REARRANGEMENT DURING REDUCTION OF CIS- AND TRANS-2-PHENYLCINNAMIC ACIDS WITH LITHIUM ALUMINIUM HYDRIDE

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REDUCTION of cis- and trans-2-phenylcinnamic acids, (I) and (II) respectively, with lithium aluminium hydride was expected to give either the saturated alcohol, 22,3-diphenylpropanol (III) or the unsaturated alcohols, 3 cis-2,3-diphenylallyl alcohol (IV) from (I)

 ${\tt PhCH}_2$. СНР h. ${\tt CH}_2$ ОН

$$\begin{array}{c} \text{Ph} \\ \text{C} = \text{C} \\ \text{CH}_2\text{OH} \end{array} \qquad \begin{array}{c} \text{Ph} \\ \text{H} \end{array} \qquad \begin{array}{c} \text{CH}_2\text{OH} \\ \text{Ph} \end{array} \qquad \begin{array}{c} \text{CH}_2\text{OH} \\ \text{Ph} \end{array}$$

L.F. Fieser, Experiments in Organic Chemistry, 3rd Edition, D.C. Heath & Co., Boston, U.S.A. p. 182 (1955).

Cf. R.F. Nystrom and W.G. Brown, J. <u>Amer. Chem. Soc.</u> 69, 2548 (1947).

³ Cf. Li Liang and W.H. Elliott, J. Amer. Chem. Soc. 74, 4089 (1952).

or trans-2,3-diphenylallyl alcohol (V) from (II) or a mixture of (III) and (IV) or (V).

Treatment of either cis-2-phenylcinnamic acid (I), m.p. 174° or trans-2-phenylcinnamic acid (II), m.p. 137° with excess of lithium aluminium hydride in refluxing ether (4 hours) gave needles (\$0\subseteq\$ from light petroleum, b.p. 40-60°), m.p. 66-67° (Found: C, 85.6; H, 6.7. C₁₅H₁₄O requires C, 85.7; H, 6.7\subseteq\$). This product has been shown by the following evidence to be 1,2-diphenylallyl alcohol (VI). In ethanol

the compound has $\lambda_{\rm max}$ 257m μ (log & 4.09) typical of a styrene but not of a stilbene system. Ozonolysis gave benzil in 94% yield. Hydrogenation over Adams catalyst at room temperature and atmospheric pressure gave 1,2-diphenylpropanol (VII), characterised as its phenylurethane, m.p. $115-116^{\circ}$.

1,2-Dirhenylallyl alcohol (VI) was recovered after treatment with acetic anhydride for several hours followed by hydrolysis with ethanolic potassium hydroxide, conditions which normally cause anionotropic rearrangement of 1-phenylallyl alcohols. This result indicates that (VI) is thermodynamically more stable than either (IV) or (V), possibly a result of steric inhibition of resonance in the uniplanar conformations of (IV) and (V).

⁴ Cf. F. Weygand and D. Tietjen, <u>Chem. Ber.</u> <u>84</u>, 625 (1951).

R.A. Morton and A.L. Stubbs, J. Chem. Soc. 1347 (1940).

E.A. Braude, J. Chem. Soc. 1902 (1949).

F. Kayser, Ann. Chim. (France) 6, 145 (1936).

⁸ H. Burton and C.K. Ingold, J. Chem. Soc. 904 (1928).

⁹ Cf. E.A. Braude and P.H. Gore, <u>J. Chem. Soc</u>. 41 (1959).