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[1]

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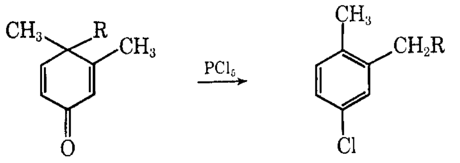
The rearrangement of 3,4-dimethyl-4-trichloromethyl-2 5-cyclohexadienone (**1**) to 4-methyl-3-(β,β,β-trichloroethyl)chlorobenzene (**2**) represents a 1,3 migration of a trichloromethyl group to an adjacent methyl group on an aromatic ring.[3] The present research was undertaken to see if a compound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

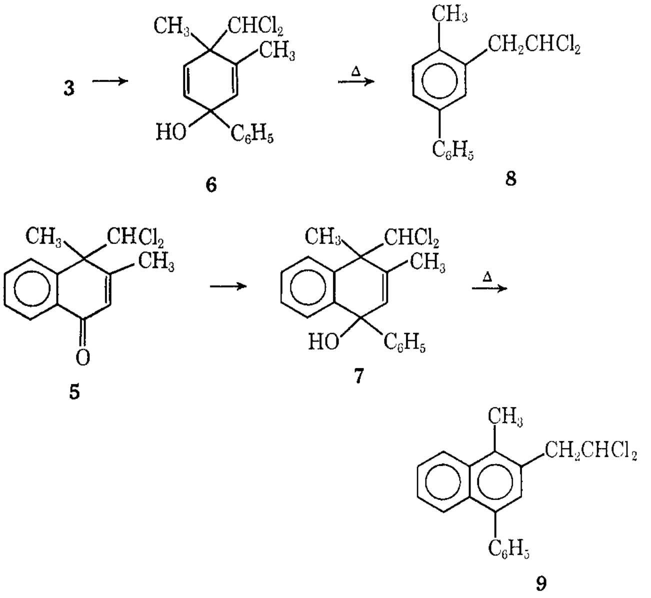


1, R = CCl_3 **2**, R = CCl_3

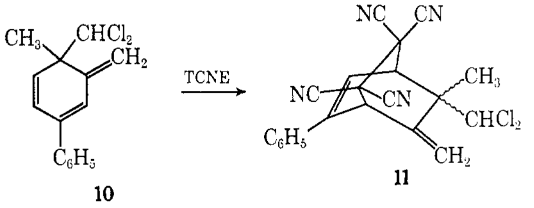
3, R = $CHCl_2$ **4**, R = $CHCl_2$

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-dichloroethyl)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 triene[5] **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[6] 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.

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[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).

Experimental Section[7]

4-Dichloromethyl-3,4-dimethyl-2,5-cyclohexadienone (3).—By the reaction of 3,4-dimethylphenol with chloroform and 15% aqueous sodium hydroxide, **3**,[4] mp 100–101°, was prepared in 15% yield.

4-Dichloromethyl-3,4-dimethyl-1-keto-1,4-dihydronaphthalene (5).—To a solution of 30.0 g (0.17 mol) of 3,4-dimethyl-1-naphthol[8] in 1 l. of 20% aqueous sodium hydroxide at 65° was added dropwise 200 g of chloroform during 1 hr. The mixture was refluxed for 2 hr, stirred at room temperature overnight, and diluted with an equal volume of water. The usual work-up afforded 8.0 g of a dark oil. Distillation and collection of the cut, bp 167–190° (1 mm), gave 5.5 g (12%) of **5** as colorless needles: mp 87.5–88.5° (from benzene–hexane); ir 6.04 μ (C=O); nmr (CCl_4) 1.81 (s, 3 H), 2.29 (d, 3 H), 6.19 (s, 1 H), 6.48 (m, 1 H), and 7.4–8.2 ppm (4 H).

Anal. Calcd for $C_{13}H_{12}Cl_2O$: C, 61.2; H, 4.7; Cl, 27.8. Found: C, 61.1; H, 5.0; Cl, 27.8.

3-(β,β-Dichloroethyl)-4-methylchlorobenzene (4).—A solution of 15.0 g (0.07 mol) of **3** and 15.2 g (0.07 mol) of phosphorus pentachloride in 160 ml of phosphorus oxychloride was refluxed for 4 hr, and then strip-distilled to remove 75% of the solvent. The remainder was left at room temperature overnight and then poured over 100 g of crushed ice. After the usual work-up, distillation gave 12.1 g (74%) of colorless **4**: bp 82.5–83.5° (0.20 mm); $n^{25}_{\rm D}$ 1.5614.

Anal. Calcd for $C_9H_9Cl_3$: C, 48.4; H, 4.1; Cl, 47.6. Found C, 48.2; H, 4.2; Cl, 47.6.

Comparative reactions of **1** and of **3** with phosphorus pentachloride in refluxing methylene chloride showed that the former required 4–6 min for complete reaction (absence of ir band near 6 μ) while the latter required 24–26 min.

Oxidation of 1 g of the above rearrangement product in 15 ml of pyridine with a solution of 1.5 g of potassium permanganate in 25 ml of water containing 15 ml of pyridine for 2 hr at room temperature and 4 hr at 60° gave 0.60 g of recovered material after the usual work-up. Acidification of the aqueous phase gave 0.20 g (66%) of 5-chloro-2-methylbenzoic acid, mp 169–170° (lit.[3a] mp 169.5–171°), identical with an authentic sample.[3a]

4-Dichloromethyl-3,4-dimethyl-1-phenyl-2,5-cyclohexadienol (6).—A solution of 5.0 g (0.024 mol) of **3** in 200 ml of dry ether was added to *ca.* 0.05 mol of phenylmagnesium bromide in 400 ml of ether. The solution was refluxed for 2 hr, cooled, and poured over 400 g of crushed ice. The organic layer was worked up as usual to give 10.4 g of a semisolid which contained **6**. After standing for 20 min, the material was filtered and 6.5 g of clear cubes of **6** (ir 2.73 μ) was obtained. As **6** is unstable at room temperature, no analysis was obtained. If heated rapidly after insertion in a bath at 80°, **6** melts at about 90°. In solution **6** is also unstable, as rearrangement to **8** occurs readily.

3-(β,β-Dichloroethyl)-4-methylbiphenyl (8).—A solution of 7.5 g (0.03 mol) of freshly prepared **6** in 100 ml of methylene chloride was refluxed for 1–2 hr and worked up as usual to give 6.9 g of an orange oil. Distillation gave 5.2 g (73%) of 3-(β,β-dichloroethyl)-4-methylbiphenyl (**8**): bp 138–140° (0.30 mm); n^{26}b 1.6059.

Anal. Calcd for $C_{15}H_{14}Cl_2$: C, 68.0; H, 5.3; Cl, 26.7. Found: C, 68.0; H, 5.1; Cl, 26.8.

The nmr and infrared spectra were consistent with the structure indicated. A 1.5-g sample of the above rearrangement product was added to a solution of 2.0 g of potassium permanganate in 45 ml of water. After refluxing for 18 hr, the mixture was filtered. Acidification of the filtrate followed by ether extraction and work-up as usual of the organic layer gave 1.05 g (88%) of 2-methyl-5-phenylbenzoic acid, mp 205–206°, identical with an authentic sample.[9]

3-(β,β-Dichloroethyl)-4-methyl-1-phenylnaphthalene (9).—A solution of 3.0 g (0.012 mol) of **5** in 200 ml of ether was added to a solution of phenylmagnesium bromide (prepared from 0.02 mol of bromobenzene in 300 ml of ether). The mixture was stirred overnight at room temperature and poured over 200 g of crushed ice. The organic layer was worked up as usual to give crude carbinol **7**, which was heated at 120° for 5 min and cooled. Distillation gave 1.7 g (57%) of recovered **5**, bp 149–168° (0.21 mm), and 1.9 g of residue. The latter was chromatographed over silica gel and purified by molecular distillation to give 1.3 g (81%, based on recovered **5**) of **9**: mp 81–82° (from hexane); nmr (CCl_4) 2.50 (s, 3 H), 3.48 (d, 2 H), 5.69 (t, 1 H), and 6.9–8.0 (1 H, aromatic region). Analysis by mass spectrometry at 70 eV gave the expected parent, parent + 2 and parent + 4 ions at *m/e* 314, 316, and 318, respectively, in a ratio of 1.0:0.64:0.13 (calculated ratio on the basis of relative isotopic abundances for the two chlorine atoms present gave 1.0:0.65:0.11).

Anal. Calcd for $C_{19}H_{16}Cl_2$: C, 72.4; H, 5.1; Cl, 22.5. Found: C, 72.2; H, 5.1; Cl, 22.7.

Trapping of 6-Dichloromethyl-6-methyl-1-methylene-3-phenyl-2,4-cyclohexadiene (10).—The color of a refluxing solution of 1.2 g of **6** and an equimolar amount of tetracyanoethylene in 30 ml of methylene chloride for 30 min changed from yellow to green to red. After the solution had cooled, the solvent was removed under dry nitrogen to give 1.50 g (91%) of a tan 1:1 adduct (**11**). Recrystallization from chloroform–hexane gave 1.2 g of **11** as colorless plates, mp 184–185° in a sealed tube (bath preheated to 170°). Attempted sublimation led to decomposition. The nmr spectrum (acetone-d_6) showed peaks at 1.52 (s, 3 H), 3.01 (s, 1 H), 3.06 (s, 1 H), 4.18 (d, 1 H, J_{HH} = 3 Hz), 5.00 (d, 1 H, J_{HH} = 3 Hz), 6.59 (s, 1 H), 6.90 (s, 1 H), and 7.4–8.0 (5 H, aromatic region). Analysis by mass spectrometry at 70 eV gave the proper parent, parent + 2 and parent + 4 ions at *m/e* 392, 394, and 396, respectively, in a ratio of 1.0:0.66:0.14 (calculated ratio on the basis of relative isotopic abundances for two chlorine atoms present gave 1.0:0.65:0.11). Other characteristic ions present were at *m/e* 357 and 359 (corresponding to loss of a chlorine atom from parent and parent + 2 ions) and at *m/e* 264 and 266 (corresponding to loss of tetracyanoethylene from parent and parent + 2 ions).

Anal. Calcd for $C_{21}H_{14}Cl_2N_4$: N, 14.3. Found: N, 14.5.

Reaction of 1 with Tri-*n*-butylphosphine.—A solution of 5.0 g (0.02 mol) of **1** and 5.2 ml(0.02 mol) of tri-*n*-butylphosphine in 50 ml of benzene was heated at reflux for 6 hr under dry nitrogen. Analysis of an aliquot by nmr and thin layer chromatography showed that one part of **1** and two parts of **3** were present. Addition of 50 ml of absolute ethanol, followed by refluxing for an additional 18 hr, gave no change in the ratio of dienones present.

Registry No.—**4**, 22242-68-8; **5**, 22242-69-9; **8**, 22242-70-2; **9**, 22242-71-3; **10**, 22242-72-4; **11**, 22242-73-5.

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(7) Melting points and boiling points are uncorrected. Analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and the Alfred Bernhardt Microanalytical Laboratory at the Max Planck Institute, Mühlheim (Ruhr), West Germany. The nmr spectra were recorded on a Varian Associates A-60 A spectrometer, employing tetramethylsilane as an internal reference. Chemical shifts are reported in parts per million downfield from tetramethylsilane. The phrase "worked up in the usual manner," used throughout this section, refers, with minor variations, to the handling of organic solutions in the following manner. The organic solution was successively washed with water and saturated sodium chloride solution and dried by filtering through a bed of anhydrous magnesium sulfate, and the solvent was removed *in vacuo*.

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Catalytic Norbornadiene–Butadiene and Norbornadiene–1,1-Dimethylallene Codimerization

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In previous papers,[1-3] we described the behavior of iron catalysts, and in particular of bis(cyclooctatetraene)iron [$Fe(COT)_2$] in the cooligomerization of some unsaturated hydrocarbons. After having studied the

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(1) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, **22**, 2037 (1967).

(2) A. Carbonaro, A. Greco, and G. Dall'Asta, *J. Org. Chem.*, **33**, 3948 (1968).

(3) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, **49**, 5129 (1968).