Synthesis and Structure of 2-t-Butylcyclohexane-1,3-dione†

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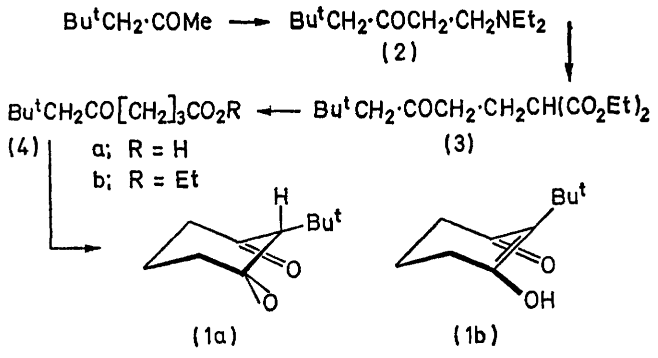
Summary 2-t-Butylcyclohexane-1,3-dione has been prepared; spectral studies suggest that it exists exclusively as the keto-tautomer (**1a**).

Many publications have dealt with the preparation of 2-substituted cyclohexane-1,3-diones,[1] which play a key role in the synthesis of steroid intermediates.[2] We herein report the preparation of the as yet elusive 2-t-butyl-1,3-cyclohexanedione (**1**), and its spectral characterization.

The hexanone (**2**), prepared from 4,4-dimethylpentan-2-one,[3] dimethylamine hydrochloride, and paraformaldehyde, was quantitatively converted into an oily methiodide, which when treated with diethyl sodiomalonate gave the oxo-diester (**3**).‡ Hydrolysis and decarboxylation of (**3**) afforded (**4a**), which was esterified giving (62% overall) the ethyl octanoate (**4b**), b.p. 93—96° at 1 mmHg.



Cyclization of (**4b**) with NaH in ether at reflux for 8 h afforded 2-t-butylcyclohexane-1,3-dione (42%), m.p. *ca.* 15—17°, b.p. 109—110° at 3 mmHg; δ ($CDCl_3$): 3·04 (s, 2-H), 2·22 (dd, CH_2CO, J 6·5 Hz), 1·5 (m, $CH_2{\cdot}CH_2{\cdot}CH_2$), and 1·05 (s, CMe_3) p.p.m. Attempted deuterium exchange of C(2)-H under various conditions failed; however, after prolonged reaction with MeOD–D_2O–OD^-, (**1**) afforded only

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† For previous paper in series: "Chiral Cyclic Olefins," see ref. 1(a).

‡ Analytical and spectral (n.m.r., i.r., m.s.) data were in accord with structural assignment.

the ring-opened oxo-acid (4; R = D) Further evidence was obtained from the simple 6-line ^{13}C n.m.r. spectrum [$\delta(C_6H_6$; Me_4Si lock): +18 (C-5), +29 (CMe_3), +30·5 (CMe_3), +33·9 (C-2), +41·3 (C-4,6), and +205 (C=O)] as well as 100 MHz ^1H n.m.r. spectra utilizing Eu(fod),[4] from which a first-order fine structure of signals for all the ring protons can be observed. The i.r. [$\nu_{max.}$ (film) 1690 and 1720 cm^{-1}] and u.v. [$\lambda_{max.}$ (hexane) 282 ($\epsilon < 100$)] spectra of (**1**) exhibit a characteristic non-enolic β-dicarbonyl absorption, as in 2,2-disubstituted cyclohexane-1,3-diones.[5]

Thus, these spectral data, as well as the unusually low m.p. (*e.g. ca.* 150—200° lower than for other alkyl substituents[1a]), indicate exceptional predominance (>98%) of the keto-tautomer (**1a**). No evidence for the presence of the enol (**1b**) was found.

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[1] Alkyl substituents: (a) G. R. Newkome, L. C. Roach, and R. C. Montelaro, *J. Org. Chem.*, 1972, **37**, 2098, and references cited therein; (b) H. Schick and G. Lehmann, *J. prakt. Chem.*, 1968, [4], **38**, 391; H. Schick, G. Lehmann, and G. Hilgetag, *Angew. Chem., Internat. Edn.*, 1967, **6**, 80, 371; (c) H. Stetter and W. Dierichs, *Chem. Ber.*, 1952, **85**, 61; aryl substituents: B. E. Betts and W. Davey, *J. Chem. Soc.*, 1961, 3333; H. Born, R. Pappo, and J. Szmuszkovicz, *ibid.*, 1953, 1779.

[2] See U. Eder, G. Sauer, and R. Wiechert, *Angew. Chem. Internat. Edn.*, 1971, **10**, 498, and references 1–5 cited therein.

[3] E. H. Man, F. C. Frostick, jun., and C. R. Hauser, *J. Amer. Chem. Soc.*, 1952, **74**, 3228.

[4] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

[5] B. Eistert and W. Reiss, *Chem. Ber.*, 1954, **87**, 92; D. J. Crispin, A. E. Vanstone, and J. S. Whitehurst, *J. Chem. Soc.* (*C*), 1970, 10.