α-HALO CARBANION INTERMEDIATES

I. SYNTHESIS OF α-CHLOROBIBENZYLS AND STILBENES VIA THE α-METALATION OF BENZYL CHLORIDES WITH n-BUTYLLITHIUM[*]

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(Received June 11th, 1965)

INTRODUCTION

The reactions of alkyl halides with organolithium compounds have been reported to proceed by a multitude of reaction paths, depending upon the particular structure of the reagents and the reaction conditions. These include halogen–metal interconversion[2,3], hydrogen–metal interconversion (metalation)[4], coupling of the organic fragments of both reagents[5], α-elimination (ref. 6, p. 93), β-elimination[**], and, more recently, direct reduction of the alkyl halide to the alkane[7].

Of these various reaction pathways, the α-elimination reactions of alkyl halides have recently received particular attention, in part due to the general resurgent interest in divalent carbon species (carbenes) as organic reaction intermediates[6,8], coupled with the important discovery of the synthesis of cyclopropanes by the reaction of alkyl halides with organolithium compounds in the presence of olefins[9-14], in which a carbene intermediate had been postulated, although recent studies have cast doubt on the general validity of this hypothesis[15-17].

Work in this laboratory, reported in part in a preliminary communication[1], disclosed that tetrahydrofuran (THF) exerted an extraordinary influence on the reaction of benzyl chloride with n-butyllithium, a very commonly compounded alkyllithium–alkyl halide reaction. At low temperatures in this solvent, the reaction proceeded almost exclusively via α-hydrogen–metal interconversion (α-metalation) to form α-chlorobenzyllithium as the transient intermediate, which reacted rapidly with excess benzyl chloride to give α-chlorobibenzyl in good yield (> 80%). The potential synthetic utility of this reaction was apparent.

To this end, this paper reports now in detail on the influence of reaction conditions upon the α-metalation reaction of benzyl chloride with n-butyllithium, and the development of a simple one-step synthesis of α-chlorobibenzyls (1,2-diarylchloroethanes), and from these, their readily-derived dehydrochlorinated products, the stilbenes. Additionally, the evidence presented here for the intermediacy of α-chloroalkyllithium compounds (potential precursors of the free carbene) and the extension of this work to other chloromethanes[17,18], which will be reported in other papers, was
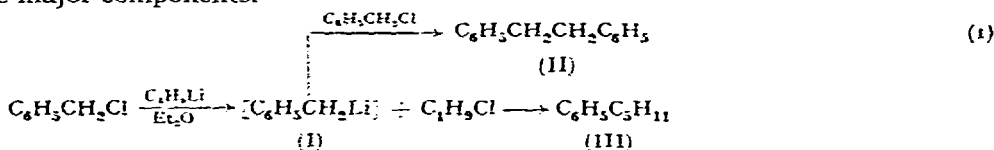
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[*] Reported in part in a preliminary communication[1].

[**] Various elimination mechanisms of organoalkali intermediates are discussed in ref. 9.

expected to have important implications with respect to proposed α-elimination mechanisms and the evidence for free carbene intermediates in the reactions of alkyl halides with organolithium compounds.

DISCUSSION

The basis for the well known and extensively used Gilman–Haubein "double titration" method for the quantitative determination of n-butyllithium is its rapid reaction with benzyl chloride in ethyl ether[19]. As such, it is probably the most commonly exercised of all the possible combinations of alkyl halides with organolithium compounds. The reaction has been suggested by Gilman and Haubein to proceed by a halogen–metal interconversion reaction (1) to form benzyllithium (I) as a transient intermediate, which was rapidly consumed in subsequent cross-coupling reactions to form a mixture of products, containing bibenzyl (II) and n-pentylbenzene (III) as the major components.

$$\begin{array}{c} \xrightarrow{\ C_6H_5CH_2Cl\ } C_6H_5CH_2CH_2C_6H_5 \hfill (\mathrm{1}) \\[4pt] (\mathrm{II}) \\[8pt] C_6H_5CH_2Cl \xrightarrow[\mathrm{Et_2O}]{C_4H_9Li} [C_6H_5CH_2Li] + C_4H_9Cl \longrightarrow C_6H_5C_5H_{11} \\[4pt] \quad\qquad\qquad\qquad\qquad (\mathrm{I}) \qquad\qquad\qquad\qquad\qquad\quad (\mathrm{III}) \end{array}$$
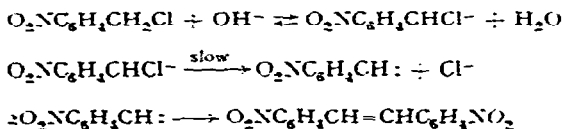
A "flash" of yellow color, typical of benzyllithium, and a "trace" of phenylacetic acid from the carbonation of the reaction mixture were offered as evidence of the intermediacy of (I).
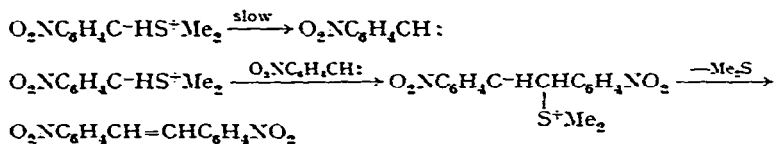
When we carried out this reaction at room temperature in tetrahydrofuran, however, there was obtained, in addition to (II) and (III), approximately a 20 % yield of *trans*-stilbene. The formation of *trans*-stilbene under these conditions was hardly consistent with a primary reaction path of halogen-metal exchange, as noted above. On the other hand, it has long been known that symmetrically substituted stilbenes are formed in the reactions of substituted benzyl chlorides with base in aqueous acetone or dioxane, when the substituents are strong electron attractors*. Thus, 4,4'-dinitrostilbene and 2,2',4,4'-tetranitrostilbene are formed from the reactions of 4-nitrobenzyl chloride and 2,4-dinitrobenzyl chloride, respectively, with alkali in aqueous dioxane or acetone. Recent kinetic data has been presented by Hanna, Iskander and Riad[20],**, which indicated a divalent carbon species was involved. In the closely related reaction of p-nitrobenzyldimethylsulfonium ions with sodium hydroxide, leading to *cis*- and *trans*-4,4'-dinitrostilbene, Swain and Thornton also predicated a carbene intermediate[21]. In this case, however, they suggested that

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* Although, interestingly enough, in pure water only normal hydrolysis products result[20].
** Rate of formation of chloride ion was 1st order in benzyl chloride, and base, and α-deuterium exchange showed proton removal to be reversible, at a rate in excess of that of Cl⁻ liberation. The following reaction sequence was suggested:

$$O_2NC_6H_4CH_2Cl + OH^- \rightleftarrows O_2NC_6H_4CHCl^- + H_2O$$

$$O_2NC_6H_4CHCl^- \xrightarrow{\ \text{slow}\ } O_2NC_6H_4CH\colon + Cl^-$$

$$2O_2NC_6H_4CH\colon \longrightarrow O_2NC_6H_4CH=CHC_6H_4NO_2$$

reaction of the carbene with the carbanion, followed by elimination to yield the stilbene rather than the less likely route of carbene dimerization:
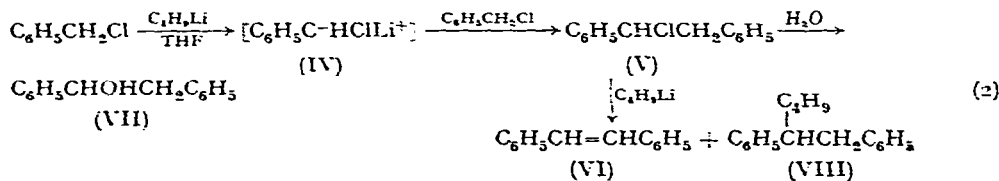
$$O_2NC_6H_4C^-HS^+Me_2 \xrightarrow{\text{slow}} O_2NC_6H_4CH:$$

$$O_2NC_6H_4C^-HS^+Me_2 \xrightarrow{O_2NC_6H_4CH:} O_2NC_6H_4C^-HCHC_6H_4NO_2 \xrightarrow{-Me_2S}$$
$$\underset{S^+Me_2}{|}$$

$$O_2NC_6H_4CH=CHC_6H_4NO_2$$

Additionally, Closs and Closs have reported the formation of 7-phenylbicyclo-[4.1.0]heptane from the reaction of benzyl chloride with n-butyllithium in ether in the presence of cyclohexene, and suggested a phenylcarbene intermediate was likely involved[14]. (Almost prophetically, Hine had cautioned that while cyclopropane formation had been used as part of the circumstantial evidence for the existence of a carbene intermediate in these reactions, it was not in itself adequate evidence, and that the benzyl chloride–butyllithium reaction required further study (ref. 6, p. 99). Closs and Closs also pointed to the possibility that the cyclopropane arose by direct reaction of the "carbene precursor" with the olefin[22].)

With this background of experience, one reasonable explanation of the formation of stilbene in this reaction was to assume an α-elimination had occurred to yield a divalent carbon intermediate structure, which yielded the stilbene by a dimerization route. or via the carbene–carbanion reaction analogous to that suggested by Swain and Thorton[21]. In exploring this reaction in greater detail, however, it became apparent that this reaction rather involved the intermediate role of α-chlorobenzyllithium and not phenylcarbene.

Evidence of an α-metalation reaction and intermediacy of α-chlorobenzyllithium

For all practical purposes, *trans*-stilbene was isolated in pure form only from those reactions run in tetrahydrofuran; the yield increased as the reaction temperature was lowered. Moreover, the presence of cyclohexene, an active "carbene-trap", produced no significant amounts of phenylnorcarane from this reaction run at —10° (*ca.* 70 vol. % cyclohexene in THF). Nor did it affect dramatically the product distribution.

A maximum yield of about 50 % was achieved at —50 to —60°. Additionally, a small amount of a yellow oil was isolated in the chromatographic separation of the products from these reactions (eluted from an alumina column with 25 vol. % methanol–benzene), which on standing several hours deposited crystals identified as 1,2-diphenylethanol (VII). 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, formed by the nucleophilic displacement of the chlorocarbanion on benzyl chloride [the 1,2-diphenylethanol arising from a small amount of hydrolysis of (V) during the workup of the reaction] according to the following reaction sequence:

$$C_6H_5CH_2Cl \xrightarrow[\text{THF}]{C_4H_9Li} [C_6H_5C^-HClLi^+] \xrightarrow{C_6H_5CH_2Cl} C_6H_5CHClCH_2C_6H_5 \xrightarrow{H_2O}$$
$$\text{(IV)} \qquad\qquad\qquad \text{(V)} \tag{2}$$
$$C_6H_5CHOHCH_2C_6H_5 \qquad\qquad \downarrow C_4H_9Li \qquad C_4H_9$$
$$\text{(VII)} \qquad\qquad\qquad\qquad C_6H_5CH=CHC_6H_5 + C_6H_5CHCH_2C_6H_5$$
$$\text{(VI)} \qquad\qquad \text{(VIII)}$$

This reaction mechanism is formally similar to that originally proposed by Kleucker[23] for the reactions of nitrobenzyl chlorides with base, and by Kharasch et al.[24] and Hauser and coworkers[25] for the reactions 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 a 2 h reaction, the yield of α-chlorobibenzyl (V) isolated was over 80%. Reaction of this compound with n-butyllithium in tetrahydrofuran at —50° gave approximately 30–40% *trans*-stilbene, and 1,2-diphenylhexane (VIII) as another product**. Hydrolysis of (V) produced the 1,2-diphenylethanol (68% yield)***.

In attempting to distill the α-chlorobibenzyl at atmospheric pressure, copious fumes of HCl were liberated and a nearly quantitative yield of *trans*-stilbene was isolated. The thermal dehydrochlorination of the α-chlorobibenzyl appeared a much more satisfactory route to the stilbenes than the basic (butyllithium) dehydrochlorination.
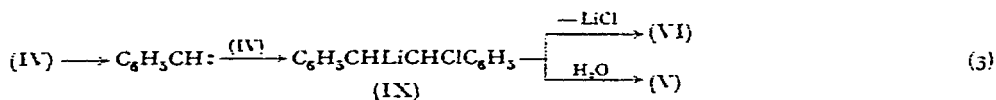
Synthetic route to the α-chlorobibenzyls and stilbenes

These results suggested that this procedure could provide a simple synthesis of α-chlorobibenzyls and stilbenes consisting of two distinct steps: first, the reaction of n-butyllithium with the substituted benzyl chloride (1:2 mole ratio) at —100° in tetrahydrofuran, and subsequently, after isolation of the α-chlorobibenzyl, thermal dehydrochlorination to give the stilbene (4).

The results obtained using this procedure with a number of substituted benzyl chlorides are summarized in Table 1. The results would indicate the procedure provides an excellent and simple synthesis of these compounds; the overall yields of stilbenes generally were very good. The procedure also seems to offer some advantages

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* It is interesting to note that Kharasch *et al.*[24] also found a marked solvent effect on this reaction. Stilbene was formed only in those reactions run in liquid ammonia. No reaction occurred in ligroin and a small amount of benzylamine was isolated in ethyl ether.

** The 1,2-diphenylhexane was eluted from the column in the same range as n-pentylbenzene and it is likely that small amounts of the former were present in the fractions identified as primarily n-pentylbenzene. A high melting compound, 175–185°, believed to be a tetraphenylbutane, was also obtained but incompletely identified.

*** While the detection of the α-chlorobibenzyl in itself has been considered good evidence of the validity of the carbanion mechanism (2) proposed[24,25], it is possible, however unlikely, to account even for its presence via the agency of a carbene intermediate via the carbene–carbanion reaction (3) to form the β-chloroalkyllithium structure (IX). Elimination of LiCl could produce the stilbene and hydrolysis would yield the α-chlorobibenzyl.

$$(IV) \longrightarrow C_6H_5CH: \xrightarrow{(IV)} C_6H_5CHLiCHClC_6H_5 \underset{\substack{\longrightarrow \\ H_2O}}{\overset{\substack{-LiCl \\ \longrightarrow}}{\Big|}} \quad (VI) \qquad (3)$$
$$(IX) \qquad\qquad (V)$$

At —100°, however, this carbene mechanism may be excluded from consideration since it requires an equimolar consumption of benzyl chloride and butyllithium for every mole of α-chlorobibenzyl formed, and under the conditions of our experiment (2 moles of benzyl chloride per mole of n-butyllithium), a maximum yield of 50% α-chlorobibenzyl could have formed (based on benzyl chloride). Moreover, the formation of (V) to the exclusion of (VI) at —100° would require structure (IX) to possess unexpected stability.
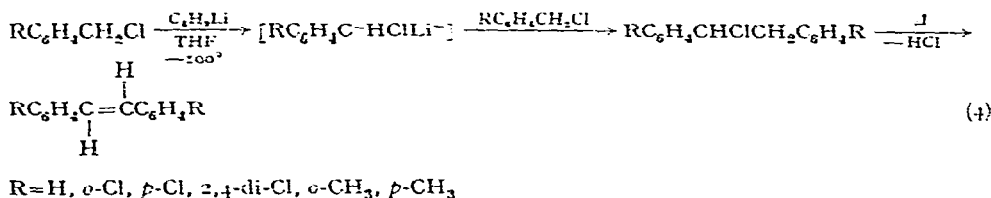
TABLE I

SYNTHESIS OF α-CHLOROBIBENZYLS AND STILBENES FROM SUBSTITUTED BENZYL CHLORIDES

Reactant	α-Chlorobibenzyl	Stilbene	Overall yield of stilbene[a]
$C_6H_5CH_2Cl$	$C_6H_5CHClCH_2C_6H_5$ b.p. 132–134° (2 mm)	$C_6H_5CH=CHC_6H_5$ m.p. 124°	95%
p-$ClC_6H_4CH_2Cl$	p-$ClC_6H_4CHClCH_2C_6H_4$-p-Cl m.p. 81–82°	p-$ClC_6H_4CH=CHC_6H_4$-p-Cl m.p. 176–176.5°	95%
$2,4$-$Cl_2C_6H_3CH_2Cl$	$2,4$-$Cl_2C_6H_3CHClCH_2C_6H_3$-$2,4$-Cl m.p. 62–63°	$2,4$-$Cl_2C_6H_3CH=CHC_6H_3$-$2,4$-Cl_2 m.p. 161–161.5°	50%
o-$ClC_6H_4CH_2Cl$	o-$ClC_6H_4CHClCH_2C_6H_4$-o-Cl b.p. 134–136° (0.5 mm)	o-$ClC_6H_4CH=CHC_6H_4$-o-Cl m.p. 98.5–99°	80%
p-$CH_3C_6H_4CH_2Cl$	p-$CH_3C_6H_4CHClCH_2C_6H_4$-p-CH_3 m.p. 52–52.5°	p-$CH_3C_6H_4CH=CHC_6H_4$-p-CH_3 m.p. 182–182.5°	85%
o-$CH_3C_6H_4CH_2Cl$	o-$CH_3C_6H_4CHClCH_2C_6H_4$-o-CH_3[b]	o-$CH_3C_6H_4CH=CHC_6H_4$-o-CH_3 m.p. 78.5–80°	55%

[a] Thermal dehydrochlorination was carried out till HCl evolution ceased. Solidification occurred on cooling and the product was recrystallized. [b] Purification was difficult since dehydrochlorination started during vacuum distillation.

over the similar route using alkali metal amides and benzyl halides. The alkali metal amides appear to be very powerful agents for the β-elimination of HCl from the intermediate α-chlorobibenzyl. Consequently, the corresponding stilbene is most often obtained along with α-chlorobibenzyl[24,25]. Additionally, handling liquid ammonia and alkali metal amides is avoided.

$$RC_6H_4CH_2Cl \xrightarrow[\text{THF}]{C_4H_9Li} [RC_6H_4C^-HClLi^-] \xrightarrow{RC_6H_4CH_2Cl} RC_6H_4CHClCH_2C_6H_4R \xrightarrow[-HCl]{\Delta}$$

$$RC_6H_4\overset{H}{\underset{H}{C}}=CC_6H_4R \qquad (4)$$

R = H, o-Cl, p-Cl, 2,4-di-Cl, o-CH_3, p-CH_3

The present reaction is limited to substituents which will not compete successfully with the α-protons for reaction with n-butyllithium. Thus, nitro-substituted benzyl chlorides do not give satisfactory yields of the dimeric chloride. The reaction is complicated, and in part, appears to involve direct reaction of n-butyllithium with the nitro group. Additionally, in agreement with a related observation of Wittig and Witt[26], this reaction occurs only with α-chloro-substituted phenylmethanes. The reaction of benzyl bromides with n-butyllithium under similar reaction conditions gave bibenzyl (88% yield) and n-pentylbenzene, presumably via reaction (1).

A number of attempts were made using various substituted benzyl chlorides to detect directly the intermediate α-chlorobenzyllithium compound by attempted carbonation, by pouring the reaction mixture into powdered dry ice shortly after mixing the reactants. The only acid ever present in large enough amounts to detect was n-valeric acid.

The reaction of the intermediate α-chlorobenzyllithium with excess of the benzyl chloride must indeed be very rapid in spite of the very low temperatures and would

TABLE 2

REACTION OF n-BUTYLLITHIUM WITH BENZYL CHLORIDE

Solvent	$C_6H_5CH_2Cl$ (mmoles)	C_4H_9Li (mmoles)	Temp. (°C)	Wt. % of material isolated by chromatography			
				$C_6H_5C_6H_{11}$	$C_6H_5CH_2CH_2C_6H_5$	$C_6H_5CH=CHC_6H_5$	$C_6H_5CHClCH_2C_6H_5$
Hexane	30	30	25	66	31		3.3
	30	30	-50	75		6.0[a]	6.0
Ethyl ether	30	30	-5	62	20	10.0[a]	8.0
	30	30	-50	64	18	4.0[a]	4.0
Dioxane	30	30	20	64	16	2.0[a]	18.0
THF	30	30	25-40	46	30	21.0	6.0
	30	30	20	51	16	19.0	10.0
	30	30	-10	32	20	30.0	16.0
	30	30	-50	32	12	50.0	7.0
	30	45	-50	45	9	43.0	3.0
THF [b]	30	30	-10	34		34.0	28.0
Hexane	30	30[c]	20	52	28	10.0	11.0

[a] Yellow oil. [b] 25 ml, plus 75 ml cyclohexane. [c] Plus 30 mmoles THF.

suggest the α-chlorobenzyl carbanion must be an exceptionally active nucleophile*. The data presented here indicate that at low temperatures in tetrahydrofuran n-butyllithium reacts with α-arylchloromethanes almost exclusively via an α-metalation reaction, leading to the formation of α-arylchloromethyllithium as the active intermediate. The unique influence of tetrahydrofuran upon this reaction is suggested to be due to its superior solvating ability for the metal cation. As a result of the electron-donating ability of the solvent satisfying the electrophilic demand of the lithium ion, the chloro carbanion is permitted a relatively greater opportunity for independent existence in THF.

The results now reported here, moreover, had stimulated us to embark several years ago on a broad study of the reactions of a wide variety of halomethanes with n-butyllithium in tetrahydrofuran at low temperatures. As will be reported in other papers, the intermediacy of α-haloalkyllithium structures provides a common reaction path.

EXPERIMENTAL

All equipment was thoroughly dried before use and "flamed out" after assembly under a purge of dry argon. Precautions were taken to exclude traces of water, carbon dioxide and other possible reactants towards active carbon lithium bonds.

Influence of reaction conditions upon the reaction of n-butyllithium with benzyl chloride

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 h, 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. × 1 in.) for chromatographic separation of the products. In a typical separation, the n-pentylbenzene was the first product eluted with petroleum ether (infrared spectrum agreed 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) was eluted with a 25 vol. % solution of benzene in petroleum ether. (Found: C, 93.3; H, 6.9. $C_{14}H_{12}$ calcd.: C, 93.3; H, 6.7 %.) The yellow oil, eventually identified as 1,2-diphenylethanol was eluted with 25 vol. % methanol–benzene, which on standing several hours deposited crystals (m.p. 64.5–65°, lit. 65°). (Found: C, 84.5; H, 7.14; O, 8.8. $C_{14}H_{14}O$ calcd.: C, 84.8; H, 7.07; O, 8.1 %.)

The results of these experiments are summarized in Table 2. It is interesting to

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* In a slightly different approach to trapping the intermediate α-chlorobenzyllithium compound, benzaldehyde was added to the benzyl chloride at —100° (in equimolar amounts) prior to adding the n-butyllithium. It was hoped that at these low temperatures the n-butyllithium would react more rapidly with the benzyl chloride than with the aldehyde, and that the intermediate α-chlorobenzyl carbanion would add to the aldehyde to yield an epoxide, as observed in the reaction of nitrobenzyl chloride and base in the presence of carbonyl compounds[18]. It was observed, however, that even at —100°, n-butyllithium adds to the benzaldehyde to give the alcoholate to the complete exclusion of reaction with benzyl chloride.

note the profound influence of tetrahydrofuran on the course of this reaction at low temperatures; stilbene is a major product. Further, very small amounts of tetra-hydrofuran influence the course of the reaction. For example, no stilbene is formed in hexane at room temperature. If, on the other hand, a 1:1 molar ratio of tetrahydro-furan–butyllithium solution in hexane is used, moderate amounts of stilbene and 1,2-diphenylethanol are formed.

Preparation of α-chlorobibenzyl, stilbene and 1,2-diphenylethanol

In a typical experiment, benzyl chloride, 10 g (78.8 mmoles), Eastman "white label", was added to 100 ml of dry THF and the solution was cooled to —100°. Then, 39.4 mmoles of *n*-butyllithium in 26 ml of hexane was added dropwise via a hypodermic syringe over a period of 15 min. After 2.5 h at —80 to —100°, the reaction was poured into 200 ml of water and the organic phase was separated. The aqueous phase was extracted with ethyl ether. The organic phases were combined, dried over sodium sulfate and vacuum stripped. A pale yellow liquid was obtained which was fractionally vacuum distilled. (Distillation at atmospheric pressure caused extensive dehydrochlorination of the α-chlorobibenzyl.) There was obtained 0.8 g of unreacted benzyl chloride, b.p. 33–36° (0.9 mm) and 7.47 g (86%) of α-chlorobibenzyl, b.p. 119–122° (1 mm), lit.[24] b.p. 110–111° (0.4 mm), n_D^{25} 1.5775, lit.[24] n_D^{25} 1.5815. (Found: C, 77.8; H, 6.13; Cl, 15.9. $C_{14}H_{13}Cl$ calcd.: C, 77.6; H, 6.04; Cl, 16.4%.)

α-Chlorobibenzyl (1.0 g) was placed in 100 ml of H_2O and refluxed overnight. The cooled mixture was extracted with ethyl ether and the ether phase was dried over Na_2SO_4 and vacuum stripped. Recrystallization of the white residue from ethanol gave prisms of 1,2-diphenylethanol, 0.62 g (68%), m.p. 63.5–65°, lit. 65° (IR spectrum was identical to the standard spectrum of 1,2-diphenylethanol, and identical to the compound isolated above chromatographically).

The α-chlorobibenzyl (0.50 g) was placed into a microdistillation assembly. As the sample was heated gently to reflux, copious evolution of HCl occurred. When no further HCl was evolved, the flask was cooled and the *trans*-stilbene product crystal-lized. Recrystallization of the residue from petroleum ether gave 0.42 g of *trans*-stilbene (> 95%) (m.p. 124°, identical infrared spectrum as the authentic sample). (Found: C, 93.3; H, 6.68. $C_{14}H_{12}$ calcd.: C, 93.4; H, 6.67%.)

The α-chlorobibenzyl (0.76 g, 4 mmoles) was dissolved in 10 ml of tetrahydro-furan and cooled to —40° to —58°. *n*-Butyllithium, 4 mmoles, in 3 ml of hexane was added slowly. The solution rapidly turned darker, finally becoming purple to dark red. After 1.5 h, the reaction was poured into cold water, the organic phase was separated, dried over sodium sulfate and vacuum-stripped to give 0.66 g of an orange-yellow liquid and moist white solid. This was placed on a 12″ ⨯ 0.5″ alumina chromato-graphic column. There was obtained 0.06 g of a clear oil (IR spectrum indicating 1,2-diphenylhexane), 0.22 g (30%) of a *trans*-stilbene (25% benzene–petroleum ether), followed by 0.10 g of a mixture of a yellowish oil and a crystalline white solid melting broadly between 175–185° (tentatively identified as a tetraphenylbutane).

Preparation of 1,2-bis(p-chlorophenyl)-1-chloroethane and 4,4′-dichlorostilbene

In the same manner as described above, 6.42 g (40 mmoles) of *p*,α-dichloro-toluene, Eastman "white label", was dissolved in 100 ml of THF. This solution was cooled to —100° and 21 mmoles of *n*-butyllithium in 14 ml of hexane was added slowly.

After 1.5 h, the reaction was poured into 200 ml of water. The organic phase was isolated as before, dried and vacuum-stripped. There was obtained 5.4 g, 95 % crude yield, of a white, crystalline solid identified as 1,2-bis(p-chlorophenyl)-1-chloroethane. The solid was recrystallized from petroleum ether–tetrahydrofuran solutions, m.p. 81–82°. (Found: C, 59.4; H, 3.95; Cl, 36.0. $C_{14}H_{11}Cl_3$ calcd.: C, 58.8; H, 3.85; Cl, 37.3 %.)

1,2-Bis(p-chlorophenyl)-1-chloroethane (0.54 g) was placed into the microdistillation assembly. Repeated heating with the microburner brought the compound to a gentle reflux and copious evolution of HCl occurred (12.3 % weight loss). After cooling, the solid residue was recrystallized from petroleum ether–THF to yield 0.47 g (quantitative yield) of transparent platelets of 4,4'-dichlorostilbene, m.p. 176–176.5°, lit.[27] 175–176° (IR spectrum was consistent with the postulated structure. Found: C, 67.6; H, 4.07; Cl, 28.5. $C_{14}H_{10}Cl_2$ calcd.: C, 67.5; H, 4.05; Cl, 28.5 %.)

Preparation of 1,2-bis(o-chlorophenyl)-1-chloroethane and 2,2'-dichlorostilbene

o,α-Dichlorotoluene, Eastman "white label", 6.29 g (39 mmoles), was dissolved in 100 ml of dry THF and cooled to −100°. A solution of 19.7 mmoles of n-butyllithium in 14 ml of hexane was added slowly. The solution became pale rose in color. After 1.5 h, the solution was poured rapidly into 200 ml of water and the organic product isolated as before. After vacuum-stripping, there was obtained a pale yellow liquid which was subsequently vacuum-distilled to give 4.5 g, 80 % of a clear liquid identified as 1,2-bis(o-chlorophenyl)-1-chloroethane, b.p. 134–136° (0.5 mm), n_D^{20} 1.596. (Found: C, 59.5; H, 4.01; Cl, 37.2. $C_{14}H_{11}Cl_3$ calcd.: C, 58.8; H, 3.85; Cl, 37.3 %.)

The 1,2-bis(o-chlorophenyl)-1-chloroethane (1.39 g) was thermally dehydrochlorinated as described. There was obtained 1.1 g, 91 %, of white needles, after two crystallizations from petroleum ether, identified as 2,2'-dichlorostilbene, m.p. 98.5–99°, lit.[28] 97–98°. (Found: C, 67.3; H, 4.02; Cl, 28.8. $C_{14}H_{10}Cl_2$ calcd.: C, 67.5; H, 4.05; Cl, 28.5 %.)

Preparation of 1,2-di-p-tolyl-1-chloroethane and 4,4'-dimethylstilbene

4-Methylbenzyl chloride, Benzol Products Co., 10.5 g (75 mmoles) was dissolved in 100 ml of anhydrous tetrahydrofuran in an argon atmosphere. The solution was cooled to −100° and 37.3 mmoles of butyllithium in 25 ml of hexane was added slowly. The solution became pale orange, which then gradually faded. After 3 h, the reaction was quenched in water and the product isolated. We obtained 8.4 g, 91 %, of a clear, pale yellow liquid, which on standing several hours crystallized into white needles, m.p. 52–52.5°, identified as 1,2-di-p-tolyl-1-chloroethane. (Found: C, 78.8; H, 7.05; Cl, 14.5. $C_{16}H_{17}Cl$ calcd.: C, 78.5; H, 6.95; Cl, 14.5 %.)

This product (1.09 g) was heated as described earlier to effect dehydrochlorination. The solid residue was then recrystallized from THF–petroleum ether to give a total of 0.80 g, 86 %, of white platelets, identified as 4,4'-dimethylstilbene (m.p. 182–182.5°, lit.[29] 180°). (Found: C, 92.2; H, 7.80. $C_{16}H_{16}$ calcd.: C, 92.3; H, 7.74 %.)

Preparation of 1,2-di-o-tolyl-1-chloroethane and 2,2'-dimethylstilbene

o-Methylbenzyl chloride, Benzol Products Co., 10.2 g (73 mmoles), was dissolved in 100 ml of anhydrous tetrahydrofuran under an argon atmosphere. After cooling to −100°, 36.8 mmoles of butyllithium was added in 24 ml of hexane. The solution

turned pale yellow-orange. After 3 h, the reaction was quenched in water and worked up as before. We obtained 8.5 g of a pale yellowish liquid, which dehydrochlorinated easily on attempted distillation, as indicated by the low chlorine analysis. (Found: Cl, 11.5. $C_{16}H_{17}Cl$ calcd.: 14.5 %.)

This product (1.28 g) was heated as described earlier and copious fumes of HCl were evolved. The solid residue was recrystallized from petroleum ether to give 0.60 g (55 % overall yield) of 2,2'-dimethylstilbene crystals (m.p. after two recrystallizations, 78.5–80°, lit. 82–83°). (Found: C, 92.3; H, 7.92. $C_{16}H_{16}$ calcd.: C, 92.3; H, 7.74 %.)

Preparation of 1,2-bis(2,4-dichlorophenyl)-1-chloroethane and 2,2',4,4'-tetrachlorostilbene

α,2,4-Trichlorotoluene (14 g, 72 mmoles), Eastman "yellow label", was dissolved in pure THF and cooled to —100°. Thereafter, 35 mmoles of n-butyllithium in 25 ml of hexane was added slowly. The solution darkened and finally became deep red-purple. After 2 h, the reaction was worked up as usual. Vacuum-stripping the dried organic phase gave 11 g of a yellow-white solid, the major amount of which was soluble in hot methanol, which on cooling yielded 6.5 g, 50 %, of a white powder identified as 1,2-bis(2,4-dichlorophenyl)-1-chloroethane, m.p. 61–62°. (Found: C, 48.2; H, 2.73; Cl, 50.3. $C_{14}H_9Cl_5$ calcd.: C, 47.4; H, 2.54; Cl, 50.1 %.)

The methanol mother liquor was stripped to yield 3.0 g of an unidentified yellow liquid. 0.4 g of the original sample was insoluble in methanol and identified as crude 2,2',4,4'-tetrachlorostilbene (m.p. 155–160°), having the same IR spectrum as the product synthesized below.

White, powdery, 1,2-bis(2,4-dichlorophenyl)-1-chloroethane (1.07 g) was thermally dehydrochlorinated as in earlier experiments and lost 0.102 g of HCl (93 % of theory). The residue was recrystallized from THF to give long needles of 2,2',4,4'-tetrachlorostilbene, m.p. 161–161.5°. (Found: C, 53.1; H, 2.60; Cl, 45.2. $C_{14}H_8Cl_4$ calcd.: C, 52.8; H, 2.52; Cl, 44.7 %.)

Reaction of benzyl bromide with n-butyllithium in THF at —100°

Benzyl bromide, 7.13 g (42 mmoles), Eastman "white label", was dissolved in 100 ml of THF and cooled to —100°. A 14 ml solution of 21 mmoles of n-butyllithium in hexane was then added slowly. A light transient orange color formed fading to colorless. After 2 h at —100°, the reaction was quenched and worked up as in earlier experiments with benzyl chlorides. Vacuum-stripping the dried organic phase yielded a white, solid residue which was rinsed with petroleum ether. The total white crystalline residue weighed 3.0 g, 88 %, identified as bibenzyl, m.p. 50–51°. The petroleum ether rinse was evaporated to give 0.40 g, 12 %, of a clear liquid identified as pentylbenzene.

Attempted trapping of the α-chlorobenzyllithium intermediates

Carbonation of the reaction mixtures of benzyl chloride and n-butyllithium, as well as p-chlorobenzyl chloride–butyllithium and o-chlorobenzyl chloride–butyllithium, under a variety of conditions was attempted. These failed to produce enough acid derivatives to analyze satisfactorily.

In an alternate approach to diverting the reaction course of the α-chlorobenzyllithium intermediate (see footnote on page 7), 12.8 g (120 mmoles) of benzaldehyde was added to 16 g (126 mmoles) of benzyl chloride in 100 ml of pure THF. After

cooling the reaction mixture to —100°, 68 mmoles of n-butyllithium was added slowly in 50 ml of hexane. A very pale yellow-orange color formed. After 1 h, the reaction was allowed to warm to room temperature. It was then poured into 200 ml of water and the organic phase separated, extracted with water, dried over sodium sulfate and vacuum-stripped to give a yellow liquid residue. Distillation at 0.5 mm gave 4.2 g of unreacted benzyl chloride and benzaldehyde, b.p. 70–110° (part of the starting material was removed in the vacuum stripping, 8.2 g [(73 %) 1-phenylpentanol, b.p. 111–112° (5 mm)]. (Found: C, 80.7; H, 10.1. $C_{11}H_{16}O$ calcd.: C, 80.5; H, 9.76; O, 9.76 %.)
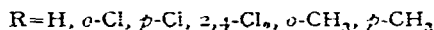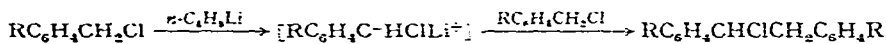
SUMMARY

The reactions of variously substituted benzyl chlorides with n-butyllithium in tetrahydrofuran at low temperatures (—100°) leads to the formation of the correspondingly substituted α-chlorobibenzyl (1,2-diarylchloroethane) in good-to-excellent yields. The corresponding symmetrically substituted stilbenes are readily formed in good yields by thermal dehydrochlorination of the α-chlorobibenzyl.

The data indicate that in tetrahydrofuran at low temperatures the reactions of benzyl chlorides with n-butyllithium proceed almost exclusively via α-hydrogen–metal interconversion (α-metalation), leading to the formation of the α-chlorobenzyllithium as the active intermediate, which is rapidly consumed by subsequent displacement on excess benzyl chloride to produce the observed product, viz.

$$RC_6H_4CH_2Cl \xrightarrow{n-C_4H_9Li} [RC_6H_4C^-HCl Li^+] \xrightarrow{RC_6H_4CH_2Cl} RC_6H_4CHClCH_2C_6H_4R$$

R=H, o-Cl, p-Cl, 2,4-Cl_2, o-CH_3, p-CH_3

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