Received December 29, 1970.

*Acta Chem. Scand.* **25** (1971) No. 1

## On the Preparation of 1,4-Diphenylcyclohexa-1,3-diene

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In connection with our studies of non-transoid conjugated exocyclic dienes<sup>1</sup> we also prepared the endocyclic diene 1,4-diphenylcyclohexa-1,3-diene, which had not then been described. In the meantime, Courlot and Le Goff-Hays<sup>2</sup> have reported its synthesis by essentially the same method that we used. They describe, however, a byproduct never observed by us, while on the other hand we found that the 1,4-diene<sup>3</sup> appears as an intermediate in our synthesis.

When the elimination of water from 1,4-diphenyl-cyclohexane-1,4-diol is carried out in benzene solution containing *p*-toluenesulphonic acid, and the water removed by azeotropic distillation, there is always formed a mixture of three products. NMR spectroscopy shows clearly that these are 1,4-diphenylcyclohexa-1,3-diene (singlets at 6.55 and 2.78 ppm), 1,4-diphenylcyclohexa-1,4-diene (multiplets at 6.30 and 3.31 ppm), and *p*-terphenyl (singlet at 7.68 ppm). When the reaction is allowed to proceed until the theoretical quantity of water is removed, the proportion of *p*-terphenyl formed is much larger than if the reaction is stopped at an early stage. Also, the ratio of conjugated to nonconjugated diene increases with time.

This easy dehydrogenation to *p*-terphenyl under acidic condition is in accord with the reported<sup>2</sup> formation of *p*-terphenyl by simply passing the 1,3-diene through alumina. A disproportionation can be excluded, since there is no indication of diphenylcyclohexene or diphenylcyclohexane in the NMR spectrum.

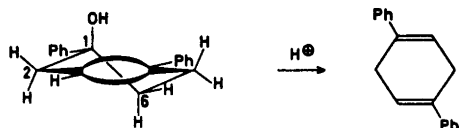
It proved impossible to separate the formed *p*-terphenyl from the diene mixture by crystallization, by chromatography, or by zone-melting. A product free from *p*-terphenyl can, however, be obtained if the complex from the reaction of cyclohexane-1,4-dione and phenyl lithium<sup>4</sup> is stirred directly with 50% aqueous sulfuric acid. A vigorous reaction takes

place, and crystals of the diene mixture precipitate after cooling and are filtered off. These yellow crystals contain no *p*-terphenyl even after 3 years' storage. Ether extraction of the filtrate yields further crystal crops, but this product is contaminated with *p*-terphenyl and is converted completely to grey-white *p*-terphenyl on long storage.

The relative quantities of 1,3- and 1,4-diene depend on the reaction time as follows:

Reaction time, min	Total yield, %	Non-conjugated, %	Conjugated, %
15	50	69	31
120	42	50	50
240	30	27	73

From this trend it seems likely that the initial dehydration product is the non-conjugated diene, and that subsequent isomerization takes place to give the conjugated diene. Complete conversion of the mixture to the conjugated isomer can be effected by refluxing in *t*-butanol containing potassium *t*-butoxide, so that it is clear that the thermodynamic equilibrium is all over on the conjugated side. This contrasts with the situation in cyclohexadiene itself, where hardly any enthalpy difference exists between the 1,3- and the 1,4-isomer.<sup>6</sup>



The preferential formation of the 1,4-isomer from the intermediate 1,4-diphenylcyclohex-3-en-1-ol in the second dehydration step suggests that stereoelectronic controlling factors are at work. In the half-chair conformation of this cyclohexene derivative only the 1-6 bond is perfectly staggered<sup>6</sup> and therefore only the axial proton in 6-position is correctly aligned

*anti* to the out-going hydroxyl group. The hydrogens in 2-position are of course more acidic, and would lead to the more stable product, but none of these are coplanar with the hydroxyl group.

**Experimental.** *1,4-Diphenylcyclohexadiene (isomer mixture).* Phenylation of cyclohexane-1,4-dione was carried out essentially as described by Müller and Sok.<sup>4</sup> To a stirred solution of phenyllithium (34 g=0.4 mol) in dry ether (250 ml) was added cyclohexane-1,4-dione (10.8 g=0.1 mol).

This solution was cooled to 0°C, and 50% sulphuric acid (175 ml) added as rapidly as the reflux would permit. After all the acid had been added, the reaction mixture was cooled, and precipitated yellow crystals were filtered off, washed with water, and dried. The filtrate was extracted with ether, and the ether solution washed with sodium carbonate and dried over sodium sulphate. After evaporation of the ether, a yellow solid was left which contained small amounts of *p*-terphenyl. The total yield of the isomer mixture was 10.5 g (=50%).

*1,4-Diphenylcyclohexa-1,3-diene.* The isomer mixture (0.2 g) was refluxed for 4 h in *t*-butanol (50 ml) containing potassium *t*-butoxide (1.4 g). After cooling, water was added, and the reaction mixture was extracted with benzene. The organic layer was dried over sodium sulphate and evaporated. Recrystallization from benzene gave yellow flakes (0.15 g=75%), m.p. 182°C (lit. 179–180°C<sup>2</sup>). Ultraviolet maxima in heptane were at 345 nm (log  $\epsilon$  4.1) and at 235 nm (log  $\epsilon$  3.7).

- Dale, J. and Kristiansen, P. O. *Chem. Commun.* **1968** 1293.
- Courlot, P. and Le Goff-Hays, O. *Bull. Soc. Chim. France* **1968** 3401.
- Griffin, C. E. and Witschard, G. *J. Org. Chem.* **27** (1962) 3334.
- Müller, E. and Sok, G. *Ber.* **70** (1937) 1990.
- Bates, R. B., Carnighan, R. H. and Staples, C. E. *J. Am. Chem. Soc.* **85** (1963) 3030.
- Elie, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Wiley, New York 1965, p. 109.

Received December 19, 1970.