

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.

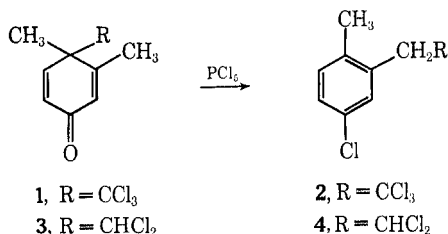
1,3 Rearrangements of the Dichloromethyl Group¹

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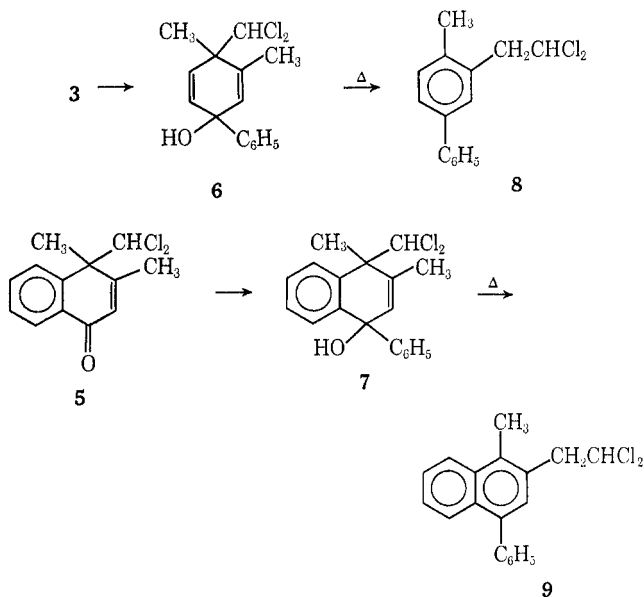
The rearrangement of 3,4-dimethyl-4-trichloromethyl-2-5-cyclohexadienone (1) to 4-methyl-3-(β,β,β -trichloroethyl)chlorobenzene (2) represents a 1,3 migration of a trichloromethyl group to an adjacent methyl group on an aromatic ring.³ The present research was undertaken to see if a compound containing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



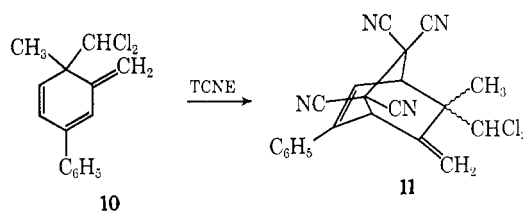
The dienones 3 and 5 were prepared by treatment of 3,4-dimethylphenol and 3,4-dimethyl-1-naphthol with chloroform and alkali.⁴ Treatment of 3 with phosphorus pentachloride yielded 4-methyl-3-(β,β -dichloro-

ethyl)chlorobenzene (4), but required long heating in phosphorus oxychloride whereas 1 reacted exothermically^{3a} to yield 2.

Both 3 and 5 were converted into the corresponding tertiary alcohols 6 and 7 on treatment with phenylmagnesium 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 triene⁵ 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*-butylphosphine⁶ 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.

(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).

(5) Compare M. S. Newman and R. M. Layton, *J. Org. Chem.*, **33**, 2338 (1968).

(6) Cf. B. Miller, *J. Amer. Chem. Soc.*, **91**, 751 (1969).