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THE REDUCTION OF 2-PHENYL-CIS- AND TRANS-CINNAMIC ACIDS WITH LITHIUM ALUMINUM HYDRIDE. THE EQUILIBRATION OF 2-PHENYL-CIS- AND TRANS-CINNAMYL ALCOHOLS AND 1,2-DIPHENYL-2-PROPENOL.

T. Axenrod, E. Bierig[1] and L.H. Schwartz
Chemistry Department, The City College of The City University
of New York, N.Y., 10031

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B. R. Brown and P. E. Brown (1) have reported that either 2-phenyl-*cis*- or *trans*-cinnamic acid (I and II, respectively) undergoes rearrangement to 1,2-diphenyl-2-propenol (III) during lithium aluminum hydride reduction. This claim was based on the following experimental results. The reduction of either of the isomeric acids resulted in the same product, an alcohol, m.p. 66-67°, λ_{max}^{EtOH} 257 mu (logε 4.09). Catalytic reduction gave 1,2-diphenyl-1-propanol (characterized as the phenylurethane) and ozonolysis gave benzil. These results are in disagreement with previous hydride reductions of acids I and II (2,3). As a result of an attempted equilibration in acetic anhydride, B.R. Brown and P.E. Brown further claimed that 1,2-diphenyl-2-propenol (III) was thermodynamically more stable than either 2-phenyl-*cis*-cinnamyl alcohol (IV) or 2-phenyl-*trans*-cinnamyl alcohol (V).

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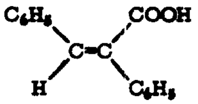
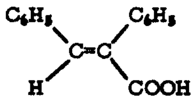
[1] Participant in the National Science Foundation's Research Program for High School Teachers, Summer 1964.



I



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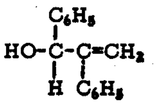

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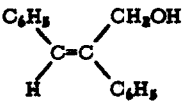

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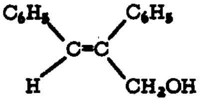

V

It occurred to us that 1,2-diphenyl-2-propenol (III) could have arisen by an allylic rearrangement during the subsequent treatment of the lithium aluminum hydride reaction mixture. To test this hypothesis, solutions of 2-phenyl-*cis*-cinnamic acid (I) and 2-phenyl-*trans*-cinnamic acid (II) were slowly added to a refluxing lithium aluminum hydride[2] slurry in anhydrous ethyl ether, and the products of the reactions were isolated under basic conditions according to the procedure of L.H. Amundsen and L.S. Nelson (4). In each case the same alcohol, m.p. 71-72°, was obtained. The n.m.r.[3] spectrum in anhydrous dimethyl sulfoxide indicated it to be either 2-phenyl-*cis*-cinnamyl alcohol (IV) or 2-phenyl-*trans*-cinnamyl alcohol (V), CH_2 (two doublets, 5.72 τ, *J* 1.8 and 5.5 c./s.), OH (triplet, 4.76 τ, *J* 5.5 c./s.), vinyl-H (triplet, 3.25 τ, *J* 1.8 c./s.), aromatic-H (multiplets, 2.90 τ and 2.69 τ). Further confirmation was obtained by catalytic reduction (5% Pd on carbon or PtO_2, atmospheric pressure) which gave an alcohol whose n.m.r. spectrum in CCl_4 was consistent with 2,3-diphenylpropanol, OH (broad

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[2] Used as supplied by Metal Hydrides, Inc., Beverly, Mass.

[3] N.m.r. spectra were measured using a Varian A-60 spectrometer with tetramethylsilane as an internal reference.

singlet, 7.65 τ), CH_2-CH (multiplet, 7.10 τ), CH_2-O (multiplet, 6.41 τ), aromatic-H (multiplet, 2.92 τ), but not with 1,2-diphenyl-1-propanol[4]. Ozonolysis in methyl acetate, followed by reductive cleavage of the ozonide (hydrogenation with Lindlar's catalyst) gave a mixture of benzaldehyde and phenylglyoxal, identified by infrared analysis. The infrared spectrum of this mixture further indicated the absence of benzil (1). Benzaldehyde was further confirmed by g.l.c. analysis (20% cyclohexanedimethanol succinate). The ultraviolet spectrum, λ_{max}^{MeOH} 257 m u (log ε 4.10), indicated our product to be 2-phenyl-*trans*-cinnamyl alcohol (V) (2) and not 2-phenyl-*cis*-cinnamyl alcohol (IV). The nature of the product obtained seems to depend on the conditions used. When 2-phenyl-*cis*-cinnamic acid (I) in ethyl ether was added to a solution (*ca.* 1 M) of lithium aluminum hydride in ethyl ether, the product obtained was mainly 2-phenyl-*cis*-cinnamyl alcohol (IV) with small amounts of both 2-phenyl-*trans*-cinnamyl alcohol (V) and 2,3-diphenylpropanol (by n.m.r. analysis). On the other hand, slow addition of the lithium aluminum hydride solution to the *cis*-acid (I) gave 2-phenyl-*cis*-cinnamyl alcohol (IV) accompanied by a small amount of 2,3-diphenylpropanol, but no 2-phenyl-*trans*-cinnamyl alcohol (V). Under the various lithium aluminum hydride conditions used, 2-phenyl-*cis*-cinnamyl alcohol (IV) did not isomerize to the *trans*-isomer (V). If, however, prior to reduction a small amount of water is added to the hydride solution, the major product from the *cis*-acid (I) is the *trans*-alcohol (V).

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[4] Catalytic reduction (5% Pd on carbon, atmospheric pressure) of 1,2-diphenyl-2-propenol, m.p. 52.0-52.5°, λ_{max}^{MeOH} 238 m u (log ε 3.92), prepared by the method of J. H. Brewster and H. O. Bayer (2), produced a mixture of diastereomeric 1-2-diphenyl-1-propanols, n.m.r. (CCl_4), methyls (two doublets, 9.01 τ , *J* 7.0 c./s. and 8.81 τ , *J* 7.0 c./s.), OH (broad singlet, 7.82 τ), CH_3C-*H* (quintuplet, 7.12 τ , *J* 7.0 c./s.), O-C-H (broad doublet, 5.55 τ , *J* 7.0 c./s.), aromatic-H (multiplet, 2.87 τ).

These results suggest that prior isomerization of the cis-acid (I) to the trans-acid (II) occurs unless basic salts (due to water) are excluded[5], and further that isomerization can be minimized by inverse addition to a solution of the hydride.

That 1,2-diphenyl-2-propenol should be thermodynamically more stable than either 2-phenyl-cis- or trans-cinnamyl alcohol (1) seemed surprising to us. An attempted equilibration of either 1,2-diphenyl-2-propenol (III) or 2-phenyl-trans-cinnamyl alcohol (V) with refluxing acetic anhydride for four hours, followed by hydrolysis with ethanolic potassium hydroxide (1,5), resulted in essentially quantitative recovery of the starting materials. We can only conclude that this method of equilibration is not applicable to the present allylic alcohol system. At best, this method of equilibration would provide thermodynamic information regarding the corresponding acetates, and not the alcohols.

We attempted to determine the equilibrium composition of the allylic alcohols III, IV and V, using the perchloric acid in aqueous dioxane method of H.L. Goering and R.E. Dilgren (6). The results, summarized in Table I, indicate that 2-phenyl-trans-cinnamyl alcohol is the thermodynamically favored isomer. Although recovery of material from each run was essentially quantitative, the n.m.r. spectra revealed the presence of other materials, possibly arising from a dismutation reaction. The nature of these materials is currently being investigated.

[5] For a similar result see, R.E. Lutz and J.S. Gillespie, Jr., J. Am. Chem. Soc., 72, 2002 (1950).

TABLE I

Equilibration of 1,2-Diphenyl-2-propenol (III), 2-Phenyl-cis-cinnamyl Alcohol (IV) and 2-Phenyl-*trans*-cinnamyl Alcohol (V).

Run	Starting Alcohol	Equilibrium Composition (%)[a,b]		
		III	IV	V
1	III[c]	14	32	54
2	IV[c]	14	35	51
3	V[c]	14	33	53
4	III[d]	14	30	56
5	IV[d]	15	31	54
6	V[d]	14	31	55

[a] Determined by n.m.r. analysis. [b] Alcohols III, IV and V comprised approximately 70% of the recovered material in each run. [c] Conditions: 55% aqueous dioxane, 0.063 M alcohol, 0.46 M $HClO_4$, temperature 95°C, heating period 20 hours, nitrogen atmosphere. [d] Conditions: 75% aqueous dioxane, 0.25 M alcohol, 0.05 M $HClO_4$, temperature 101°C, heating period 87 hours, sealed tube.

REFERENCES

1. B. R. Brown and P. E. Brown, Tetrahedron Letters, 191 (1963).
2. J. H. Brewster and H. O. Bayer, J. Org. Chem., **29**, 105 (1964).
3. R. E. Lutz and E. H. Rinker, Jr., J. Am. Chem. Soc., **77**, 366 (1955); H. E. Zimmerman, L. Singer and B. S. Thyagarajan, J. Am. Chem. Soc., **81**, 108 (1959).
4. L. H. Amundsen and L. S. Nelson, J. Am. Chem. Soc., **73**, 242 (1951).
5. H. Burton and C. K. Ingold, J. Chem. Soc., 904 (1928).
6. H. L. Goering and R. E. Dilgren, J. Am. Chem. Soc., **81**, 2556 (1959).