The Acetylation of Homo-enolate Anions: A New Synthesis of Cyclopropyl Acetates

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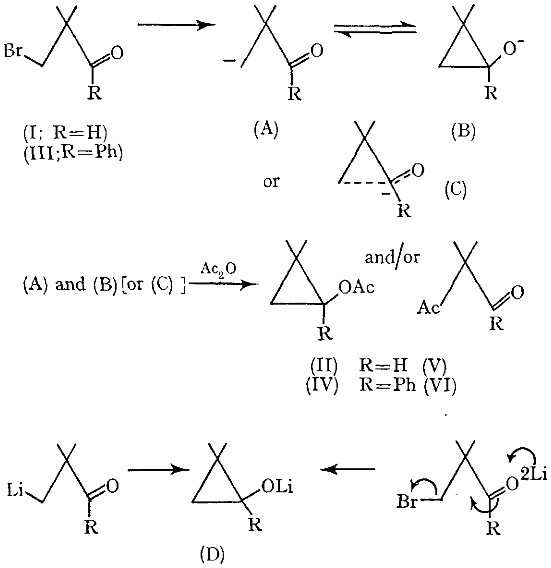
NICKON *et al.* have invoked the concept of homo-enolisation to account for the racemisation, by strong base at elevated temperatures, of optically active camphenilone.[1] In order to study the implications of this concept we have attempted to generate homo-enolate anions by the action of an alkali metal on a β-halogenated aldehyde (I) or ketone (III). Acylation of the anion could give two products (II) and (IV) or (V) and (VI) but only the cyclopropyl acetates (II) and (IV) were isolated.



Oxidation of 3-bromo-2,2-dimethylpropanol,[2] by the method of Barton,[3] gave 3-bromo-2,2-dimethylpropionaldehyde (I)† (50%)[4] b.p. 62—68°/23 mm. Slow addition of this bromoaldehyde, in ether, to a stirred suspension of finely cut lithium, in ether under nitrogen, at 10° during 6 hours and subsequent addition of the filtered solution to an excess of acetic anhydride gave, after work-up and distillation (100°/26 mm.), 2,2-dimethylcyclopropyl acetate (II)† (40—60% $\nu_{\max}^{\text{film}}$ 1740, 1230 cm.$^{-1}$, $\delta_{\text{Me}_4\text{Si}}^{\text{CCl}_4}$ 1·05, 1·03 (2, s, 6H, *gem*-Me) 1·97 (s, 3H, —OCOMe) ABX pattern, 4 peaks centred at δ 3·68 (1H X portion, >CHOCO—), 6 peaks 1·03—0·41 (≃ 2H AB portion, ring —CH$_2$). The structure was confirmed by a comparison of the spectra with those of an authentic sample prepared by Baeyer–Villiger oxidation[5] of 2,2-dimethylcyclopropyl methyl ketone.[6] Treatment of 3-bromo-2,2-dimethylpropiophenone (III)[4] under similar conditions produced 2,2-dimethyl-1-phenylcyclopropyl acetate (IV) (49%), confirmed by independent synthesis by the method of Freeman.[7]

It is interesting to enquire whether the intermediate lithium homo-enolate anion exists as an equilibrium mixture of two anions (A) and (B), as a delocalised anion (C) (subsequent acetylation being kinetically controlled‡) or as a covalent compound (D). The anion (D) could arise by either the internal attack of an alkyl-lithium on the carbonyl group or by addition of electrons to the carbonyl group followed by an intramolecular alkylation (see Scheme).

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† Analytical figures consistent with this formula have been obtained.

‡ Preliminary experiments indicate that protonation with water or boric acid probably gives the corresponding cyclopropanol. (*cf.* C. H. De Puy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, 1964, **29**, 2813). We have noted that 2,2-dimethylcyclopropanol has recently been prepared by this method (U. Schöllkopf, J. Paust, Ali Al-Azrak, and H. Schumacher, *Chem. Ber.*, 1966, **99**, 3391).

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