4. *The Inversion of α-Substituted Hydroxyhydrindeneacetic Acids.*

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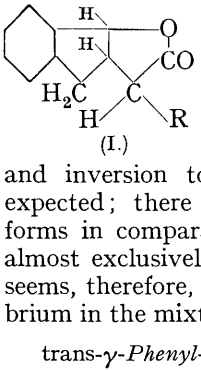

(I.)

It has been shown (J., 1934, 1296) that lactones of type (I) undergo inversion at the α-carbon atom when $R = CH_2Ph$ but not when $R = Me$ or *n*-Bu and it was suggested that the difference is due to the electron affinity of the benzyl group. We have now found that inversion takes place when $R = CH_2\cdot CH_2Ph$ or $CH_2\cdot C_6H_4Br$ (*p*), thus confirming the suggestion that the phenyl group aids inversion and supporting the hypothesis that it is the electron affinity of the phenyl group which assists the process. The *lactone* (I*a*; $R = CH_2\cdot CH_2Ph$) was readily formed from the corresponding *acid*, and inversion took place much more slowly than when $R = CH_2Ph$, as would be expected; there was also an indication that the equilibrium mixture contained the two forms in comparable amounts. When $R = CH_2Ph$, the equilibrium mixture contained almost exclusively the *b* form of the lactone. The substitution of $CH_2\cdot CH_2Ph$ for CH_2Ph seems, therefore, to affect not only the speed of inversion but also the position of equilibrium in the mixture formed.

trans-*γ-Phenyl-α-1-hydroxyhydrindene-2-butyric Acid.*—Ethyl β-phenylethylacetoacetate (23·4 g.; Auwers and Moller, *J. pr. Chem.*, 1925, **109**, 124) and solutions of sodium (2·3 g. in 50 c.c.) and of 2-bromo-1-hydroxyhydrindene (21·3 g. in 50 c.c.) in absolute alcohol were mixed and boiled for 2 hours. The product of hydrolysis by alcoholic caustic potash, liberated by acidification, was a thick oil, which partly crystallised on addition of benzene. The *acid* was recrystallised from benzene (yield, 4 g.); m. p. 131° (Found: C, 76·7; H, 6·95. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%).

cis-*Lactone* (I*a*; $R = CH_2\cdot CH_2Ph$).—The preceding acid (4 g.) was boiled for 2 hours with an acetic acid solution of hydrogen bromide (20 c.c.). The acetic acid and hydrogen bromide were then distilled under reduced pressure and the *lactone* was dissolved in benzene, shaken with sodium bicarbonate solution, dried, recovered, and crystallised from benzene; m. p. 94° (yield, 2·65 g.) (Found: C, 81·6; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

cis-*Lactone* (I*b*; $R = CH_2\cdot CH_2Ph$).—The lactone (I*a*) (0·5 g.) was boiled with 25 c.c. of alcoholic *N*-sodium hydroxide: after $\frac{1}{2}$ hour the original lactone (m. p. 94°) was recovered, but after 5 hours an oil was obtained which solidified when scratched and then crystallised (m. p. 73—74°) slowly from light petroleum. When heated in a sealed tube for 2 hours at 150°, the same quantities of lactone and alkali gave a product, m. p. 72—74°, which, crystallised from light petroleum, gave a *lactone*, m. p. 88° (0·19 g.), and a mixture of lactones, m. p. 73—74° (0·18 g.). Similar products were obtained when the original lactone (0·5 g.) was heated with caustic potash (1 g. in 5 c.c. of water) for 3 hours at 130° (Found for the lactone, m. p. 88° : C, 81·5; H, 6·5; *M*, 274·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%; *M*, 278. Found for the lactone mixture, m. p. 73—74° : C, 80·6, 80·4, 80·6; H, 6·9, 6·75, 6·5%; *M*, 273·6. Consistently low results for carbon were obtained with this substance).

trans-β-p-*Bromophenyl*-α-1-*hydroxyhydrindene*-2-*propionic Acid.*—Ethyl *p*-bromobenzylacetoacetate (b. p. 218—220°/40 mm.; 30 g.), sodium (2·3 g.), and absolute alcohol (50 c.c.) were mixed and to the cold solution 2-bromo-1-hydroxyhydrindene (21·3 g.) in absolute alcohol (50 c.c.) was added. Next day the mixture was boiled for 2 hours and was then neutral. The crude acid (10 g.), on crystallisation from benzene, gave the desired *acid*, m. p. 175° (Found : Br, 21·95. $C_{18}H_{17}O_3Br$ requires Br, 22·2%), and a mixture of this acid with β-*p*-bromophenylpropionic acid. This mixture on treatment with phosphorus pentachloride gave a product which after treatment with water yielded the *cis*-lactone described below and β-*p*-bromophenylpropionic acid.

cis-*Lactone* (I*a*; R = *p*-$C_6H_4Br{\cdot}CH_2$).—The preceding acid (2 g.) was heated on a water-bath for 2 hours with a saturated solution of hydrogen bromide in acetic acid (20 c.c.) The *lactone* obtained, m. p. 134°, was soluble in ethyl alcohol and benzene–light petroleum (Found : Br, 23·5. $C_{18}H_{15}O_2Br$ requires Br, 23·3%). The same lactone was obtained by the action of phosphorus pentachloride on a chloroform solution of the acid.

cis-*Lactone* (I*b*; R = *p*-$C_6H_4Br{\cdot}CH_2$).—The above lactone (0·5 g.) was heated on a water-bath for 2 hours with alcoholic caustic potash (1 g. in 5 c.c.). The neutral product was crystallised from alcohol; m. p. 110° (Found : Br, 23·1. $C_{18}H_{15}O_2Br$ requires Br, 23·3%). A mixture of the two lactones melted at 122°.

Acetoxy-acid.—*trans*-β-*p*-Bromophenyl-α-1-hydroxyhydrindene-2-propionic acid (1 g.) was heated under reflux with acetic anhydride (5 c.c.) at 150—160° for 3 hours, and the acetic anhydride then distilled off. The residue, washed with benzene and dilute sodium bicarbonate solution, had m. p. 252°; it was dissolved in aqueous alcohol, and added to sodium bicarbonate solution. On acidification the *acetoxy*-acid (0·9 g.) was obtained, m. p. 171° after crystallisation from benzene (Found : Br, 20·0. $C_{20}H_{19}O_4Br$ requires Br, 19·85%); mixed with the original acid, it melted at 152°.

No isomeric acetoxy-acid was obtained from the mother-liquor of the original acid.

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