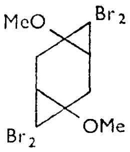
243. 4-*Hydroxybenzocyclobuten*-1-*one and its Derivatives.*

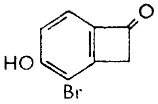
By G. M. ISKANDER and F. STANSFIELD.

4-Hydroxybenzocyclobuten-1-one (IV) was obtained by catalytic hydrogenation of the 3-bromo-derivative [1] (II), the synthesis of which was simplified. These compounds, with aqueous sodium hydroxide, gave the corresponding *o*-toluic acid derivatives (V, R = H and R = Br, respectively) by fission of the cyclobutenone ring. Like carboxylic acids, of which they are vinylogues, they are probably associated.

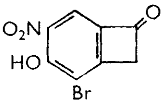
THE preparation of the 3-bromo- (II) and 3-bromo-5-nitro- (III) derivatives of 4-hydroxybenzocyclobutenone from the bis(dibromocarbene) adduct (I) by prolonged boiling with aqueous alcoholic silver perchlorate or nitrate, respectively, has already been reported.[1] The former compound (II) has now been obtained much more easily, though in somewhat lower yield, by allowing a solution of the adduct (I) and silver sulphate in 98% sulphuric acid to stand at room temperature for 24 hr. Precipitation of silver bromide occurred rapidly on mixing.



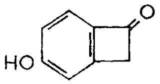
(I)



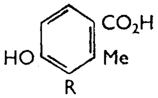
(II)



(III)



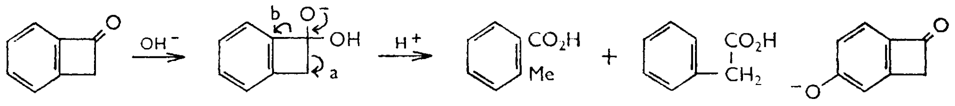
(IV)



(V)

Catalytic hydrogenation of the bromo-compound (II) in ethanol with palladium on charcoal gave 4-hydroxybenocyclobuteneone (IV), the structure of which is substantiated by u.v., i.r., and n.m.r. spectra. Solutions of this compound, on warming in presence of air and acid, gave insoluble polymeric material, though it is stable in the solid state. Reduction of the bromo-derivative (II) with nickel–aluminium alloy in aqueous sodium hydroxide solution gave 4-hydroxy-2-methylbenzoic acid (V, R = H).

Cava and Muth [2] have shown that the parent compound, benzocyclobutenone (VI), readily undergoes fission with aqueous sodium hydroxide solution at room temperature by addition of hydroxyl ion and ring-opening by each of two routes, (a) and (b), giving *o*-toluic and phenylacetic acids. We found that alkaline fission of 4-hydroxybenzocyclobutenone (IV) gave only the toluic acid derivative (V, R = H), presumably because in alkaline solution route (b) is excluded, owing to the high electron density on the para-position of the phenoxide ion (VII). This effect would also be expected to oppose the addition of hydroxyl ion to the carbonyl group, thereby retarding fission, and this was observed. The hydroxy-compound (IV) was converted into the acid (V, R = H) only to the extent of *ca.* 10% at room temperature in 10% sodium hydroxide solution during 48 hr., but conversion of more than 95% occurred on boiling for 45 min. By contrast, the bromohydroxy-compound (II) gave the acid (V, R = Br) very rapidly, fission being complete in 24 hr. at room temperature with the reagent, thus indicating a similar rate to that found by Cava [2] for the unsubstituted compound (VI).



(VI) (VII)

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[1] Birch, Brown, and Stansfield, *J.*, 1964, 5343.

[2] Cava and Muth, *J. Amer. Chem. Soc.*, 1960, **82**, 652.

Although these hydroxy-ketones (II and IV) gave normal dinitrophenylhydrazones, they are vinylogues of carboxylic acids and dissolve in potassium hydrogen carbonate solution. Like carboxylic acids, they are probably associated, as shown by, *e.g.*, their high melting points and by their infrared spectra as Nujol mulls. In the latter, the hydroxyl stretching frequencies of both these compounds occur as broad bands with many minor peaks between 2800 and 2100 cm.$^{-1}$, as with dimeric carboxylic acids,[3] though covering a wider range. This association would also explain the low frequency of the carbonyl stretching vibrations which appear as strong multiplets centred at 1730 and 1720 cm.$^{-1}$ for the ketones (II) and (IV), respectively. It is significant that the nitro-compound (III), in which association is probably prevented by the large substituents on both sides of the hydroxyl group, gives a single carbonyl peak at much higher frequency (1770 cm.$^{-1}$), whilst 3-bromo-4-methoxybenzocyclobutenone [1] absorbs at 1750 cm.$^{-1}$. Benzocyclobutenone also shows a doublet [2] at 1773 and 1755 cm.$^{-1}$. The nitro-compound (III) shows weak absorption, characteristic of a chelated hydroxyl group centred at 3100 cm.$^{-1}$, and minor peaks below 2800 cm.$^{-1}$ are absent.

The ultraviolet spectra, in ethanol, are complex, like that of benzocyclobutenone.[2]

EXPERIMENTAL

3-*Bromo*-4-*hydroxybenzocyclobutenone*.—4,4,8,8-Tetrabromo-1,5-dimethoxytricyclo[5,1,0,0^{3,5}]-octane [1] (10 g.) and silver sulphate (15 g.) were dissolved by shaking with sulphuric acid (98%; 55 ml.) in a stoppered flask, and the solution, from which silver bromide began to precipitate almost immediately, was allowed to stand in the dark at room temperature for 24 hr. The product was poured, with stirring, on to crushed ice (250 g.), sodium chloride (20 g.) stirred in, and the mixture filtered on a sintered glass funnel. The solid was thoroughly extracted with boiling water (1·5 l.) (charcoal) and the hot filtrate allowed to cool, finally in the refrigerator. The bromo-compound was filtered off, washed with water, and dried, giving almost colourless crystals (1·55 g., 35% theoretical) identical with the product previously reported.[1]

With Brady's reagent, the compound gave a 2,4-*dinitrophenylhydrazone* forming small orange-coloured crystals from ethyl acetate, m. p. 251—252° (Found: C, 42·7; H, 2·5; Br, 20·1; N, 14·5. $C_{14}H_9BrN_4O_5$ requires C, 42·75; H, 2·3; Br, 20·35; N, 14·3%), $\lambda_{max.}$ ($CHCl_3$) 383 mμ, $\varepsilon_{max.}$ 33,000.

4-*Hydroxybenzocyclobutenone*.—The above bromo-compound (2·13 g.) dissolved in absolute ethanol (70 ml.) was hydrogenated at room temperature and pressure in presence of acid-washed charcoal (0·5 g.), a solution of palladium chloride (0·2 g.) in dilute hydrochloric acid (0·1N; 20 ml.) being added in portions until there was no further hydrogen uptake (total uptake *ca.* 1 mol.). After filtration, the filtrate and washings were rapidly concentrated in vacuum to *ca.* 8 ml. (undue heating and exposure to air gave polymeric material), cooled in ice, and the crystalline product filtered off, washed with a little cold alcohol, and dried (0·90 g.). On recrystallisation from boiling water (charcoal), then from benzene, 4-*hydroxybenzocyclobutenone* formed stable colourless leaflets, m. p. 184° (Found: C, 71·6; H, 4·7. $C_8H_6O_2$ requires C, 71·6; H, 4·5%), giving a violet ferric chloride colour in aqueous solution, $\lambda_{max.}$ EtOH (in mμ; $\varepsilon_{max.}$ in parentheses): 226 (8300), 267 (7900), 301 (9600), 337 (8700). The p.m.r. spectrum in acetone showed a singlet at very low field (1 proton, OH group), a multiplet centred at 7·15 p.p.m. (3 protons, aromatic), and a singlet at 3·80 p.p.m. (2 protons, CH_2 group). Infrared data are given in the previous section.

With Brady's reagent, the compound gave a 2,4-*dinitrophenylhydrazone* separating from ethyl acetate as long orange-red needle crystals (deep red on filtering, changing colour on drying), m. p. 268° (decomp.) (Found: C, 53·4; H, 3·3; N, 17·9. $C_{14}H_{10}N_4O_5$ requires C, 53·5; H, 3·2; N, 17·8%), $\lambda_{max.}$ ($CHCl_3$) 385 mμ, $\varepsilon_{max.}$ 29,000.

Reductive Fission of 3-*Bromo*-4-*hydroxybenzocyclobutenone*.—Nickel–aluminium alloy (50 : 50; 10 g.) was added in small portions over 3 hr. with mechanical stirring to a solution of the bromo-compound (2·60 g.) and sodium hydroxide (19 g.) in water (150 ml.), the temperature being kept below 35°. After stirring for a further 2 hr., the solution was filtered, the solid washed with small amounts of water, and the combined filtrate and washings acidified with conc. hydrochloric

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[3] Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1959, p. 163.

acid and cooled in the refrigerator. The colourless crystalline product was filtered off, washed, and dried (0·67 g., m. p. 175—178°) and was free from bromine. After recrystallisation from water, then benzene, the 4-hydroxy-2-methylbenzoic acid melted at 178—180° (lit.,[4] m. p. 177—178°) (Found: C, 63·3; H, 5·4. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%).

Alkaline Fission of 4-*Hydroxybenzocyclobutenone*.—(*a*) The compound (0·10 g.) was dissolved in sodium hydroxide solution (10% w/v; 3·5 ml.) and the clear solution allowed to stand for 48 hr. at room temperature. After acidification with conc. hydrochloric acid and ice-cooling, the product was filtered off, washed with a little water, and dried (0·08 g.). Comparison of its i.r. spectrum (as Nujol mull) with those of the starting material and of 4-hydroxy-2-methylbenzoic acid indicated *ca.* 10% conversion.

(*b*) Repetition of the experiment, but with boiling of the solution under reflux for 45 min. instead of allowing it to stand, gave almost pure acid (0·06 g.) containing less than 5% starting material.

Alkaline Fission of 3-*Bromo*-4-*hydroxybenzocyclobutenone*.—The bromo-compound (0·10 g.) was dissolved in a solution of sodium hydroxide (2 g.) in water (12 ml.) and the solution allowed to stand at room temperature for 24 hr. After acidification of the solution with conc. hydrochloric acid and ice-cooling, the 3-*bromo*-4-*hydroxy*-2-*methylbenzoic acid* was filtered off, washed, dried (0·06 g.), and crystallised from boiling water, giving colourless needles, m. p. 200° (Found: C, 41·45; H, 3·1; Br, 34·4. $C_8H_7BrO_3$ requires C, 41·6; H, 3·0; Br, 34·6%), $\nu_{max.}$ (Nujol) 3480, 2620, and 2500 (OH); 1680 cm.$^{-1}$ (CO).

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[4] Tiemann and Schotten, *Ber.*, 1878, **11**, 778.