An Aberrant Michael Condensation

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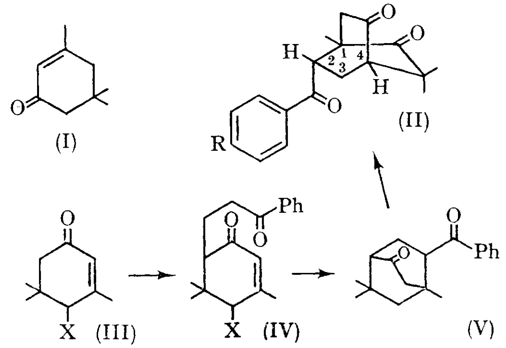
IN our studies on the scope and mechanism of the thermal Michael condensation,[1,2] we have treated β-dimethylaminopropiophenone with isophorone (I) at its boiling point for 1 hr. Distillation afforded a red oil (71%), which, on trituration with ether, yielded a colourless crystalline product* ($C_{18}H_{20}O_3$) of m.p. 183° (methanol) accounting for 35—40% of the distillate. This product showed $\nu_{CO}(CCl_4)$ 1733 and 1688 cm.$^{-1}$ and Ph·CO· absorption in the ultraviolet region. Its n.m.r. spectrum showed three singlet resonances (τ 8·72, 8·91, and 9·01) and a sharp 1 × H triplet at τ 6·17 (J = 8·8 c./sec.), but no vinylic signal. On this evidence we were unable to formulate the product: in particular we were unable to account for the extra oxygen atom or to assign the low-field triplet signal. An analogous product* ($C_{18}H_{19}O_3Br$), m.p. 173—174° (methanol), which showed the same spectroscopic features, was formed by the reaction of isophorone with β-dimethylamino-*p*-bromopropiophenone and has been examined by single crystal *X*-ray methods using three-dimensional data. Its structure is as shown (II; R = Br) and its halogen-free analogue is thus (II; R = H).

Crystals of (II; R = Br) are monoclinic, space group $P2_1/c$, with 4 molecules in a unit cell of dimensions a = 17·71, b = 9·25, c = 10·63 Å, β = 106·5°. Some 2000 independent structure amplitudes were derived from equi-inclination Weissenberg photographs taken with a small needle crystal rotating about c. The position of the heavy atom was found by Patterson methods; the other non-hydrogen atoms were found from the first electron-density distribution derived from bromine phases and observed amplitudes. The atomic parameters have been refined by further electron-density calculations and by full matrix, least squares methods. R is now 0·13, and further refinement is in progress.†



Even with the knowledge of the structure, a confident assignment of the low-field triplet is not possible, but this detail was resolved by the observation that after deuterium exchange (D_2O–OD^-) the signal disappeared. It can therefore be assigned to the C-2 proton, strongly deshielded by a conformationally frozen aroyl group. A study of molecular models confirms that non-bonded interactions severely limit rotation about the

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* Acceptable analytical figures were obtained.

† Using computer programmes devised by Professor D. W. J. Cruickshank, Dr. J. G. Sime, D. McGregor, K. W. Muir, R. Pollard, J. G. F. Smith, and other members of the Glasgow Crystallography Group.

CO–C-2 bond and although the aromatic ring is free to rotate about the Ph–CO bond [the aromatic proton signal in (II; R = Br) is a symmetrical A_2B_2 quartet] the C-2 proton is permanently in the deshielding zones of the C=O and the aromatic ring. The extra carbonyl group arises from peroxide or hydroperoxide present in the original sample of isophorone, for freshly purified material yields products of the expected molecular weight,[2] and the base-catalysed conversion of hydroperoxides into ketones is well authenticated.[4] Aside from this, the reaction is remarkable as a double Michael reaction in which the isophorone functions in turn both as donor and acceptor molecule (*viz.* III → IV → V; X = O_2H or = O), decomposition of the hydroperoxide occurring at some point in the sequence. The participation of αβ-enones as donors is well known,[5] but in the present instance, the orientation of the product (IV) is strikingly abnormal and appears to be equally abnormal in peroxide-free reactions on αβ-unsaturated ketones[2] under thermal Michael conditions.

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