Anal. Calcd for  $C_{11}H_{10}O_2$ : C, 75.86; H, 5.75. Found: C, 75.85; H, 5.73.

Registry No.—4, 22242-74-6; 4 semicarbazone, 22242-75-7; 5, 22297-83-2; 5 semicarbazone, 22242-76-8; 6, 22242-77-9; 6 semicarbazone, 22242-78-0; 8, 22242-79-1; 9, 22242-80-4; 10, 22242-81-5; 11, 22242-82-6; 13, 22242-83-7; 15, 22242-84-8; 18, 22242-85-9.

# The Coupling of Phenyllithium with trans- and cis-1-Chloro-2-butene<sup>1</sup>

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### Received July 2, 1969

The recent report by Wawzonek, *et al.*,<sup>2</sup> on the reaction of 1-chloro-2-butene with phenyllithium prompts us to communicate our results on the same system, and to point out that the apparent loss of geometrical integrity<sup>2</sup> is due solely to the use of impure starting materials.

According to Wawzonek, et al.,<sup>2</sup> the addition of trans-1-chloro-2-butene (1a) to phenyllithium yields 3-phenyl-1-butene (2), trans- and cis-1-phenyl-2-butene (3a and 3b), and trans-1-methyl-2-phenylcyclopropane (4) in an 18:54:16:11 distribution; similarly, cis-1-chloro-2butene (1b) is alleged to give the same products in the distribution 23:7:67:3.

CH<sub>3</sub>CH=CHCH<sub>2</sub>Cl + PhLi 
$$\rightarrow$$
  
la, trans  
b, cis  
CH<sub>3</sub>CHCH=CH<sub>2</sub> + CH<sub>3</sub>CH=CHCH<sub>2</sub>Ph +  $\rightarrow$   
Ph 3a, trans Ph CH<sub>3</sub>  
2 b, cis 4

The commercially available crotyl chloride assumed by these workers to be *trans*-1-chloro-2-butene is, in fact, a mixture of 1a, 1b, and 3-chloro-1-butene (1c). The first two components have the same retention times on most glpc columns, but can be separated on  $\beta$ , $\beta'$ -oxydipropionitrile.<sup>3</sup> A pure sample (>99%) of *trans*-1-chloro-2-butene (1a) can be obtained by preparative glpc of the commercial material (*ca.* 85% 1a, 15% 1b, and 1% 1c). Similarly, the reaction mixture (*ca.* 5% 1a, 92% 1b, and 3% 1c) from treatment of *cis*-1-hydroxy-2-butene<sup>4a</sup> with thionyl chloride<sup>4b</sup> can be separated by preparative glpc, yielding pure (>99%) *cis*-1-chloro-2-butene (1b).

The results from the reactions of 1a, 1b, and the commercial mixture of 1a and 1b with phenyllithium are summarized in Table I. No geometric isomerization

(1) Support of this work by the Robert A. Welch Foundation is gratefully acknowledged as is the assistance of the National Science Foundation in the purchase of a Varian Associates  $\Lambda$ -56/60A Spectrometer.

TABLE I THE REACTION OF 1-CHLORO-2-BUTENE WITH PHENYLLITHIUM<sup>a</sup>

Starting	Total yield,	Product distribution, %			
chloride	% <sup>b</sup>	2	3a	3b	4
1a	55	22.6	66.0	0ª	11.4
1b	<b>42</b>	23.5	0 <i>d</i>	71.8	4.7
1a + 1b°	63	15.7	62.3	12.4	9.7

<sup>a</sup> The allylic chloride was added to a slight excess of phenyllithium in ether, and the reaction mixture was refluxed for 2 hr. <sup>b</sup> Total yields were determined by quantitative glpc using ethylbenzene as an internal standard. <sup>c</sup> The product distribution was determined by glpc of the crude reaction mixture. <sup>d</sup> None present by the limits of glpc detection. <sup>e</sup> Commercially available crotyl chloride (Aldrich Chemical Co., Inc.).

occurs during the course of the reaction. Control experiments establish that neither 1a nor 1b isomerizes during the reaction, nor is either converted into allylic bromide by reaction with lithium bromide present in the phenyllithium solution; all of the products are stable under the reaction conditions. The clean stereochemistry, therefore, makes it unnecessary to invoke<sup>2</sup> the ionization mechanism<sup>5</sup> which we have argued against earlier.<sup>6</sup>

Cyclopropane 4 undoubtedly arises via a mechanism analogous with that established previously for allyl chloride,<sup>6</sup> concluding with the addition of phenyllithium across the double bond of 3-methylcyclopropene. The fact that 4 is nearly exclusively trans should not be taken as evidence against this mechanism in the light of the known directing effects of a methyl group on the Diels-Alder reactions of cyclopropenes.<sup>7</sup>

We have also investigated the coupling reaction of phenyllithium with 3-chloro-1-butene and with 3-chloro-2-methyl-1-propene- $3,3-d_2$ ; we will report these results, as well as those from all of the dimethyl allyl chlorides, in a future publication.

#### **Experimental Section**

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector) and utilized the following columns: A,  $\beta_i\beta'$ -oxydipropionitrile (15%) on 80/100 Chromosorb P,  $1/_8$  in. × 10 ft; B, a  $1/_8$  in. × 30 ft column composed of a 20-ft section of diethyleneglycol succinate (20%) on 80/100 Chromosorb P, HMDS and a 10-ft section of Bentone 34 (10%) on 80/100 Chromosorb P, HMDS. All yields were determined by glpc using an internal standard; areas were measured with a Disc integrator. Preparative glpc was performed on a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector) and utilized the following columns: C,  $\beta_i\beta'$ -oxydipropionitrile (15%) on 80/100 Chromosorb P,  $3/_8$  in. × 10 ft; D, XF-1150 (10%) on 45/60 Chromosorb P,  $3/_8$  in. × 10 ft.

Nmr spectra were obtained on a Varian Associates A-56/60A spectrometer; ir spectra were obtained on a Beckman IR-8.

Materials.—Crotyl chloride was purchased from Aldrich Chemical Co., Inc.; preparative glpc (column C) yielded pure (>99%, column A) trans-1-chloro-2-butene (1a). Pure (>99%, column A) cis-1-chloro-2-butene (1b) was obtained by preparative glpc (column C) of the reaction mixture<sup>4b</sup> from cis-crotyl alcohol<sup>4a</sup> and thionyl chloride. Phenyllithium in ether was prepared in the usual manner and was standardized by the Gilman method.<sup>8</sup> All reactions involving lithium reagents were run under an argon atmosphere.

**Reaction of 1-Chloro-2-butene with Phenyllithium.**—Pure trans-1-chloro-2-butene (1a, 0.90 g, 0.01 mol) in 5 ml of ether was added dropwise over 15 min to 15 ml (0.012 mol) of 0.8 N

<sup>(2)</sup> S. Wawzonek, B. J. Studnicka, and A. R. Zigman, J. Org. Chem., 34, 1316 (1969).

<sup>(3)</sup> L. J. Brubacher, L. Treindl, and R. E. Robertson, J. Amer. Chem. Soc., **90**, 4611 (1968).

<sup>(4) (</sup>a) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950); (b) S. H. Sharman, F. C. Caserio, J. C. Leak, and W. G. Young, *ibid.*, **80**, 5965 (1958).

<sup>(5)</sup> S. J. Cristol, W. C. Overhults, and J. S. Meek, ibid., 73, 813 (1951).

<sup>(6)</sup> R. M. Magid and J. G. Welch, ibid., 90, 5211 (1968).

<sup>(7) (</sup>a) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **35**, 3796 (1963);
(b) M. A. Battiste, *Tetrahedron Lett.*, 3795 (1964).

<sup>(8)</sup> H. Gilman and A. H. Haubein, J. Amer. Chem. Soc., 66, 1515 (1944).

phenyllithium in ether; 0.50 g of ethylbenzene was present as an internal standard. The reaction mixture was refluxed for 2 hr and was then hydrolyzed with 10 ml of water. The ether layer was separated, dried (calcium sulfate), and analyzed (column B), giving the yield and product distribution reported in Table I.

In the same manner, *cis*-1-chloro-2-butene (1b) and commercial crotyl chloride were allowed to react with phenyllithium. The results of these reactions are summarized in Table I.

Separation and identification of the various products was performed on the reaction mixture from 22.8 g of commercial crotyl chloride. The ether layer was concentrated and separated by preparative glpc (column D) into three components. The first in order of elution was identified (nmr) as 3-phenyl-1-butene (2), the second (nmr, ir, comparison with a commercial sample, Matheson Coleman and Bell) as *trans*-1-phenyl-2-butene (3a), and the third (nmr) as a mixture of *cis*-1-phenyl-2-butene (3b) and *trans*-1-methyl-2-phenylcyclopropane (4). This last mixture was separated into its two components by column chromatography on 15% silver nitrate on silica gel.

Controls on Reagent and Product Stability.—Aliquots taken at various times from the reaction mixtures of phenyllithium with 1a and 1b were analyzed by glpc (column A) and showed no isomerization (geometric or positional) of the starting chloride and no conversion into an allylic bromide. Each of the hydrocarbon products was refluxed for 2 hr in excess phenyllithium in ether containing an internal standard; all four compounds survived this treatment unchanged.

**Registry No.**—Phenyllithium, 591-51-5; 1a, 4894-61-5; 1b, 4628-21-1.

# 1,3 Rearrangements of the Dichloromethyl Group<sup>1</sup>

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# Received April 7, 1969

The rearrangement of 3,4-dimethyl-4-trichloromethyl-2 5-cyclohexadienone (1) to 4-methyl-3- $(\beta,\beta,\beta$ -trichloroethyl)chlorobenzene (2) represents a 1,3 migration of a trichloromethyl group to an adjacent methyl group on an aromatic ring.<sup>3</sup> The present research was undertaken to see if a compound containing a dichloromethyl group would undergo a similar rearrangement.



The dienones 3 and 5 were prepared by treatment of 3,4-dimethylphenol and 3,4-dimethyl-1-naphthol with chloroform and alkali.<sup>4</sup> Treatment of 3 with phosphorus pentachloride yielded 4-methyl-3- $(\beta,\beta$ -dichloro-

(1) This work was taken from the Ph.D. thesis of W. X. Bajzer, The Ohio State University, 1968, and was supported in part by National Science Foundation Grant 5552.

(2) Goodyear Research Fellowship, 1967-1968, and Dissertation Fellowship, The Ohio State University Graduate School, 1968.

(3) (a) M. S. Newman and L. L. Wood, Jr., J. Amer. Chem. Soc., 81, 6450
(1959); (b) see M. S. Newman and F. Bayerlein, J. Org. Chem., 28, 2804
(1963), for a similar rearrangement.

(4) K. von Auwers and G. Keil, Ber., 35, 4207 (1902).

ethyl)chlorobenzene (4), but required long heating in phosphorus oxychloride whereas 1 reacted exothermically<sup>3a</sup> to yield 2.

Both 3 and 5 were converted into the corresponding tertiary alcohols 6 and 7 on treatment with phenyl-magnesium bromide. As both 6 and 7 were unstable to heat, they were not analyzed. The crude carbinols were heated to yield 8 and 9, respectively.



The rearrangement of 6 to 8 was shown to proceed through the intermediate triene<sup>5</sup> 10 by trapping the latter with tetracyanoethylene (TCNE) to yield the adduct 11. No attempt to trap a similar triene in the case of 7 was made.



Attempts were made to improve the yields of **3** by generation of dichlorocarbene in different ways, but the yields were never better than those obtained by the conventional Reimer-Tiemann procedure. The partial reduction of **1** to **3** by heating with tri-*n*-butylphosphine<sup>6</sup> in benzene was accomplished. Thus, the route to a dichloromethylcyclohexadienone *via* a trichloromethylcyclohexadienone may prove superior to the Reimer-Tiemann route, since the yields of trichloromethylcyclohexadienones are often good.

Several unsuccessful attempts to introduce fluorine into 1 were made. The details may be found in the Ph.D. thesis cited in ref 1.

<sup>(5)</sup> Compare M. S. Newman and R. M. Layton, J. Org. Chem., 33, 2338 (1968).

<sup>(6)</sup> Cf. B. Miller, J. Amer. Chem. Soc., 91, 751 (1969).