

Fig. 2.—Bond angles and distances of triclinic tetraphenylporphine; bonds to hydrogen atoms are broken.

The molecular configuration of triclinic tetraphenylporphine is markedly different from that of the tetragonal form, showing that the porphine system is flexible. Their bond lengths and angles, however, are consistent if the one crystallographically independent pyrrole ring in the tetragonal case is compared to an average of the two independent ones in the triclinic case. Such averaging, however, ignores significant differences between the two types of pyrrole ring. Preliminary results⁴ from this laboratory on silver tetraphenylporphine indicate the possibility of obtaining triclinic crystals of metalloporphines⁵ and thereby observing intramolecular differences among their pyrrole rings also.

The crystallographic details of this structure determination will appear elsewhere.

(4) R. Shapiro and A. Tulinsky, in preparation.

(5) The structures of tetragonal forms of nickel etioporphyrin-II (M. B. Crute, *Acta Cryst.*, **12**, 24 (1959)), nickel etioporphyrin-I (E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963)), and copper tetraphenylporphine (E. B. Fleischer, *ibid.*, **85**, 1353 (1963)), which is isomorphous to tetragonal tetraphenylporphine, have been reported.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

STUART SILVERS
A. TULINSKY

RECEIVED JANUARY 4, 1964

The Influence of Tetrahydrofuran on the Reaction of *n*-Butyllithium with Benzyl Chloride: Halogen-Metal Interconversion vs. α -Hydrogen-Metal Interconversion

Sir:

We wish to report an extraordinary influence of tetrahydrofuran upon the mechanism of the reaction of benzyl chloride with *n*-butyllithium. Earlier studies had indicated that this reaction proceeded *via* halogen-metal interconversion (1), leading to the formation of benzylolithium (I) as a transient intermediate which was rapidly consumed in subsequent coupling reactions to form the observed products, bibenzyl (II) and *n*-amylbenzene (III).^{1,2} When we carried out this reaction at room temperature in tetrahydrofuran, however, there was obtained, in addition to II and III, approximately a 20% yield of *trans*-stilbene. As this

(1) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(2) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

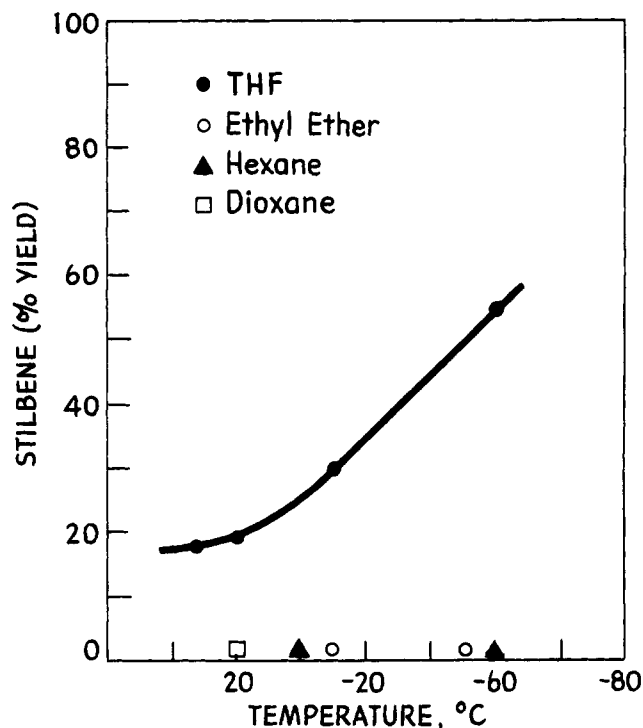
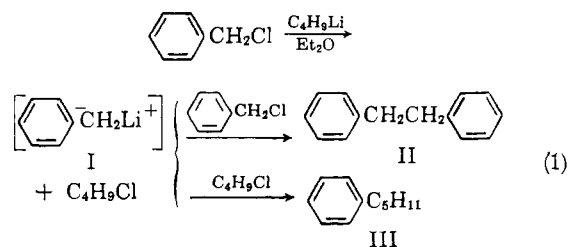


Fig. 1.—The influence of solvent and temperature upon the formation of stilbene from *n*-butyllithium and benzyl chloride.

reaction provides the basis for a widely used analytical method for the quantitative determination of butyllithium, and inasmuch as the presence of stilbene could not be readily accommodated in the proposed mechanism above, we decided to explore how the reaction conditions, such as solvent and temperature, influenced the course of this reaction.³ Figure 1

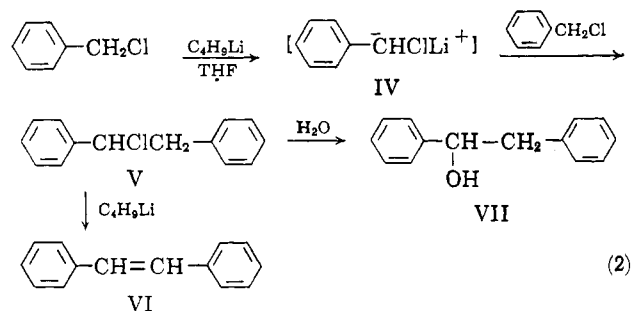


shows how the yield of *trans*-stilbene was affected by these reaction conditions. The unique influence of tetrahydrofuran as a solvent for this reaction, particularly at low temperatures, is evident from this figure.⁴ Additionally, a small amount of a yellow oil was isolated in the chromatographic separation of the products from the tetrahydrofuran reactions (eluted

(3) The procedure adopted was as follows: At the prescribed temperature, 30 ml. of a solution of *n*-butyllithium in heptane (1 mmole/ml.) was added slowly (5 min.) to a solution of 3.8 g. (30 mmoles) of benzyl chloride in 100 ml. of the appropriate solvent under argon. After 2 hr., the reaction was poured into an equal volume of a 50-50 water-petroleum ether (b.p. 37-54°) mixture. The organic phase was separated, dried over Na_2SO_4 , and vacuum stripped. A representative portion of the residue was placed on an alumina column (24 in. \times 1 in.) for chromatographic separation of the products. In a typical separation, the *n*-amylbenzene was the first product eluted with petroleum ether (infrared spectrum identical with authentic sample), followed closely by bibenzyl (m.p. 52°, lit. 52.5°, no depression in mixture melting point, identical infrared spectrum as authentic sample). *trans*-Stilbene (m.p. 124-125°, lit. 124°, identical infrared and ultraviolet spectra with authentic sample). *Anal.* Calcd for $\text{C}_{11}\text{H}_{12}$: C, 93.3; H, 6.7. Found: C, 93.3; H, 6.9, was eluted with a 25 vol.-% solution of benzene in petroleum ether.

(4) Even very small amounts of tetrahydrofuran exert a discernible effect. Thus, little or no stilbene was detected when the reaction was run in hexane at room temperature. In contrast, when a 1-1 molar ratio of tetrahydrofuran-butyllithium (30 mmoles of each) in hexane (100 ml.) was used, approximately a 10% yield of *trans*-stilbene was isolated after 2 hr. reaction.

with 25 vol.-% methanol-benzene) which, on standing several hours, deposited crystals identified as 1,2-diphenylethanol (VII, m.p. 64.5–65°, lit. 65°). *Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.8, H, 7.07, O, 8.1. Found: C, 84.5, H, 7.14, O, 8.8. The presence of both stilbene and 1,2-diphenylethanol suggested that a substantial part of the reaction in tetrahydrofuran involved the formation of α -chlorobibenzyl (V) as an intermediate product (the 1,2-diphenylethanol arising from a small amount of hydrolysis of V during the work-up of the reaction) according to the following reaction sequence.⁵



This reaction mechanism is formally similar to that suggested by Kharasch, *et al.*,⁶ and others,⁷ for the reaction of benzyl chloride with alkali metal amides in liquid ammonia.

We set out to isolate the α -chlorobibenzyl intermediate by adjusting the stoichiometry of the reagents (2 moles of benzyl chloride per mole of *n*-butyllithium), by adding the *n*-butyllithium to the tetrahydrofuran solution of the benzyl chloride, and by using very low reaction temperatures (-100°). After 2 hr. reaction, the yield of α -chlorobibenzyl (V) isolated was over 80% (b.p. 110–112° at 0.5 mm.). *Anal.* Calcd. for $C_{14}H_{13}Cl$: Cl, 16.4. Found: Cl, 16.2. Hydrolysis of V yielded the 1,2-diphenylethanol and base-catalyzed or thermal dehydrochlorination gave *trans*-stilbene. In agreement with the related observation of Wittig and Witt,⁸ this reaction occurs only with α -chlorosubstituted phenylmethanes. The reaction of benzyl bromide with butyllithium under the same conditions³ gave only bibenzyl (88% yield) and amylbenzene, presumably *via* reaction 1.

These data indicate that at low temperatures in tetrahydrofuran *n*-butyllithium reacts with benzyl chloride, practically exclusively by attack of the α -hydrogen atoms (eq. 2), to form α -chlorobenzyl lithium (IV) (or perhaps more accurately, the α -chlorobenzyl carbanion) as a transient intermediate. It is suggested that the unique effect of tetrahydrofuran may be related to its superior solvating ability for the metal cation, and that we are observing the reaction of the dissociated butyllithium (butyl anion displacement on the α -hydrogen). On this basis, one might expect the

(5) It has been known for a long time that symmetrically substituted stilbenes are formed in the reaction of substituted benzyl chlorides with base in aqueous acetone or dioxane, when the substituents on the benzyl chloride are strong electron attractors. Thus, 4,4'-dinitrostilbene is formed from 4-nitrobenzyl chloride and alkali in aqueous acetone or dioxane. Recent evidence has been presented [S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 217 (1961)] indicating that this reaction proceeds *via* α -elimination to form phenylmethylene which dimerizes to form the stilbene. In the early part of this work, we suspected that a similar mechanism could be involved. We attempted to "trap" any carbene as phenylnorcaradiene by using tetrahydrofuran containing cyclohexene (ca. 70 vol.-% cyclohexene at -10°) as the reaction solvent. No phenylnorcaradiene was detected, nor was any appreciable difference noted in the product distribution, using the same procedure as in ref. 3.

(6) M. S. Kharasch, W. Nudenberg, and E. K. Fields, *J. Am. Chem. Soc.*, **66**, 1276 (1944).

(7) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956).

(8) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941).

nature of alkali metal to be of subordinate importance; a point presently being studied. We are also studying the utility of this reaction scheme as a general synthesis for substituted α -chlorobibenzyls and stilbenes.

Acknowledgment.—Infrared and ultraviolet spectral data, which were of considerable help in the identification of these products, were obtained by Mr. John E. Forrette.

BORG-WARNER CORPORATION RESEARCH CENTER
DES PLAINES, ILLINOIS

DONALD F. HOEG
DONALD I. LUSK

RECEIVED NOVEMBER 22, 1963

Total Synthesis of *dl*-Garryine and *dl*-Veatchine¹

Sir:

Very recently we reported² the total synthesis of *dl*-atisine performed in a stereospecific manner. This communication presents a total synthesis of garryine and veatchine, representative garrya alkaloids, in the racemic form.

The pentacyclic dimesyl derivative II, synthesized from the tricyclic conjugated ketone I as described in the preceding paper,² was refluxed with collidine to afford the olefin III,³ m.p. 200–200.5°, in 78% yield.

Sterically controlled hydroboration⁴ of III with bis-3-methyl-2-butylborane followed by oxidation and hydrolysis yielded the desired 1,2-diol V, m.p. 242–245°, purified *via* its acetone (m.p. 228–230°), in 53% yield, and the isomeric 1,3-diol VI, m.p. 262–263°, in 18% yield. Here, no epimeric *endo*-hydroxy compounds were isolated. The 1,2-diol V was smoothly racemized by refluxing a methanolic dioxane solution of its monobrosyl derivative VII with aqueous potassium hydroxide to the bridged ketone VIII having a desired configuration, m.p. 215–217° ($\nu_{\text{max}}^{\text{CHCl}_3}$ 1739 cm^{-1}), in 70% yield. This compound was also synthesized by the following alternative route involving more reaction steps but with higher selectivity. The acetoxy olefin III after hydrolysis (IV, m.p. 189–191°, 203–204°) was epoxidized with perbenzoic acid to give exclusively the *exo*-epoxide IX, m.p. 258–259.5°, which was rearranged with diethyl aluminum chloride to the ketol X, m.p. 242–243° ($\nu_{\text{max}}^{\text{CHCl}_3}$ 1744 cm^{-1}). This compound after ketalization (XI, m.p. 220–221°) was oxidized to the ketone XII, m.p. 205–206° ($\nu_{\text{max}}^{\text{CHCl}_3}$ 1738 cm^{-1}), which on a modified Wolff-Kishner reduction⁵ (XIII, m.p. 198.5–200°) and subsequent deketalization led to the ketone VIII mentioned earlier. By this route the last compound was obtained from the olefin III in an over-all yield (32%) comparable to that (37%) in the former procedure.

Wittig condensation of VIII afforded the *exo*-methylene derivative XIV, m.p. 136–137° ($\nu_{\text{max}}^{\text{CHCl}_3}$ 1659, 882 cm^{-1}), in 90% yield. At this stage it was necessary to replace the protecting N-mesyl group by another suitable one. Thus XIV was demesyated by Birch reduction and the resulting secondary amine XV, m.p. 68–71°, was converted into the N-carbomethoxy derivative XVI, an oil. Introduction of the hydroxyl group at the 19 α position was carried out in a way similar to that previously reported²: XVI underwent bromination with N-bromosuccinimide followed by epoxidation and debromination with zinc to give the allylic alcohol

(1) Angularly Substituted Polycyclic Compounds. XII.

(2) W. Nagata, T. Sugawara, M. Narisada, T. Wakabayashi, and Y. Hayase, *J. Am. Chem. Soc.*, **85**, 2342 (1963).

(3) All compounds show reasonable infrared spectra and those for which melting points are recorded give satisfactory compositional analyses.

(4) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960); G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **85**, 2072 (1963).

(5) W. Nagata, *et al.*, to be published.