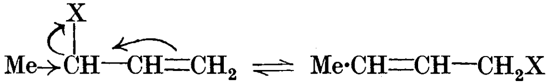
LXIV.—*Mobile Anion Tautomerism. Part III. A Comparison of the Activation of Three-carbon Anionotropic Systems by Alkyl and by Aryl Groups.*

By HAROLD BURTON.

IN Part II (Burton, J., 1928, 1650) it was shown that the activation of the three-carbon anionotropic system (I) $\mathrm{Ph{\cdot}CHX{\cdot}CH{:}CH_2} \longrightarrow \mathrm{Ph{\cdot}CH{:}CH{\cdot}CH_2X}$ (II) by the phenyl group causes a complete conversion of (I) into (II) in suitable solvents. The conditions for the change are dependent on the anionic stability of X (*i.e.*, strengths of acids HX) and also on some molecular property of the solvent closely related to its dielectric constant. The migratory power of X is in the order Br $>$OAc; $\mathrm{O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2}(p)>$OH.

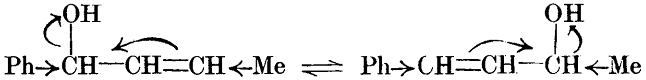
In the system (III$\rightleftharpoons$IV) the mobility of X is much smaller. For instance, each alcohol yields its own acetyl derivative on boiling

(III.)  (IV.)

$$\mathrm{Me{\rightarrow}\overset{X}{C}H{-}CH{=}CH_2 \rightleftharpoons Me{\cdot}CH{=}CH{-}CH_2X}$$

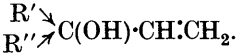
with acetic anhydride (Baudrenghien, *Bull. Soc. chim. Belg.*, 1922, **31**, 160; compare Prevost, *Ann. Chim.*, 1928, **10**, 147), and although both alcohols yield the same bromide (α-bromo-Δ^{β}-butene) (Bouis, *ibid.*, 1928, **9**, 410; Prevost, *loc. cit.*), hydrolysis of this with aqueous alkali carbonate yields 60% of (III) and 40% of (IV). The *p*-nitrobenzoates should resemble the acetates in their stability, and this has been verified for *α-methylallyl* p-*nitrobenzoate* by the author's method (*loc. cit.*) of boiling an acetic anhydride solution for 6 and 24 hours. In each experiment the substance was unchanged.

In consequence of the pronounced difference in activating power of the phenyl and the methyl group a direct comparison of the two was made by examining an anionotropic system terminated at one end by a phenyl and at the other by a methyl group. No difficulty was experienced in the preparation by the usual Grignard method of *α-phenyl-γ-methylallyl alcohol* (V) and the isomeric γ-phenyl-α-methylallyl alcohol (VI) (Klages, *Ber.*, 1902, **35**, 2650).

(V.)  (VI.)

$$\mathrm{Ph{\rightarrow}\overset{OH}{C}H{-}CH{=}CH{\leftarrow}Me \rightleftharpoons Ph{\rightarrow}CH{=}CH{-}\overset{OH}{C}H{\leftarrow}Me}$$

Although it was not possible to prepare a homogeneous *p*-nitrobenzoyl derivative or bromide from either of these alcohols, the alcohol (V) was smoothly and completely converted into the acetate of (VI) by boiling with acetic anhydride. The completeness of the change shows the remarkable property of activating anionotropic systems possessed by the phenyl group. As it also promotes activation in prototropic systems (Ingold and Shoppee, this vol., p. 447), this group is able, by tautomeric electron-displacements of either sign (see Ingold and Shaw, J., 1927, 2918) promoted by the requirements of the system, to absorb an electric charge of either sign produced by the ionisation of an attached atom or group. It is the separation of X as the ion ($X^\ominus$) that is the key process, and therefore it follows that the influence (represented by $\rightarrow$ in III) is probably a *compensating* influence.

From the work of Ingold and others (J., 1927, 997; 1928, 3125) on the decomposition of quaternary ammonium hydroxides it follows that the influence (represented by $\rightarrow$ in III) of the alkyl group in increasing the toleration of C_a for the shared sextet left by the separation of $X^\ominus$ should reach its maximum at about *n*-hexyl. Even then the activation may not be as great as that produced by phenyl or by *gem*-dialkyl groups,  $\begin{smallmatrix}R'\searrow\\R''\nearrow\end{smallmatrix}C(OH)\cdot CH{:}CH_2$. Compounds of this structure have been shown (Locquin and Wouseng, *Compt. rend.*, 1922, **174**, 1711; **175**, 100) to give the derivatives

$$CR'R''{:}CH\cdot CH_2\cdot OAc$$

on acetylation, and the substituted acraldehydes

$$CR'R''{:}CH\cdot CHO$$

on oxidation in acid media. It is hoped to test the action of the *n*-hexyl group on anionotropic systems when some of the experimental difficulties have been surmounted.

EXPERIMENTAL.

α-*Methylallyl* p-*nitrobenzoate*, $CHMe(O\cdot CO\cdot C_6H_4\cdot NO_2)\cdot CH{:}CH_2$, was obtained by heating a mixture of methylvinylcarbinol (8·4 g.), *p*-nitrobenzoyl chloride (23·8 g.), and pyridine (150 c.c.) on the water-bath for 15 hours. The oil which separated when the product was poured into water gradually solidified, and the *ester* crystallised from alcohol in almost colourless needles, m. p. 43—44° (Found : C, 59·9; H, 4·9. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). When the *p*-nitrobenzoate (5 g.) was boiled with acetic anhydride (10 c.c.) for 6 and for 24 hours, and the solutions were poured into water, unchanged material was obtained in each case.

α-*Phenyl*-γ-*methylallyl Alcohol* (V).—The Grignard reagent prepared from magnesium (12 g.), bromobenzene (94 g.), ether (200 c.c.), and a trace of iodine was cooled below 0°, and a solution of crotonaldehyde (35 g.) in ether (125 c.c.) added during 1·5 hours. The mixture was stirred for a further 4 hours and then decomposed with ice and saturated ammonium chloride solution. The *alcohol* (51 g.; yield, 70%) was obtained from the ethereal extract as a colourless mobile oil, b. p. 121·5—123·5°/14 mm. (Found : C, 80·7; H, 8·05. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%). An attempt to prepare the *p*-nitrobenzoyl derivative in pyridine solution gave an ill-defined solid, m. p. about 60°, which was probably a mixture of *cis*- and *trans*-isomerides and could not be purified by repeated crystallisation from alcohol. The bromide obtained by the action of a 30% solution of hydrogen bromide in glacial acetic acid decomposed on distillation.

γ-Phenyl-α-methylallyl alcohol (VI) was prepared from magnesium methyl iodide and cinnamaldehyde as described by Klages (*loc. cit.*). During the vacuum distillation of the alcohol, small drops of water formed. [This tendency for formation of phenylbutadiene (Straus, *Ber.*, 1909, **42**, 2882) is enhanced by the presence of small amounts of acid substances.] The phenylurethane crystallised from light petroleum or dilute alcohol in clusters of colourless needles, m. p. 92—93° (Klages gives m. p. 94—95°) (Found : C, 76·4; H, 6·4. Calc. for $C_{17}H_{17}O_2N$: C, 76·4; H, 6·4%). Attempts to prepare the *p*-nitrobenzoate and the bromide gave results similar to those obtained with the isomeride.

A prototropic change analogous to $Ph{\cdot}CH(OH){\cdot}CH{:}CH_2 \longrightarrow Ph{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ (Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; see also Burton and Ingold, J., 1928, 908; Shoppee, *ibid.*, p. 2567) is not undergone by either of the above alcohols in presence of 20% alcoholic potassium hydroxide or 5% sodium ethoxide solution.

γ-Phenyl-α-methylallyl Acetate, $CHPh{:}CH{\cdot}CHMe{\cdot}OAc$.—Either of the alcohols (V) and (VI) (10 g.) was boiled with acetic anhydride (15 c.c.) for 6 hours. The residue obtained after removal of the excess of acetic anhydride gave on distillation 6·3 g. of the *acetate*, b. p. 141—144°/15 mm. (Found: C, 76·3; H, 7·35. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), together with a dark-coloured, high-boiling residue.

When the acetate was hydrolysed with an excess of 5% sodium ethoxide solution, and the product worked up in the usual way, γ-phenyl-α-methylallyl alcohol, b. p. 130°/11 mm., was obtained: it was further characterised by the m. p. and mixed m. p. of its phenylurethane. When a solution of the acetate in chloroform was treated with ozonised oxygen for 36 hours, and the ozonide decomposed by boiling with water for 2—3 hours, no volatile aldehyde (Schiff's reagent) was evolved. Benzoic acid, identified by mixed

m. p., separated from the cooled solution. The mother-liquor on evaporation gave a further small quantity of benzoic acid and had a strong odour of pyruvic acid. Pyruvic acid phenylhydrazone, m. p. 185° (decomp.) (compare Bamberger and Grob, *Ber.*, 1901, **34**, 548), was obtained by the action of phenylhydrazine acetate on the residue. The acid was apparently formed by the hydrolysis and further oxidation of the intermediate α-acetoxypropaldehyde.

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