3-Bromomethylindene-2-carboxylic Acid

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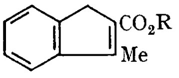
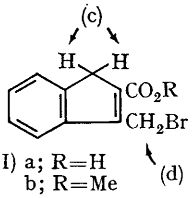
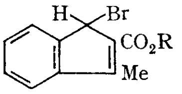
3-BROMOMETHYLINDENE-2-CARBOXYLIC ACID (IIa), required as a possible intermediate in the preparation of 1-hydroxymethylindane-2-carboxylic acid, can be prepared by a method based on that used for the preparation of 3-methylindene-2-carboxylic acid (Ia)[1] wherein ethyl α-benzylacetoacetate is treated with cold, concentrated sulphuric acid. Ethyl γ-bromo-α-benzylacetoacetate dissolved in cold, concentrated sulphuric acid, left for a few hours and then poured into ice and water produced a bromo-acid, m.p. 245°, with decomposition, which gave the correct analysis for the required compound (IIa). This melting point was the same as that of a bromo-acid made by Roser (*loc. cit.*) by the action of bromine upon an acetic acid solution of his original 3-methylindene-2-carboxylic acid, and to which he assigned the structure 1-bromo-3-methylindene-2-carboxylic acid (IIIa). The bromo-acid was therefore prepared by Roser's method and then appeared to be identical with the bromo-acid prepared as described above; mixed melting-points, accompanied by decomposition, were unchanged and the infrared spectra were identical. It was also found that the methyl esters of the bromo-acids prepared as above appeared identical with each other and with the bromo-ester obtained by brominating in chloroform solution the methyl ester of 3-methylindene-2-carboxylic acid.



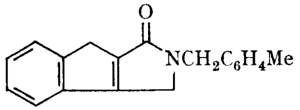
(I) a; R=H
b; R=Me



(II) a; R=H
b; R=Me



(III) a; R=H
b; R=Me



(IV)

An acid of the structure (IIa) might be expected to form a lactone readily but the bromo-acid concerned did not so react. However a lactam (IV) corresponding to this lactone was readily prepared. The bromomethyl acid readily reacted with *p*-toluidine to form the 3-*p*-toluidinomethyl acid whose toluene-*p*-sulphonyl derivative when treated with cold concentrated sulphuric acid gave a compound to which the structure (IV) was assigned. An isoindolinone, assigned a similar structure has been prepared from phthalide[2] so that (IV) may be regarded as derived from the hitherto unprepared lactone and this in turn supports the structure (IIa) for the parent bromo-acid rather than the structure (IIIa) assigned by Roser (*loc. cit.*).

These conclusions are supported by evidence from the n.m.r. spectra and I am indebted to Dr. D. H. Williams for the following report on the spectra of the three compounds (Ib), (IIa), and (IIb).

"The structures assigned to (Ib) and (IIa) are supported in some detail by their n.m.r. spectra. The spectrum of (Ib) contains a four-proton multiplet centred at τ 2·7 p.p.m. (aromatic protons) and a three-proton singlet at τ 6·26 p.p.m. (methoxyl protons). A three-proton triplet ($J \sim$ 2·5 c./sec.) is evident at τ 7·54 p.p.m. and a two-proton quartet ($J \sim$ 2·5 c./sec.) at τ 6·49 p.p.m.; these signals are assigned to the vinylic methyl group and the methylene protons, respectively, the splitting arising due to a pronounced mutual homoallylic coupling.

The spectrum of (IIa) in deuterated dimethyl sulphoxide solution contains signals due to four aromatic protons as a multiplet in the τ 2·2—2·6 p.p.m. region, and two two-proton singlets at τ 4·88 and 6·22 p.p.m., associated with protons c and d respectively (see IIa); this spectrum rules out the alternative structure (IIIa) for the bromo-acid. Attention is drawn to the large difference in the homoallylic coupling in (Ib) and (IIa). Also, no significant homoallylic coupling is observed between the protons c and d of the methyl ester (IIb) (spectrum run in deuterochloroform) derived by esterification of (IIa)."

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[1] (a) H. von Pechmann, *Ber.*, 1883, **16**, 516; (b) W. Roser, *Annalen*, 1888, **247**, 157.

[2] D. H. Peacock, *J. Chem. Soc.*, 1951, 891.