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CIS- AND TRANS-4,6-DI-T-BUTYLCYCLOHEXANE-1,3-DIONE

N.W.J. Pumphrey and M.J.T. Robinson
The Robert Robinson Laboratories,
University of Liverpool

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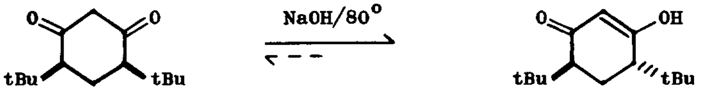
IN the course of preparing derivatives of cyclohexane required as intermediates for syntheses of alicyclic and heterocyclic compounds of fixed conformation we have observed an unprecedented cis to trans isomerisation of a 1,3-dialkylcyclohexane derivative.

Catalytic hydrogenation of 4,6-di-t-butylresorcinol in alkaline solution over Raney nickel at 20° and 100 atm. during 4 days gave a nearly quantitative yield of cis-4,6-di-t-butylcyclohexane-1,3-dione (I), m.p. 50-51°, which is not enolised in the solid state and which shows a much lower tendency to enolise in solution than is usual for cyclohexane-1,3-diones. The dione (I) is converted by dilute sodium hydroxide into the trans-isomer (II) in 95% yield. The trans-dione (II), m.p. 136-137°, is enolised in the solid state, and in polar



I   II

solvents its degree of enolisation is similar to other enolisable cyclohexane-1,3-diones. Both diones were converted by sodium hypobromite in methanol into 2,2-dibromo-derivatives and diazomethane into enol methyl ethers. The configurations of the two 2,2-dibromodiketones were established by their proton magnetic resonance spectra in deuterochloroform. The $C_{(4)}$-, $C_{(5)}$-, and $C_{(6)}$-protons form an A_2XY group in the *cis* isomer and an A_2X_2 group in the *trans* isomer, as would be expected if the latter is inverting rapidly; the less clearly resolved spectra of the parent diketones confirm these configurations. It is interesting that the $C_{(2)}$-protons in each isomer gave a sharp singlet which was apparently due to accidental equivalence rather than to rapid chemical exchange since the addition of 1-2 molecular equivalents of methanol did not alter the spectra of the diketones.

Although the isomerisation in alkali relates to the enolate anions while the enolisation equilibria involve changes in the bonding of the oxygen atom, it is clear that anomalies must be expected in chemical and conformational equilibria involving 2-t-butylcyclohexanones if there are changes in the relative positions of the t-butyl group and the oxygen atom. We believe, therefore, that *cis*- and *trans*-2,4- and -2,6-di-t-butylcyclohexanone [1,2] are most unsuitable models for the

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[1] N.L. Allinger and H.M. Blatter, *J. Amer. Chem. Soc.* **83**, 994 (1961).

[2] B. Rickborn, *ibid.* **84**, 2414 (1962).

chair and boat conformations of cyclohexanone, and we are restudying the conformational equilibrium in cyclohexanone.[3]

Satisfactory analyses and spectra were obtained for all the compounds mentioned. Proton magnetic resonance spectra were determined with a Varian A60 spectrometer.

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[3] W.D. Cotterill, N.W.J. Pumphrey and M.J.T. Robinson, unpublished work.