

290. *The Composition of the Ponndorff–Meerwein Reduction
Product of Mesityl Oxide.*

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Mesityl oxide is reduced by aluminium *isopropoxide* to a mixture of $\alpha\gamma$ -trimethylallyl alcohol (III) and a small quantity of the isomeride (IV); this is held to confirm the conclusion of Dupont and Menut that mesityl oxide contains a significant amount of the isomeride (II). Some $\alpha\gamma$ -trimethylallyl esters are unstable, and the alcohol itself is readily dehydrated, resembling a tertiary alcohol. Catalytic dehydration of the alcohol sometimes leads to the abnormal product, $\alpha\gamma$ -dimethylbutadiene, the course of the reaction apparently being dependent on the experimental conditions.

In view of a recent paper by Dupont and Menut (*Bull. Soc. chim.*, 1939, **6**, 1215), in which from an examination of the Raman spectra of mesityl oxide and derivatives thereof it is concluded that this substance is a mixture of (I) with 20% of (II), we desire to place on record certain observations made in this laboratory. Although the above-mentioned



workers were in no case able to effect a separation of the isomeric ketones (I) and (II), we have succeeded in isolating, in a pure condition, derivatives of the isomeric alcohols (III) and (IV) to which (I) and (II) respectively give rise, from the reduction products of ordinary mesityl oxide.

Dupont and Menut, and also Deux (*Compt. rend.*, 1938, **207**, 920), describe the reduction of the ketone to the corresponding unsaturated alcohol by the Ponndorff–Meerwein method, but record neither full experimental details nor the yield obtained; Lund (*Ber.*, 1937, **70**, 1520) was able to obtain only δ -methylpentan- β -ol by this reaction. By the interaction of mesityl oxide and aluminium *isopropoxide*, using the procedure of Arcus and Kenyon (*J.*, 1938, 698), we have obtained a product, b. p. 127–140°, in some 18% yield. This

yielded a *p*-xeny lurethane identical with the *p*-xeny lurethane from $\alpha\gamma\gamma$ -trimethylallyl alcohol (III), prepared by the method of Bacon and Farmer (J., 1937, 1065), which has a well-authenticated structure. On heating with phthalic anhydride and pyridine, our product yielded, however, a small quantity of the hydrogen phthalate of δ -methyl- Δ^{δ} -penten- β -ol (IV) (Kenyon and Young, J., 1938, 1452); the hydrogen phthalic ester of $\alpha\gamma\gamma$ -trimethylallyl alcohol is not formed under these conditions (see below). The yield of phthalate corresponded to a proportion of 3.2% of (II) in the reduction product, but owing to the poor yield and impure condition of the latter it is impossible to draw any precise conclusions from the data as to the quantitative composition of mesityl oxide. The result does, however, present chemical evidence for the heterogeneity of this material, although it may be noted that, as Arcus and Kenyon (*loc. cit.*) observed *cis-trans* interconversion of isomerides during the reduction of butylideneacetone, the Ponndorff-Meerwein reduction might possibly also result in an $\alpha\gamma$ shift of the double bond.

$\alpha\gamma\gamma$ -Trimethylallyl alcohol is best prepared by the interaction of β -methylcrotonaldehyde and methylmagnesium bromide as described by Bacon and Farmer (*loc. cit.*), but their yield (50% of crude product) has now been increased to 75% of pure distilled alcohol by dilution of both Grignard reagent and aldehyde with a large proportion of ether. Since β -methylcrotonaldehyde is obtainable in 30% yield from ordinary amyl alcohol (Fischer and Löwenberg, *Annalen*, 1932, 494, 263), it should be possible to prepare $\alpha\gamma\gamma$ -trimethylallyl alcohol in 22.5% yield from this starting material. The alternative Grignard reaction, between "activated" magnesium, *isocrotyl* bromide, and acetaldehyde (Krestinski, *Ber.*, 1922, 55, 2754), was found to be sluggish and incomplete, and the product was impure and could not be conclusively identified as $\alpha\gamma\gamma$ -trimethylallyl alcohol.

The hydrogen phthalic ester of $\alpha\gamma\gamma$ -trimethylallyl alcohol, owing to the ease with which it eliminates phthalic acid, cannot be prepared by warming the alcohol with phthalic anhydride in pyridine; it was obtained by interaction of the potassio-derivative of the alcohol in benzene solution with phthalic anhydride. It was an unstable oil which deposited phthalic acid immediately on warming; the other product appeared to be, not a hexadiene, but polymerised material. The acetate is more stable, and was readily prepared in the usual manner, although Krestinski (*loc. cit.*) observed the formation of some hexadiene after long heating of the alcohol with acetic anhydride. Attempts to prepare the *p*-nitrobenzoate were unsuccessful.

The instability of $\alpha\gamma\gamma$ -trimethylallyl esters would appear to be due to the facilitation of electron-release to, and splitting off by ionisation of, the ester group (V). As the second-



ary carbon atom is virtually under the electron-repelling influence of all three methyl groups, the structure presents some analogy to that of a tertiary alcohol. Esters of the isomeride (IV) are in contrast much more stable (Duveen and Kenyon, J., 1936, 1451*). An inspection of the probable electronic effects (VI) suggests that electron-release to the functional group is much reduced, and furthermore that the double bond would be expected to open rather than to undergo a shift of position. Support for this view is provided in Dupont and Menut's observation (*loc. cit.*) that δ -methyl- Δ^{δ} -penten- β -ol (IV) is hydrogenated much faster than $\alpha\gamma\gamma$ -trimethylallyl alcohol.

Catalytic Dehydration of $\alpha\gamma\gamma$ -Trimethylallyl Alcohol.—Bacon and Farmer found (*loc. cit.*) that $\alpha\gamma\gamma$ -trimethylallyl alcohol on catalytic dehydration gave $\alpha\alpha$ -dimethylbutadiene and a trace of $\alpha\gamma$ -dimethylbutadiene, both characterised by their maleic anhydride adducts. On the other hand, Dupont and Menut (*loc. cit.*) described the dehydration as yielding only the $\alpha\gamma$ -compound, identified by its Raman spectrum. Dehydration carried out on specimens of this alcohol prepared in the present investigation gave the surprising result that in all cases the product was entirely the $\alpha\gamma$ -diene; unfortunately, the reaction was not carried out on material *freshly* prepared by Bacon and Farmer's method. Dr. Farmer has,

* In this paper the alcohol (IV) was erroneously described as $\alpha\gamma\gamma$ -trimethylallyl alcohol.

however, informed us in a private communication that further unpublished experiments indicate that the subject is more complicated than appears from his paper, and that in many dehydrations two isomeric dienes may appear in varying proportions according to variations in the catalyst, or possibly the experimental conditions. It thus appears that the nature of the catalytic dehydration product is not a reliable guide to the structure of an unsaturated alcohol. Formation of the abnormal product appears to be due more probably to an $\alpha\gamma$ -shift rather than to "1 : 4 dehydration" as postulated by the French authors.

EXPERIMENTAL.

Ponndorff–Meerwein Reduction of Mesityl Oxide.—Mesityl oxide (66 g.) was reduced by aluminium isopropoxide (from 8.0 g. of aluminium) by the procedure of Arcus and Kenyon (*loc. cit.*). The product yielded, besides low- and high-boiling material, two fractions, b. p. 127–135° (8.2 g.) and b. p. 135–150° (mostly 138–140°) (2.5 g.; n_D^{18} 1.4370), which both yielded *p*-xeny lurethanes, m. p. 90–91°, undepressed by authentic $\alpha\gamma\gamma$ -trimethylallyl *p*-xeny lurethane (from β -methylcrotonaldehyde; see below) but strongly depressed by methylisobutylcarbinyl *p*-xeny lurethane (m. p. 94°). The reduction product still contained unreduced mesityl oxide.

2.14 G. of the combined fractions above were warmed with 3 g. of phthalic acid in pyridine (2 g.) for 1 hr. and left overnight; after trituration with dilute hydrochloric acid the chloroform-soluble portion of the product was extracted with aqueous ammonia; after acidification, any ester present was re-extracted with chloroform, leaving phthalic acid behind. This extract on evaporation left 0.44 g. of a solid product, which was only partly soluble in hot light petroleum (b. p. 60–80°); the latter solution on partial evaporation and cooling deposited 0.17 g. of *dl*- δ -methyl- Δ^8 -penten- β -yl hydrogen phthalate, which after further recrystallisation had m. p. 79°, m. p. in admixture with an authentic specimen (Kenyon and Young, *loc. cit.*) 79–81°. The weight of ester corresponds to 0.069 g. of δ -methyl- Δ^8 -penten- β -ol, so the original reduction product contained at least $0.069/2.14 \times 100 = 3.2\%$ of this alcohol.

Methylisobutylcarbinyl p-xeny lurethane, prepared from the *dl*-alcohol, formed colourless needles, m. p. 94° (Found : N, 5.2. $C_{19}H_{23}O_2N$ requires N, 4.7%). [*dl*-Methylisobutylcarbinyl hydrogen phthalate (Pickard and Kenyon, J., 1911, 99, 45) has been crystallised for the first time; after recrystallisation from light petroleum it forms colourless plates, m. p. 41–42.5°.]

Preparation of $\alpha\gamma\gamma$ -Trimethylallyl Alcohol by the Grignard Reaction.—30 G. of β -methylcrotonaldehyde (b. p. 62–64°/60 mm.) in dry ether (150 c.c.) were run slowly into methylmagnesium bromide (from 10 g. of magnesium) in about 250 c.c. of ethereal solution kept at –15° to –20°, and the product decomposed immediately with ice and ammonium chloride. The dried ethereal extract yielded $\alpha\gamma\gamma$ -trimethylallyl alcohol (26 g.) distilling at 48–52°/16 mm.; only a little colourless resin remained behind. The alcohol had n_D^{20} 1.4251, d_4^{20} 0.8475 [Bacon and Farmer (*loc. cit.*) give b. p. 55°/20 mm., n_D^{17} 1.4318, d_4^{17} 0.8448]; the *p*-xeny lurethane formed microscopic needles from light petroleum, m. p. 91° (Found : N, 5.0. $C_{19}H_{21}O_2N$ requires N, 4.8%).

$\alpha\gamma\gamma$ -Trimethylallyl Hydrogen Phthalate.—Potassium (2 g.) was "powdered" under benzene (25 c.c.), and a slight excess of $\alpha\gamma\gamma$ -trimethylallyl alcohol added dropwise with cooling, followed by phthalic anhydride (7.4 g.). The alkaline aqueous extract was acidified and extracted with chloroform; from the dried extract the solvent was removed in a vacuum, leaving the hydrogen phthalic ester as a viscous oil. Separation of phthalic acid occurred on warming or after about 2 weeks' standing (less with impure specimens). A small quantity was kept in benzene at room temperature for a few weeks; phthalic acid, m. p. 193–194°, was removed, and the filtrate distilled; a dark gummy residue was left. The benzene distillate contained nothing which would react with maleic anhydride. A solution of the phthalate in formic acid and chloroform yielded deposited phthalic acid and a high-boiling tarry material only.

$\alpha\gamma\gamma$ -Trimethylallyl acetate was obtained by heating the alcohol (1.0 g.) with acetic anhydride (1.0 g.) on the steam-bath for 2 hours. It had b. p. 46°/14 mm., n_D^{18} 1.4291, d_4^{20} 0.8794 [Krestinski (*loc. cit.*) gives b. p. 140–146°/760 mm.].

Catalytic Dehydration of $\alpha\gamma\gamma$ -Trimethylallyl Alcohol.—Specimens of the alcohol (a) from mesityl oxide, freshly prepared, (b) from mesityl oxide, 12 months old, and (c) from β -methylcrotonaldehyde, 6 months old, were distilled with small quantities of iodine. All gave $\alpha\gamma$ -dimethylbutadiene, b. p. 76.5–77.5°, n_D^{17} 1.4430; the maleic anhydride addition product was formed in good yield, was completely soluble in light petroleum, and had m. p. 57°, undepressed

by a specimen of the adduct prepared from authentic $\alpha\gamma$ -dimethylbutadiene. The same result was obtained from specimen (a) when aniline hydrobromide was used as catalyst.

Thanks are due to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries, Ltd., for grants, also to the Department of Scientific and Industrial Research for a maintenance grant to one of us (D. P. Y.).

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[Received, October 21st, 1940.]
