127. *Reduction of the Carbonyl Group in Unsaturated Ketones, and the Interconversion of Geometrical Isomerides during such Reduction.*

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The unsaturated ketone *n*-butylideneacetone is reduced by aluminium *iso*propoxide to α-methyl-γ-*n*-propylallyl alcohol without simultaneous etherification or reduction of the double bond. Since both the *cis*- and the *trans*-form of the ketone yield identical products, this reagent appears to facilitate interconversion of geometrical isomerides.

During an experimental study of the reactions of *n*-propylpropenylcarbinol (Arcus and Kenyon, this vol., p. 312), the preparation of dl-*α-methyl-γ*-n-*propylallyl alcohol* (I) became

$$\text{(I.)}\quad \mathrm{CHPr^{a}{:}CH{\cdot}CHMe{\cdot}OH} \qquad\qquad \mathrm{CHPr^{a}{:}CH{\cdot}COMe}\quad \text{(II.)}$$

desirable. It has now been prepared by the reduction of *n*-butylideneacetone (II), the *cis*- and *trans*-forms of which were described by Eccott and Linstead (J., 1930, 905). The *cis*-form was prepared by condensing *n*-butaldehyde with acetone and allowing the (exothermic) reaction to proceed unchecked. The slow addition of *n*-butaldehyde to a cooled mixture of acetone and alkali yields the ketol $\mathrm{CHPr^{a}(OH){\cdot}CH_2{\cdot}COMe}$, which, on dehydration with anhydrous oxalic acid gives the *trans*-form of (II). These isomerides have different physical constants and yield different semicarbazones.

Reduction was effected with a solution of aluminium *iso*propoxide in *iso*propyl alcohol by the Ponndorf–Meerwein method (Meerwein and Schmidt, *Annalen*, 1925, **444**, 221;

$$\mathrm{COR_1R_2 + CHMe_2{\cdot}O{\cdot}al \rightleftharpoons {\cdot}COMe_2 + CHR_1R_2{\cdot}O{\cdot}al}$$

Ponndorf, *Z. angew. Chem.*, 1926, **39**, 138) : Lund (*Ber.*, 1937, **70**, 1520) has shown that, by this method, unsaturated ketones yield mainly the *iso*propyl ethers of the unsaturated alcohols initially produced. In the present instance the reaction was stopped as soon as the evolution of acetone had markedly diminished, and although some polymerisation was observed, neither the *iso*propyl ether nor the saturated alcohol was encountered.

From the product of reduction of the *cis*- and of the *trans*-isomeride of the ketone it was possible in each case to isolate—by means of the hydrogen phthalic ester—only one, and the same, alcohol. Since Eccott and Linstead (*loc. cit.*) found the isomeric ketones strongly resistant to configurative change and to yield high-boiling products with alkaline catalysts, it appears very probable that interconversion of geometrical isomerides occurs at the stage when the alcohols exist as aluminium alkoxides.

The identity of α-methyl-γ-*n*-propylallyl alcohol was demonstrated by catalytic reduction to methyl-*n*-amylcarbinol.

Experimental.

Reduction of cis-n-*Butylideneacetone.*—The crude ketone, b. p. 71—77°/16 mm., prepared by the method of Eccott and Linstead (*loc. cit.*), was dried by addition of an equal volume of dry benzene and removal of the latter by distillation through a column; the remaining ketone had b. p. 80°/27 mm. By the special procedure of Eccott and Linstead it furnished a semicarbazone having, after three recrystallisations from aqueous alcohol, m. p. 155°.

This material (132 g.) was added to a solution of aluminium *iso*propoxide in *iso*propyl alcohol (3N, 620 c.c.; prepared by the procedure of Lund, *loc. cit.*), and the mixture heated on a steam-bath in a flask fitted with a return condenser through which water at 65—70° was circulated; acetone distilled over, but the *iso*propyl alcohol was returned. After 4 hours the excess of *iso*propyl alcohol was removed under diminished pressure, and the residue decomposed with ice and dilute sulphuric acid. From an ethereal extract, washed, and dried with potassium carbonate, the crude alcohol, b. p. 69°/17 mm., was obtained. This (39 g.) was heated with a suspension of phthalic anhydride (51 g.) in pyridine (27 g.) at 60—70° for 2 hours, and the cooled product extracted with dilute aqueous ammonia. Extraction of the acidified ammoniacal solution with ether yielded a crystalline product (73 g.), which after two crystallisations from light petroleum gave dl-*α-methyl-γ*-n-*propylallyl hydrogen phthalate* in needles, m. p. 67° (Found, by titration with NaOH : *M*, 262. $\mathrm{C_{15}H_{18}O_4}$ requires *M*, 262).

dl-*α-Methyl-γ-*n*-propylallyl alcohol.* Steam was passed through a solution of the hydrogen phthalic ester (16 g.) and sodium hydroxide (5·4 g.) in water (27 c.c.); extraction of the distillate yielded the *alcohol*, b. p. 66—67°/16 mm., $n_D^{18°}$ 1·4391, $d_{4°}^{17°}$ 0·834 (Found: C, 73·8; H, 12·4. $C_7H_{14}O$ requires C, 73·6; H, 12·4%). Its p-*nitrobenzoate*, formed by adding *p*-nitrobenzoyl chloride (1·6 g.) to a solution of the alcohol (1·0 g.) in pyridine (0·7 g.) and after an interval heating the mixture at 60° for an hour, separated from light petroleum in plates, m. p. 29·5° (Found: C, 64·6; H, 6·6. $C_{14}H_{17}O_4N$ requires C, 63·8; H, 6·5%). Its p-*xenylurethane*, prepared by heating a mixture of the alcohol (1·2 g.) with *p*-xenylcarbimide (2·0 g.) on the steam-bath for an hour, separated from ether–light petroleum in needles, m. p. 87° (Found: C, 77·4; H, 7·35. $C_{20}H_{23}O_2N$ requires C, 77·7; H, 7·5%).

Reduction of trans-n-*Butylideneacetone.*—The ketol (heptan-δ-ol-β-one), prepared according to Eccott and Linstead (*loc. cit.*), b. p. 99°/15 mm., was dehydrated with anhydrous oxalic acid, and the resulting *trans-n*-butylideneacetone, b. p. 61—63°/12 mm., dried by the method described above. It furnished, by the procedure indicated above, a semicarbazone having, after three recrystallisations, m. p. 126°, not increased by further recrystallisation. This material (160 g.), reduced in the same manner as the *cis*-isomeride, yielded the crude alcohol, b. p. 64°/14 mm. This was converted into its hydrogen phthalic ester (100 g.) which, after recrystallisation from light petroleum, formed needles, m. p. 67° alone or when mixed with the hydrogen phthalate of the alcohol obtained by the reduction of the corresponding *cis*-ketone.

Reduction of dl-*α-Methyl-γ-*n*-propylallyl Alcohol to* dl-*Methyl-*n*-amylcarbinol.*—The alcohol (3·3 g.) in ether (24 c.c.) was reduced with hydrogen at 2 atm., in the presence of the platinum catalyst of Adams, Voorhees, and Shriner ("Organic Syntheses," **8**, 92). The solution yielded *dl*-methyl-*n*-amylcarbinol, b. p. 64—65°/13 mm., $n_D^{17°}$ 1·4226; the hydrogen phthalate had m. p. 57·5° (Pickard and Kenyon, J., 1911, **99**, 45, recorded b. p. 73·5°/20 mm., $n_D^{20°}$ 1·4209; *dl*-hydrogen phthalic ester, m. p. 57—58°).

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