

dium sulfate) and the ether was removed. The residual mixed alcohols were directly subjected to glpc analysis or were acetylated with a 30% molar excess of acetyl chloride in benzene solution, and the undistilled acetates were subjected to glpc analysis.

**Borohydride Reduction of Substituted Decalones (9b, 9c, 10b, and 10c).**—The ketone (0.012 mol) was added to a stirred solution of sodium borohydride (0.012 mol) in methanol at 0°. The reaction was continued for 4 hr, whereupon dilute hydrochloric acid was added to bring the solution to pH 4. Methanol was evaporated and the residue was continuously extracted with ether. After drying and evaporation of the ether, the mixed alcohols were methylated with ethereal diazomethane if appropriate (*i.e.*, in the case of 9b and 10b). The mixed ester-alcohols were acetylated as before with acetyl chloride and the analysis was carried out on the undistilled acetates.

**Analysis.**—Analyses were performed on an Aerograph Model 600 HyFi with flame ionization detector. The columns were either 15 ft by 1/8 in. stainless steel packed with 10% Carbowax 20M on acid-washed Chromosorb, 80–100 mesh, or 20 ft by 1/8 in. stainless steel packed with FFAP on acid-washed Chromosorb, 80–100 mesh. The oven was operated at constant temperatures varying from 180 to 230° ± 2°.

The composition of the product mixtures was compared before and after acetylation only for *trans*-1-decalone (10a) and *trans*-2-decalone (9a). In these cases, agreement was ±2%—within experimental error—and thereafter only the acetates were determined. The calibration of the column was carried out using authentic samples of *trans-trans*-1-decalyl acetate, *trans-cis*-2-decalyl acetate, and the acetate of methyl *trans-cis*-2-hydroxy-10-decalincarboxylate. In cases where authentic samples were not available, the identifications of equatorial hydroxyl (as acetate) and axial hydroxyl (as acetate) was made by relative retention times.

No attempt was made to isolate the products of the reductions. Reductions of all ketones were essentially complete as shown by the absence of other than trace amounts of unreduced ketone in the infrared spectra. The percentages reported in all cases are relative percentages of reduced materials.

**Registry No.**—Sodium borohydride, 16940-66-2; 9a, 23646-48-2; 9b, 23595-68-8; 9c, 23595-69-9; 10a, 21370-71-8; 10b, 23595-70-2; 10c, 23595-71-3.

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### A Simple and Quantitative Method of Preparation of *cis*-Stilbene and Its Deuterated Analog, Ph—CD=CD—Ph

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In the course of studies of the chemistry of radical ions and dianions of diphenylacetylene, we discovered a simple and quantitative method for synthesis of *cis*-stilbene and of its deuterated analog, Ph—CD=CD—Ph. To our knowledge, no method which yields quantitatively pure *cis* isomer, without admixture of the *trans*-stilbene, has been yet described in the literature.<sup>1</sup>

(1) (a) O. H. Wheeler and H. N. Battle de Fabon, *J. Org. Chem.*, **30**, 1473 (1965). (b) K. N. Campbell and E. E. Young, *J. Amer. Chem. Soc.*, **65**, 965 (1943). Electrolytic reduction of toluene on spongy Ni cathode yields 80% *cis* isomer. (c) It is claimed that hydrogenation of acetylene on 5% palladium on BaSO<sub>4</sub> gives excellent yields of *cis* olefins: R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965, p. 69. However, this reaction was not checked for the toluene reduction.

Ten milliliters of 10<sup>-2</sup> M solution of diphenylacetylene in tetrahydrofuran is treated with metallic lithium at -78°. The chunks of lithium metal used for the reduction are previously washed with a cold (-78°) solution of diphenylacetylene which is subsequently decanted in a high-vacuum system. The reaction is over in *ca.* 1–2 hr and yields a slurry which is removed from the excess of metal by pouring it through a narrow tube into another container. Thereafter a solution of methanol, or deuterated methanol, is added and the protonated products are allowed to warm to room temperature. It should be stressed that all the operations, including the protonation, have to be performed at -78°, preferentially on a high-vacuum line. Whenever the reacting mixture is allowed to warm, even to -60°, other products, including *trans*-stilbene, are formed.

The alkali is extracted with water and the organic layer is extracted with carbon tetrachloride. The alkali-free layer is then dried with anhydrous MgSO<sub>4</sub>, the solvent is evaporated, and the residual *cis*-stilbene (or deuterated *cis*-stilbene) is then isolated. The yield is quantitative. No difficulties are expected in scaling up this preparation.

The product was identified by its uv spectrum, a single sharp peak at 280 mμ characteristic of the *cis* isomer (the *trans* isomer gives a double peak at 298 and 310 mμ and a shoulder at 322 mμ). Its identity was also proved by vpc using a silicone column which separates the isomers (checked with original samples). Finally, the nmr spectrum gives two sharp peaks, one at 393.5 cps, the other at 428 cps, intensities being in the expected ratio 1:5. The deuterated product gives only one peak at 428 cps with no other peaks visible in the spectrum. The nmr spectrum of the *trans* isomer is much more complex, with seven peaks in the range 430–447 cps and the olefinic peak at 421 cps.

It is interesting to point out that the reduction with sodium under similar conditions gives several products, including the *trans* isomer, but none of the *cis* isomer. Apparently, the alkali salts of the dianions of diphenylacetylene have well-defined geometry, namely, the lithium salts being *cis* while the sodium salt appears to be of *trans* form.

The addition of LiCl to the cold (-80°) solution of the sodium salt in THF precipitates the red lithium salt which, on protonation, gives pure *cis*-stilbene.

The organolithium salts often are dimeric,<sup>2</sup> and we tentatively suggest that this tendency of forming quadrupoles may be responsible for the *cis* structure of the dilithium salt. Thus the two lithium cations could be located one above and the other below the plane of the hydrocarbon framework, each interacting with *both* lone electron pairs of the carbanions and with one half of the π-electron cloud. Of course, this geometry requires a *cis* form of the salt.

**Registry No.**—*cis*-Stilbene, 645-49-8; deuterated *cis*-stilbene, 3947-91-9.

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(2) M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience Publishers, New York, N. Y., 1968, Chapter VIII.