105. *Studies in Chelation. Part V. Hydroxyacetylhydrindenes.*

By Wilson Baker.

From theoretical considerations Mills and Nixon (J., 1930, 2510) considered it probable that in the molecule of hydrindene the bond common to the two rings is single (as in I and II). This was supported by the facts that both 5-hydroxy- and 5-amino-hydrindene showed chemical reactivity only in position 6 and not in the alternative ortho-position 4. It was, however, pointed out that *o*-4-xylenol also is reactive chiefly in position 6, so that the influences of the hydrindene ring other than a possible strain effect could afford an explanation of the chemical reactivity of the 5-substituted hydrindenes in position 6.

Support for the original hypothesis has been obtained from two independent sources. Sidgwick and Springall (*Chem. and Ind.*, 1936, **55**, 476; J., 1936, 1532) showed that the dipole moment of 5 : 6-dibromohydrindene was in very close agreement with the moment calculated on the assumption of a fixed double bond between carbon atoms 5 and 6, evidence which indicates a fixation of the links in hydrindene in the resting state of the molecule, unlike the previous evidence based on chemical reactivity. The same conclusion was reached by Fieser and Lothrop (*J. Amer. Chem. Soc.*, 1936, **58**, 2050), who observed that 5-hydroxy-6-methylhydrindene refuses to couple with diazo-compounds, though 5-hydroxy-4 : 7-dimethylhydrindene couples readily in position 6.

To obtain further evidence on the structure of hydrindene, 5-*hydroxy*-6-*acetylhydrindene* (I) and 5-*hydroxy*-4-*acetylhydrindene* (II) were examined. It has been shown (Parts I, II, and III, Baker, J., 1934, 1684; Baker and Lothian, J., 1935, 628; 1936, 274) that chelation between the hydroxyl and the acetyl group in *o*-hydroxyacetophenones and in β-hydroxy-ketones depends upon the presence of a double bond between the carbon atoms bearing these groups,* and this fact furnishes a new method for the detection of a fixed double or single link in a simple aromatic structure. Moreover this method is free from certain objections (Sutton and Pauling, *Trans. Faraday Soc.*, 1935, **31**, 939) which can be raised against arguments based on the formation in preponderating amount of one product in a chemical reaction in cases where two isomers might be produced (Mills and Nixon, *loc. cit.*). Such objections can hardly apply, however, to the experiments of Fieser and Lothrop (*loc. cit.*).

If fixation of the aromatic links in compounds (I) and (II) occurs as postulated by Mills and Nixon, then it is evident that 5-hydroxy-6-acetylhydrindene (I) should exhibit a greater degree of chelation than 5-hydroxy-4-acetylhydrindene (II). It must be pointed out, however, that even if in simple hydrindenes the double bonds are definitely fixed as in (I) and (II), in the case of the hydroxyacetylhydrindene (II) it is not to be expected that the compound will behave like a completely non-chelated compound, since chelation between

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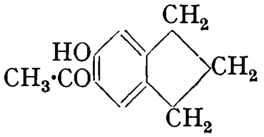
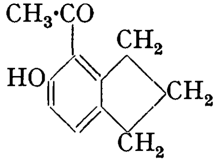
* The reason for this which was advanced in Part I requires a slightly new interpretation in view of our increased knowledge of the nature of " co-ordinately linked hydrogen " (see Sidgwick, *Ann. Reports*, 1934, **31**, 41).

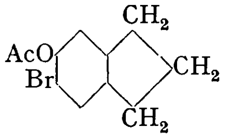
hydroxyl and acetyl groups may well be a more powerful influence in fixing the bonds in an aromatic nucleus than fusion with a *cyclo*pentane ring. In the case of (I) these two effects reinforce each other, in the case of (II) they are in opposition.



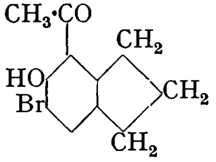
(I.)



(II.)



(III.)



(IV.)

Examination of the physical properties of (I) and (II) shows that both are considerably chelated, but that (II) is less highly chelated than (I) in accordance with expectation. (I) is readily soluble in light petroleum and benzene, and easily volatile in steam, (II) is very much less soluble in hydrocarbon solvents (probably partly explicable by its higher m. p., which may itself be due to its greater association) and almost involatile in steam. The following table gives some of the physical properties of the two compounds, the difference in degree of chelation being clearly indicated by the greater depression of the melting point of (II) under water as compared with that of (I), in spite of its higher melting point. For purposes of comparison the properties of 5-hydroxyhydrindene are also recorded.

	M. p., dry.	M. p., wet.	Depression.	Critical solution temp.
5-Hydroxy-6-acetylhydrindene (I)	59·5°	57·6°	1·9°	>265°
5-Hydroxy-4-acetylhydrindene (II)	124·5	119	5·5	>265
5-Hydroxyhydrindene	53·5	36·5	17	*ca.* 200

The critical solution temperatures of the compounds (I) and (II) in water could not be reached owing to darkening above 250°. Both give chelate copper derivatives soluble in chloroform.

5-Hydroxy-6-acetylhydrindene (I) was prepared from 5-*acetoxyhydrindene* by treatment with aluminium chloride in carbon disulphide, and appeared to be the sole product of the reaction. The position of the acetyl group is inferred from the known reactivity of 5-hydroxyhydrindene in position 6 and by the fact that the compound differs from 5-hydroxy-4-acetylhydrindene (II), which was prepared by the following method.

5-Hydroxyhydrindene was converted into 6-bromo-5-hydroxyhydrindene (Mills and Nixon, *loc. cit.*; these authors established the position of the bromine atom in this compound), and thence by acetylation into 6-*bromo*-5-*acetoxyhydrindene* (III). Compound (III) when heated with aluminium chloride in carbon disulphide underwent slow conversion into 6-*bromo*-5-*hydroxy*-4-*acetylhydrindene* (IV), which when reducėd with zinc dust in sodium hydroxide solution gave 5-hydroxy-4-acetylhydrindene (II). Confirmation of the position of the acetyl group in this compound was afforded by the fact that, whilst (IV), in which the carbonyl group might be expected to be sterically hindered by the methylene group in position 3, merely suffers loss of the bromine atom when reduced with zinc dust and sodium hydroxide, 5-hydroxy-6-acetylhydrindene (I), where such a steric effect could not be operative, is reduced under exactly the same conditions to the corresponding pinacol. This observation will be the subject of a further communication. The formation of (IV) from (III) is a noticeably much slower reaction than the conversion of 5-acetoxyhydrindene into (I), a result to be expected if the double bonds are fixed, and which may be compared with the experiments of Fieser and Lothrop to which reference has already been made.

An isomer of (IV) of unknown constitution, whose chemical properties are identical with those of (IV), was produced in one reaction when (III) was heated with aluminium chloride and carbon disulphide for a much longer period than normal.

EXPERIMENTAL.

5-*Aminohydrindene.*—Hydrindene (313 g.) gave 5-acetylhydrindene (313 g.) and thence the oxime (295 g.) [acetylhydrindene (100 g.), alcohol (500 c.c.), water (300 c.c.), hydroxylamine hydrochloride (75 g.), and crystalline sodium acetate (200 g.), heated on the steam-bath for 4 hours, cooled, product collected]. The oxime gave 5-acetamidohydrindene (252 g.) [oxime

(80 g.) was added to a mixture of acetic acid (720 g.) and acetic anhydride (280 g.), saturated with dry hydrogen chloride at 0°, and after 48 hours the crystals of a hydrochloride were isolated, stirred into water, collected and washed], and then 5-aminohydrindene (176 g.) by hydrolysis for 2 hours with four times its weight of concentrated hydrochloric acid on the water-bath, addition of alkali, extraction with ether, and distillation (cf. Borsche and Pommer, *Ber.*, 1921, **54**, 107).

5-*Hydroxyhydrindene*.—This compound was prepared from 5-aminohydrindene, as a quantity of this substance was available. It is, however, most readily obtained from hydrindene *via* the 5-sulphonic acid (Cook and Linstead, J., 1934, 952). Borsche and John (*Ber.*, 1924, **57**, 658) obtained only a 17% yield from 5-aminohydrindene. 5-Aminohydrindene (16 g.) was dissolved in water (140 c.c.) and concentrated sulphuric acid (25 c.c.), rapidly cooled to − 10°, and a solution of sodium nitrite (8·4 g.) in water (40 c.c.) slowly added. The diazo-solution was run into aqueous copper sulphate (200 c.c. saturated at 15°) through which steam was passing, and 5-hydroxyhydrindene, m. p. 53·5°, was extracted from the distillate with ether (yield 11 g.; 69%).

5-*Acetoxyhydrindene*.—To a solution of 5-hydroxyhydrindene (10 g.) in *N*-sodium hydroxide (90 c.c.; 1·2 mols.) was added ice, and then acetic anhydride (8·4 g.; 1·1 mols.) in one portion with vigorous shaking. The oily product was shaken in ether with dilute sodium hydroxide solution, then water, dried by calcium chloride, and distilled. 5-*Acetoxyhydrindene* distilled at 136°/18 mm. as a colourless oil with an odour of phenyl acetate (Found: C, 75·2; H, 6·6. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). It solidified in a freezing mixture and then had m. p. 16—17°. The yield was almost quantitative.

5-*Hydroxy*-6-*acetylhydrindene* (I).—5-Acetoxyhydrindene (5 g.), dissolved in carbon disulphide (10 c.c.), was treated with coarsely crushed aluminium chloride (10 g.). After the somewhat vigorous reaction had abated, the mixture was heated on the water-bath for 2 hours and subsequently treated with dilute hydrochloric acid. The oily product was obtained solid (4·4 g.) by steam distillation and after crystallising twice from a small volume of methyl alcohol formed prismatic needles, m. p. 59° (Found: C, 74·9; H, 6·9; *M*, 179. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%; *M*, 176). 5-*Hydroxy*-6-*acetylhydrindene* in alcoholic solution gives with ferric chloride a rather intense reddish-blue colour, becoming slate-grey on dilution with water; with dilute sodium hydroxide solution it gives a very sparingly soluble, yellow sodium salt, and its alcoholic solution when treated with aqueous copper acetate yields a copper derivative dissolving in chloroform with a green colour. For complete purification the substance was converted into its *acetyl* derivative by boiling with excess of acetic anhydride for 4 hours; this separated as a solid when the mixture was shaken with water and crystallised from light petroleum (b. p. 60—80°) in thick diamond-shaped plates, m. p. 88° (Found: C, 71·4; H, 6·9; *M*, 210. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·4%; *M*, 218). Hydrolysis with dilute alcoholic sodium hydroxide for a few minutes regenerated 5-hydroxy-6-acetylhydrindene (I), which, crystallised from methyl alcohol and then light petroleum (b. p. 40—60°), had m. p. 59·5°.

6-*Bromo*-5-*acetoxyhydrindene* (III).—5-Hydroxyhydrindene (10 g.) was converted into 6-bromo-5-hydroxyhydrindene (Mills and Nixon, *loc. cit.*), and thence by refluxing with acetic anhydride (50 c.c.) for 4 hours into 6-*bromo*-5-*acetoxyhydrindene*. After the excess of acetic anhydride, the acetate distilled at 169°/16 mm. as a colourless oil (16·3 g.) (Found: C, 51·6; H, 4·2; Br, 31·6. $C_{11}H_{11}O_2Br$ requires C, 51·8; H, 4·3; Br, 31·4%).

6-*Bromo*-5-*hydroxy*-4-*acetylhydrindene* (IV).—A mixture of 6-bromo-5-acetoxyhydrindene (5 g.), carbon disulphide (10 c.c.), and aluminium chloride was heated on the water-bath for 5 hours and the product was decomposed with very dilute hydrochloric acid, extracted in ether, and shaken with dilute aqueous sodium hydroxide (unchanged 6-bromo-5-acetoxyhydrindene remained in the ethereal layer). Acidification of the yellow aqueous layer gave an oily product, which solidified; crystallised from a little methyl alcohol (yield, 1 g.), and then from light petroleum (b. p. 40—60°), it formed thin yellow prisms, m. p. 102—103° (Found: C, 51·6; H, 4·4; Br, 31·9; *M*, 258. $C_{11}H_{11}O_2Br$ requires C, 51·8; H, 4·3; Br, 31·4%; *M*, 255). When the *compound* was heated with dilute alcoholic potassium hydroxide for 4 hours at 100°, the bromine atom was not eliminated.

Bromohydroxyacetylhydrindene, m. p. 115°.—In an experiment similar to the above, the mixture was heated for 36 hours. The oil resulting from decomposition of the aluminium complex did not solidify and was collected in ether and distilled under diminished pressure, b. p. about 200°/16 mm. The yellow distillate solidified in contact with methyl alcohol, and was crystallised first from methyl alcohol and then light petroleum (b. p. 40—60°) and obtained in colourless prisms, m. p. 115° (Found: C, 51·7; H, 4·2; Br, 31·4; *M*, 255. $C_{11}H_{11}O_2Br$

requires C, 51·8; H, 4·4; Br, 31·4; *M*, 255), depressed to 70—85° by 6-bromo-5-hydroxy-4-acetylhydrindene. The bromine atom in this *substance* was not eliminated by heating with dilute alcoholic potassium hydroxide for 4 hours at 100°. It dissolved in hot dilute sodium hydroxide to a yellow solution, depositing a sparingly soluble, pale yellow sodium salt on cooling. Its alcoholic solution gave a dull purplish colour with ferric chloride.

5-*Hydroxy*-4-*acetylhydrindene* (II).—6-Bromo-5-hydroxy-4-acetylhydrindene (IV) (0·35 g.), dissolved in 2% aqueous sodium hydroxide (10 c.c.), was heated for 6 hours on the water-bath with zinc dust (3·5 g.). The filtered solution was acidified, and the resulting solid crystallised twice from dilute alcohol, forming faintly amber-coloured, flat prisms, m. p. 124·5° (Found: C, 75·0; H, 7·0; *M*, 181, 183. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%; *M*, 176). It gave a dull greenish colour with alcoholic ferric chloride, dissolved in sodium hydroxide solution with a pale yellow colour, and in concentrated sulphuric acid a bright lemon-yellow solution was produced which on dilution with a little water became more orange-yellow and then pale violet. Its alcoholic solution when treated with aqueous copper acetate gave a copper derivative, which dissolved in chloroform with a green coloration. 5-Hydroxy-4-acetylhydrindene also was obtained by similar reduction of the bromohydroxyacetylhydrindene, m. p. 115°.

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