The 2,4-Dibenzylidenecyclobutanone Anion: a Unique Intermediate Leading to 2,4-Dibenzylidenecyclobutanone Dimer

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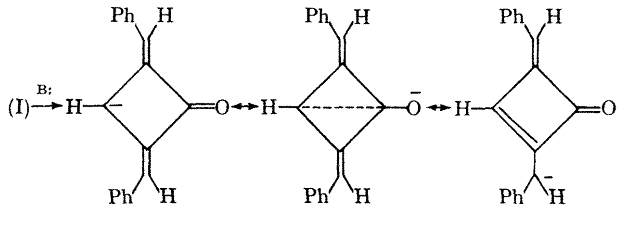
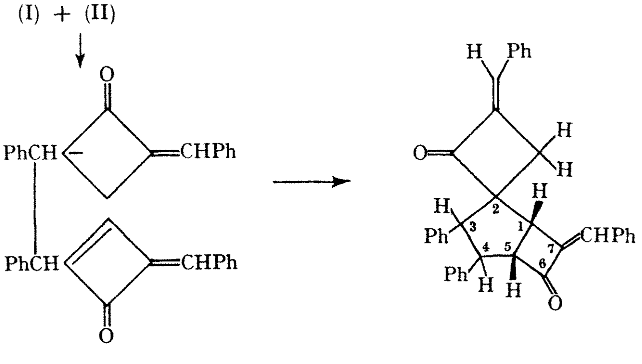
Summary The title non-classical enolate anion is involved in a base-catalysed reaction leading to a dimer, $C_{36}H_{28}O_2$, whose structure has been established.

SELF-CONDENSATION of a 2% solution of 2,4-dibenzylidenecyclobutanone (I) in 0·001M-ethanolic sodium hydroxide (45°, 10 min.; 25°, 50 min.) produces pale yellow spears, m.p. 191—192°, of a dimer, $C_{36}H_{28}O_2$ (31%); ν_{KBr} 1746, 1734 (C=O), 1638 cm.$^{-1}$ (C=C); λ_{max} (EtOH) nm. (ϵ) 318 (50,500), 233 (21,400), 227 (20,500), 220sh (25,600); M^+ 492. The dimer forms a mono-2,4-dinitrophenylhydrazone, m.p. 279—280° (prisms from ethylene dichloride); ν_{KBr} 1735 cm.$^{-1}$ (C=O). Benzaldehyde was produced by osmium tetroxide–sodium periodate oxidation of the dimer. These data, when compared with those of Conia[1] and Thieme[2] on (I) and 2-benzylidenecyclobutanone, in addition to the n.m.r. spectra of the dimer and certain of its deuterioderivatives, support dimer structure (IV), 7-benzylidene-3,4-diphenyl-2-spiro-(2-oxo-3-benzylidenecyclobutyl)-bicyclo[3,2,0]heptan-6-one. Another dimer of (I) (m.p. 223—235°; structure undetermined) has been reported by Thieme.[2]

Our previous results on base-catalysed self-condensation of $\alpha\beta$-unsaturated ketones[3] suggest that the dimerization occurs by Michael addition of (I), anion, (II), to (I), followed by Michael cyclization of acyclic intermediate (III) to (IV).



(IIa) (IIb) (IIc)



(III) (IV)

Anion (II) is unique in that, unlike other $\alpha\beta$-unsaturated ketone derived anions, its carbonyl group cannot participate in classical enolate anion resonance. However, delocalization of the negative charge on oxygen is very likely involved in its stabilization. It does not undergo rapid deuterium exchange under the conditions of the dimerization reaction since in EtOD the dimer product is found to have but one deuterium at C-5, as required by the mechanism; the rate-limiting step appears to be proton abstraction from (I).

The n.m.r. spectrum† of this C-5 monodeuterio-dimer, $C_{36}H_{27}DO_2$, was simplified in the bicycloheptanone ring proton region relative to the spectrum of (IV). The four ring protons which appear in (IV) as a complex multiplet are reduced to three: the two benzylic protons at C-3 and C-4 appear as an AB quartet at τ 5·72 and 5·98 (J 7 Hz) and the C-1 proton as a doublet at τ 5·86 (J 1 Hz) due to weak coupling to the C-7 benzal vinyl proton. The phenyl protons (20) appear as three sharp peaks at τ 2·75, 2·82, and 2·88; the methylene group of the spirocyclobutanone ring as a triplet at τ 7·20 (J 2·5 Hz) due to coupling with the adjacent benzal vinyl proton which appears as a triplet at τ 3·48 (J 2·5 Hz).

[$^2H_{10}$]-2,4-Dibenzylidenecyclobutanone (two =CH, τ 2·89, triplet, J 2·5 Hz; CH_2, 6·23, triplet, J 2·5 Hz), prepared from C_6D_5CHO, dimerized in ethanol to $C_{36}H_8D_{20}O_2$, which revealed the C-7 benzal vinyl proton as a doublet at τ 2·79 (J 1 Hz). [$^2H_{12}$]-2,4-Dibenzylidenecyclobutanone, (CH_2, τ 6·22, singlet), prepared from [$^2H_6$]-benzaldehyde, dimerized in EtOD to $C_{36}H_3D_{25}O_2$ having the cyclobutanone ring methylene at τ 7·17 (doublet, J 1·7 Hz) and the C-1 ring proton at τ 5·73 (singlet). Dimerization of [$^2H_{12}$]-2,4-dibenzylidenecyclobutanone in ethanol gave $C_{36}H_4D_{24}O_2$ having the ring cyclobutanone methylene at τ 7·33 (measurement in 1 : 1-[$^2H_8$]-toluene–$CDCl_3$; doublet, $J < 1$ Hz) and the C-1, C-5 protons as an AB quartet (τ 5·93, 6·12, J 9 Hz). Dimers of (I) having phenyl substituents have been prepared which show n.m.r. spectra very similar to that of (IV).

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† N.m.r. spectra determined in deuteriochloroform with tetramethylsilane internal standard with Varian A-60 spectrometer, except as noted.

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[2] P. Thieme, *Chem. Ber.*, 1968, **101**, 378.
[3] A. T. Nielsen and D. W. Moore, *J. Org. Chem.*, 1969, **34**, 444; A. T. Nielsen and S. Haseltine, *ibid.*, 1968, **33**, 3264; A. T. Nielsen, H. Dubin, and K. Hise, *ibid.*, 1967, **32**, 3407; A. T. Nielsen and H. Dubin, *ibid.*, 1963, **28**, 2120.