

XXXVI.—*Mobile Anion Tautomerism. Part IV. The Stability of Some α - and γ -Alkylallyl Alcohols and their Esters. 2:4-Dimethylcinnamyl Alcohol.*

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It has been emphasised in previous parts of this series that the migratory power of X in the simple three-carbon anionotropic system, (I) $R \cdot CHX \cdot CH : CH_2 \rightleftharpoons R \cdot CH : CH \cdot CH_2 X$ (II), depends on three factors: (i) the group R, (ii) some molecular property of the solvent closely related to the dielectric constant, and (iii) the anionic stability of X (*i.e.*, strengths of the acids HX). With regard to factor (iii), the migratory power of X is in the order $Br > O \cdot CO \cdot CCl_3 > O \cdot CO \cdot C_6H_4 \cdot NO_2(p)$; $OAc > OH$, the position of the trichloroacetoxy-group following from the recent work of Prévost (*Ann. Chim.*, 1928, **10**, 160). Prévost has shown that esterification of trichloroacetic acid with either methylvinylcarbinol, $CHMe(OH) \cdot CH : CH_2$, or crotyl alcohol, $CHMe : CH \cdot CH_2 \cdot OH$, gives in each case the same mixture of about 55% of methylvinylcarbinyl trichloroacetate and about 45% of crotyl trichloroacetate. Furthermore, the action of potassium trichloroacetate on crotyl bromide

(α -bromo- Δ^{β} -butene) also gives the same mixture of the isomeric trichloroacetates. The explanation advanced by Prévost to account for the formation of the same mixture is that "trichloroacetic acid esterifies solely by the effect of hydrogen ions in liberating the tri-polar ion $\text{CH}_3 \cdot \overset{+}{\text{C}}\text{H} \cdot \overset{-}{\text{C}}\text{H} \cdot \overset{+}{\text{C}}\text{H}_2$; the trichloroacetoxy-group subsequently combining at one or other of the positive poles."

An alternative explanation is that the esters of types I and II are first formed and that these subsequently undergo interconversion to give an equilibrium mixture. It is probable that Prévost considered this aspect, since he states that the isomeric trichloroacetates are not isomerised even above 100° . No experimental details of the attempted interconversions are given and one may presume that Prévost merely heated the esters alone below their boiling points. Consideration of the experimental conditions under which esterification is carried out indicates that the mixture of either alcohol and trichloroacetic acid would have a moderately high dielectric constant; this would tend to decrease as reaction proceeded. In Prévost's experimental procedure, esterification is far from complete (yield of esters, 45—46%), so that rearrangement of the isomeric trichloroacetates would be expected to occur if such an explanation is the correct one. On the other hand, the dielectric constants of the pure esters would be relatively small and long heating would be necessary to effect any interconversion (see Burton, J., 1928, 1650).

The author's method (*loc. cit.*) being used, methylvinylcarbinyl and crotyl trichloroacetates were heated in acetic anhydride (dielectric constant = 20.5) for 6 hours at the boiling point; in each case the equilibrium mixture of about 55% of the former and 45% of the latter ester was obtained. This shows definitely that the explanation suggested above is probably the correct one, and that Prévost's failure to effect isomerisation was due to unsuitable experimental conditions.

It would be expected that esterification of trichloroacetic acid with butylvinylcarbinol would afford a mixture with the equilibrium displaced in the direction II. Unfortunately, this has not been capable of verification, as the attempted esterification gave rise to none of the expected esters.

In Part III (J., 1929, 455) it was pointed out that the influence of the n -alkyl group in activating the simple three-carbon anionotropic system should reach its maximum at about n -hexyl. It was also stated that "even then the activation may not be as great as that produced by the phenyl or by *gem*-dialkyl groups." It is now shown that the n -hexyl and *iso*amyl groups are very similar to the

methyl group in their activating power. For instance, α -*n*-hexylallyl *p*-nitrobenzoate, like α -methylallyl *p*-nitrobenzoate, is recovered unchanged when an acetic anhydride solution is boiled for 6 and 24 hours; and acetylation of α -isoamylallyl alcohol with an excess of acetic anhydride gives the corresponding acetate, as does methylvinylcarbinol. The pronounced difference in activating power of the alkyl and the phenyl group is again emphasised in experiments with α -*m*-4-xylylallyl alcohol, which are described in the experimental portion. The conversion of this alcohol into 2 : 4-dimethylcinnamyl alcohol is of interest in view of the very limited methods available for the synthesis of cinnamyl alcohols.

EXPERIMENTAL.

Methylvinylcarbinol and butylvinylcarbinol were prepared by Delaby's method (*Compt. rend.*, 1922, 175, 967).

Butylvinylcarbinyl p-nitrobenzoate, prepared by the pyridine method, crystallises from cold alcohol in colourless plates, m. p. 24—25° (Found: C, 63.8; H, 6.5. $C_{14}H_{17}O_4N$ requires C, 63.9; H, 6.5%).

Esterification of Trichloroacetic Acid with Methylvinylcarbinol.—This was carried out in the manner described by Prévost (*loc. cit.*). The yield of mixed esters, b. p. 70—90°/10 mm., was 45—46%. Fractionation of the mixture in a vacuum, by means of a Dufton column (50 cm.), gave approximately equal amounts of two well-defined fractions, the mid-piece being rejected. Further distillation under reduced pressure and collection of the middle fractions only, afforded methylvinylcarbinyl trichloroacetate, b. p. 69.5—70.5°/8 mm., $n_{D_{461}}^{18}$ 1.46390 (Found: C,* 33.4; H, 3.0. Calc.: C, 33.1; H, 3.2%), and crotyl trichloroacetate, b. p. 86—86.5°/9 mm., $n_{D_{461}}^{18}$ 1.47596 (Found: C, 33.4; H, 3.4%). The refractive indices were measured with a Pulfrich instrument, the green line of the mercury arc being used, with an auxiliary slit to increase the accuracy of setting. The drum of the instrument was used, so the differences between the observed indices are more accurate than the absolute values. The pure esters and mixtures were measured rapidly one after another at the same temperature. The mixtures obtained from three similar experiments showed $n_{D_{461}}^{18}$ 1.46947, 1.46947, and 1.46932 respectively; hence content of methylvinylcarbinyl trichloroacetate = 54, 54 and 55% respectively.

Conversion of the Esters into the Equilibrium Mixture.—Either of the esters (10 g.) was boiled with acetic anhydride (20 c.c.) for 6 hours. The yellow solution was poured into water and extracted with ether, and the extract was washed repeatedly with sodium

* The values for C are all somewhat high owing to the large chlorine content of the esters.

carbonate solution until free from acid and dried. The residue from the ethereal extract gave, in addition to a main fraction, b. p. 70—90°/10 mm., high-boiling material, showing that some decomposition had taken place. The mixed esters were redistilled three times and analysed (Found : C, 33·6, 33·5; H, 3·1, 3·5%). The refractive indices of the mixtures were 1·46916 and 1·46932; hence content of methylvinylcarbinyl trichloroacetate = 56 and 55%.

α-n-Hexylallyl Alcohol (Δ^{α} -Nonen- γ -ol), $C_6H_{13}\cdot CH(OH)\cdot CH:CH_2$.—The Grignard reagent prepared by the method of Gilman and McCracken (*J. Amer. Chem. Soc.*, 1923, **45**, 2463) from magnesium (12 g.), *n*-hexyl bromide (82 g.), ether (200 c.c.), and a trace of iodine was cooled below 0°, and a solution of acraldehyde (33 c.c.) in ether (150 c.c.) added during 2 hours. The mixture was stirred for a further 4 hours and then decomposed with ice and saturated ammonium chloride solution. Distillation of the oil from the ethereal extract gave 36 g. of a mobile oil, b. p. 88—95°/16 mm., which gave high values for carbon and hydrogen and was not purified by further fractionation. When the oil was heated with *p*-nitrobenzoyl chloride (50 g.) and pyridine (350 c.c.) on the water-bath for 2 hours, and the mixture poured on ice, a solid (35 g.) was obtained. This was collected, washed with cold light petroleum, drained on porous earthenware, and crystallised from a concentrated alcoholic solution at 0—5°; *α-n-hexylallyl p-nitrobenzoate*, m. p. 36—37°, then separated in almost colourless plates (Found : C, 65·8; H, 7·2. $C_{16}H_{21}O_4N$ requires C, 66·0; H, 7·2%).

Hydrolysis of the *p*-nitrobenzoate (14·5 g.) by boiling with 5% alcoholic potassium hydroxide solution (100 g.) for 2 hours, the product being worked up in the usual way, gave *α-n-hexylallyl alcohol* as a colourless mobile oil, b. p. 89°/12 mm. (Found : C, 75·7; H, 12·8. $C_9H_{18}O$ requires C, 76·05; H, 12·7%).

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-isoAmylallyl Alcohol, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH:CH_2$.—The Grignard reagent prepared from magnesium (12 g.), *isoamyl* bromide (76 g.), ether (300 c.c.), and a trace of iodine was treated during 2 hours with a solution of acraldehyde (30 c.c.) in ether (150 c.c.) as for the hexyl analogue. Decomposition of the product with ice and ammonium chloride and careful fractionation of the product obtained afforded 14 g. of the *alcohol*, b. p. 73—74°/16 mm., as a colourless mobile oil (Found : C, 75·05; H, 12·6. $C_8H_{16}O$ requires C, 75·0; H, 12·5%). A crystalline *p*-nitrobenzoate could not be prepared by the pyridine method.

α-isoAmylallyl acetate, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OAc)\cdot CH:CH_2$, was

obtained by boiling a mixture of the above alcohol (14 g.) and acetic anhydride (20 c.c.) for 9 hours and working up the product in the usual way. The ester is a colourless mobile oil, b. p. 83—84°/18 mm. (Found : C, 70·5; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%). Hydrolysis with an excess of boiling 5% alcoholic potassium hydroxide solution regenerated the above alcohol.

α-m-4-Xylylallyl Alcohol, $C_6H_3Me_2 \cdot CH(OH) \cdot CH : CH_2$.—To the well-cooled Grignard reagent prepared from magnesium (12 g.), *m-4-iodoxylylene* (116 g.), ether (200 c.c.), and a trace of iodine, a solution of acraldehyde (33 c.c.) in ether (150 c.c.) was added during 2 hours. The mixture was stirred for a further 3 hours, and the very gummy product decomposed with ice and ammonium chloride solution. Distillation of the residue from the ethereal extract afforded a fraction (12 g.), b. p. 130—140°/15 mm., which on redistillation gave the impure *alcohol*, b. p. 129—131°/12 mm., as a colourless mobile oil (Found : C, 80·1; H, 8·8. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%). The *phenylurethane*, m. p. 105—106°, crystallises from light petroleum in clusters of colourless fine needles (Found : C, 77·0; H, 6·8. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8%).

2 : 4-Dimethylcinnamyl Alcohol, $C_6H_3Me_2 \cdot CH : CH \cdot CH_2 \cdot OH$.—A mixture of *α-m-4-xylylallyl alcohol* (8 g.) and acetic anhydride (10 c.c.) was boiled for 6 hours and then fractionated. The *2 : 4-dimethylcinnamyl acetate*, b. p. 168—170°/17 mm., obtained was hydrolysed with a slight excess of 5% alcoholic potassium hydroxide solution, giving *2 : 4-dimethylcinnamyl alcohol*, which was obtained as a pleasant-smelling, straw-coloured, viscous liquid, b. p. 162—164°/19 mm. (Found : C, 80·8; H, 8·6. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%). The *phenylurethane* separated from light petroleum in colourless needles, m. p. 82—83° (Found : C, 77·0; H, 6·9. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8%).

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