Solutions containing ionic detergents were made up by adding the desired weight of the solid to the stock solutions just before mixing with diazonium salt solutions. No volume change effects were observable. Because of the larger quantities of Triton X-100 needed this detergent was added to the stock acetate buffer before the final dilution to the mark with water.

**Registry No.**—*p*-Nitrophenyldiazonium ion, 14368-49-1; S salt, 93-01-6; R salt, 148-75-4.

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## The Reaction of Phenyllithium with Allyl Chloride. Addition of Phenyllithium to Lithiated Cyclopropenes

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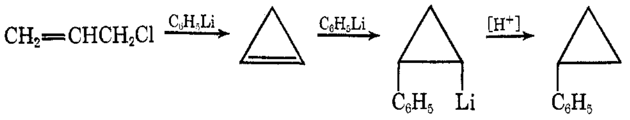
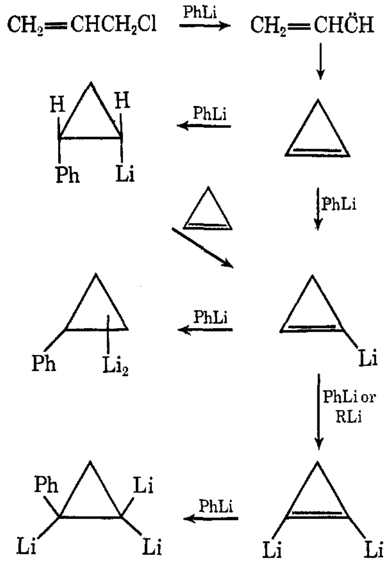
The formation of phenylcyclopropane from the reaction of phenyllithium with allyl chloride in ether has been the subject of at least four proposed mechanisms.[1,2] The mechanism which has gained the most impressive confirmation[3] is 1,1 elimination to form cyclopropene, followed by addition of phenyllithium to the double bond and protolysis of the 2-phenylcyclopropyllithium thus formed. The principal difficulty with this mechanism is that the source of the proton in the last step has not been found. It has been reported by two groups[2,3] that, if reaction mixtures were treated with deuterium oxide, the phenylcyclopropane isolated contained no deuterium, apparently ruling out water in the isolation procedure as the proton source. Magid[3] has suggested ether, allylbenzene, and allyl chloride as proton sources, but the first two are too slow in their reactions with phenylcyclopropyllithium[3] to account for the lack of deuterium incorporation with $D_2O$ after a reaction run under mild conditions,[2] and the last is unsuitable under at least some conditions since allyl-1,1-$d_2$ chloride gives phenylcyclopropane containing only one deuterium[3] (confirmed in this work).



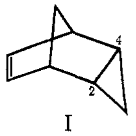
The source of the proton for the last step and hence a strong confirmation of the cyclopropene mechanism has now been found to be cyclopropene itself. If the reaction is run with a 1.50 mole ratio of phenyllithium to allyl chloride (as opposed to ratios 0.75–1.20 previously used), followed by a deuterium oxide quench, the isolated phenylcyclopropane contains an average deuterium content of 1.47 atoms (combustion analysis) and includes $d_1$, $d_2$, and $d_3$ species (mass spectrometry). The deuterium atoms were shown to be exclusively on the cyclopropane ring by quantitative integration of the H nmr and D nmr spectra, with 0.37 atoms in the $\alpha$ position and 1.10 atoms in the $\beta$ positions. A control showed that treatment of phenylcyclopropane with phenyllithium, followed by a deuterium oxide quench, gave no detectable deuterium incorporation. It is concluded that phenylcyclopropane does in fact arise from addition of phenyllithium to cyclopropene, and that di- and trideuterated phenylcyclopropanes form as a result of addition of phenyllithium to the metalated cyclopropenes, 1-lithiocyclopropene and 1,2-dilithiocyclopropene (Scheme I).

Scheme I



The source of protons to make phenylcyclopropane in the absence of sufficient phenyllithium is then seen to be cyclopropene, certainly the best proton acid in the medium.

Two other observations serve to confirm the mechanism shown in Scheme I. The first is that, when a reaction mixture of allyl chloride and methyllithium was quenched with deuterium oxide and the resulting cyclopropene was allowed to react with cyclopentadiene, the adduct I was obtained with 1.48 atoms/molecule of deuterium, all of it being in the 2 and 4 positions, according to H nmr and D nmr spectra, in which the multiplet at $\delta$ 1.31 was assigned to $C_2$ and $C_4$. The presence of 1,2-dilithiocyclopropene in a reaction mixture very similar to the phenyllithium mixture was thus supported, although the experiment did not exclude the possibility of base-catalyzed exchange of unlithiated or monolithiated cyclopropene with deuterium oxide.



I

A second observation pertinent to the mechanism in Scheme I is the finding that 3-phenyl-1,5-hexadiene (II) is a minor (2–5%) product of the reaction of phenyllithium with allyl chloride. When the reaction was run with allyl-1,1-$d_2$ chloride, the II formed contained almost no proton at $C_3$, while positions $C_4$ and $C_6$

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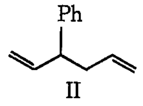
[1] S. Wawzonek, B. Studnicka, H. J. Bluhm, and R. E. Kallio, *J. Amer. Chem. Soc.*, **87**, 2069 (1965).

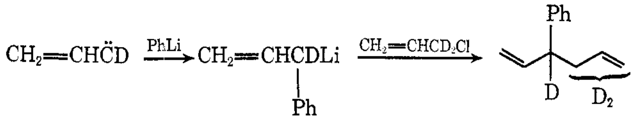
[2] D. E. Applequist and M. A. Lintner, *J. Org. Chem.*, **31**, 3062 (1966).

[3] R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **90**, 5211 (1968), and earlier references cited therein.



II

shared two deuterium atoms (by pmr integration). A reasonable explanation is that the vinylcarbene or carbenoid intermediate is trapped by phenyllithium to give 1-phenylallyllithium, which couples with allyl chloride.



$$CH_2{=}CH\ddot{C}D \xrightarrow{PhLi} CH_2{=}\underset{\displaystyle Ph}{\underset{|}{CHCDLi}} \xrightarrow{CH_2{=}CHCD_2Cl}$$

It is pertinent that allylbenzene isolated from a phenyllithium–allyl chloride reaction with a deuterium oxide quench shows no deuterium incorporation.

### Experimental Section[4]

**The Reaction of Allyl Chloride with Phenyllithium.**—To 50 ml of a 1.2 *N* solution of phenyllithium (0.06 mol) at 0° in ether[5] was added dropwise 3.06 g (0.04 mol) of allyl chloride in 5 ml of ether, while the vapor above the stirred solution was swept slowly (60 min) with argon through a dewar condenser at −70° into a solution of 6.60 g (0.100 mol) of freshly distilled cyclopentadiene in 150 ml of methylene chloride at 0°. The mixture in the first flask was then treated with 50 g of water and heated to reflux for 5 min, while the argon flow was continued, now through the Dewar condenser at 0°. The phases were then separated, the aqueous phase was washed with 10 ml of ether, and the ether phases were combined and dried ($MgSO_4$).

Distillation and analytical gc (0.25 in. × 10 ft 20% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 Chromosorb P column at 125°, flow rate 100 ml/min) showed allylbenzene at 7.0 min, phenylcyclopropane at 13.3 min, and 3-phenyl-1,5-hexadiene at 19.6 min in a ratio of 68:22:10, respectively. Preparative gc (0.375 in. × 5 ft 20% 1,2,3-tris(2-cyanoethoxy)propane on 45/60 Chromosorb A column at 135°, flow rate 100 ml/min) gave 1.184 g (0.01004 mol, 25.2%) of allylbenzene, 0.334 g (0.00284 mol, 7.1%) of phenylcyclopropane, and 0.156 g (0.00099 mol, 4.9%) of 3-phenyl-1,5-hexadiene. Comparison of the published nmr and infrared spectra of allylbenzene[6,7a] and phenylcyclopropane[7b,8] with those of the isolated samples established their respective identities. The 3-phenyl-1,5-hexadiene was identified by comparison of the infrared spectrum with the published spectrum:[7c] nmr ($CCl_4$) $\delta$ 7.19 (s, 5, phenyl), 5.86 (m, 2, –CH=), 5.02 (m, 4, $CH_2$=), 3.30 (m, 1, PhCH), and 2.46 (m, 2, $-CH_2-$); mass spectrum (25 eV) *m/e* 158.

*Anal.* Calcd for $C_{12}H_{14}$: C, 91.09; H, 8.91. Found: C, 89.93; H, 8.72.

Distillation of the methylene chloride from the contents of the second flask and preparative gc of the higher boiling material (0.375 in. × 7 ft 20% SE-30 on 45/60 Chromosorb A column) gave 0.492 g (0.00464 mol, 11.6%) of the known[9] *endo*-tricyclo-[3.2.1.0$^{2,4}$]oct-6-ene: 220-MHz nmr ($CCl_4$) $\delta$ 5.66 (m, 2, $C_{6,7}$), 2.76 (m, 2, $C_{1,5}$), 1.80 (m, 1, $C_8$), 1.71 (m, 1, $C_8$), 1.31 (m, 2, $C_{2,4}$), 0.56 (m, 1, $C_3$), and 0.35 (m, 1, $C_3$).

The deuterium oxide quench was carried out in the same manner (without the cyclopropene trap) with the exception that 75 g (3.75 mol) of deuterium oxide (99.5%) was used as the quenching agent. Preparative gc gave phenylcyclopropane with average deuterium content (falling-drop analysis) 1.47; 220-MHz nmr ($CCl_4$) $\delta$ 7.02 (m, 5, phenyl), 1.82 (m, 0.61, benzylic), 0.86 (m, 1.68, trans to phenyl), and 0.63 (m, 1.24, cis to phenyl); mass spectrum (20 eV) *m/e* (rel intensity) 118 (35.57), 119 (87.35), 120 (100.00), 121 (39.36), 122 (4.43); 15.351-MHz D nmr ($CD_2Cl_2$) 3.52 (m, 0.37, benzylic) and 4.60 ppm upfield of $CD_2Cl_2$ (m, 1.10, ring methylene). In the mass spectrum, the ratio of the *m/e* 118 peak to the *m/e* 119 peak was 0.408. The ratio of the *m/e* 117 peak to the *m/e* 118 peak in a reference spectrum was 0.388, indicating few, if any, $d_0$ molecules (within the experimental error). The nmr and mass spectra of the isolated allylbenzene and 3-phenyl-1,5-hexadiene showed no evidence of deuterium incorporation.

**The reaction of allyl-1,1-$d_2$ chloride with phenyllithium** was carried out as described above, without the cyclopropene trap, utilizing 3.11 g (0.0396 mol) of the dideuterated allyl chloride[10] and 76.2 ml of a 0.78 *N* solution of phenyllithium (0.0594 mol) in ether. Analytical gc of the product showed only the allylbenzene, but isolation of the products *via* preparative gc (0.900-ml injections) gave small amounts of the phenylcyclopropane and 3-phenyl-1,5-hexadiene. The phenylcyclopropane mass spectrum (20 eV) showed *m/e* (rel intensity) 118 (33), 119 (100), 120 (13), indicating at least 97% $d_1$ (*vide supra*). Allylbenzene showed nmr ($CCl_4$) $\delta$ 7.17 (s, 5, phenyl), 5.90 (m, 1.0, –CH=), 5.00 (m, 0.6, $CH_2$=), and 3.34 (d, 1.3, PhCH–); mass spectrum (20 eV) *m/e* (rel intensity) 119 (5), 120 (100), 121 (11); indicating 68% 3,3-$d_2$-allylbenzene and 32% 1,1-$d_2$-allylbenzene. 3-Phenyl-1,5-hexadiene showed nmr ($CCl_4$) $\delta$ 7.19 (s, 5.0, phenyl), 5.86 (m, 2.0, –CH=), 5.02 (m, 3.5, $CH_2$=), 3.30 (broad m, maximum of 0.1, PhCH–), and 2.46 (m, 0.4, $-CH_2-$).

**The reaction of methyllithium with allyl chloride** was carried out as described for the phenyllithium reaction, with the second flask charged with 23.3 g (0.353 mol) of freshly distilled cyclopentadiene in 300 ml of methylene chloride, and the first flask charged with 505 ml of a 1.07 *N* solution of methyllithium in ether (0.540 mol). The allyl chloride (13.78 g, 0.180 mol) in 25 ml of ether was added to the cooled methyllithium solution over a 40-min period, and the resulting solution was stirred at room temperature for 30 min, heated to gentle reflux for 7 min, and stirred for an additional 60 min at room temperature. The ice water bath was then replaced, the condenser coolant was changed to Dry Ice and carbon tetrachloride, and the reaction mixture was quenched with 18.30 g (0.916 mol) of deuterium oxide. The volatile products were swept into the second flask, which was cooled with an ice water bath. After the deuterium oxide addition was complete, the first flask was heated at gentle reflux for 15 min, and the second flask was then disconnected. Preparative gc gave 0.800 g (0.00754 mol, 4.2%) of *endo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene, whose 220-MHz nmr spectrum was identical with that described above, the only exception being that the signal at $\delta$ 1.31 integrated for only 0.52 protons. The average deuterium content (falling-drop analysis) was found to be 1.48, and the D nmr spectrum showed only one absorption at 5.89 ppm upfield of deuteriochloroform, corresponding to the $C_2$ and $C_4$ positions.

**Registry No.**—Phenyllithium, 591-51-5; allyl chloride, 107-05-1; 3-phenyl-1,5-hexadiene, 1076-66-0; phenylcyclopropane, 873-49-4; allylbenzene, 300-57-2; methyllithium, 917-54-4.

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(4) The nuclear magnetic resonance spectra were obtained by Mr. Robert L. Thrift, Mr. Joseph M. Timko, and Mr. Steven K. Silber. The microanalyses were determined by Mr. Josef Nemeth and his associates.

(5) Prepared from lithium metal (0.01% sodium, Lithium Corp. of America) and bromobenzene according to R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).

(6) "JEOLCO NMR Spectra," Japan Electron Optics Laboratory Co., Ltd., New Tokyo Bldg., Marunouchi, Chiyoda-ku, Tokyo, Japan, spectrum 100–112.

(7) "Sadtler Standard Spectra," The Sadtler Research Laboratories, Philadelphia, Pa., 1962, (a) spectrum 13701; (b) spectrum 12108; (c) spectrum 2792.

(8) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, spectrum 528.

(9) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

(10) Allyl-1,1-$d_2$ alcohol was obtained by the procedure of R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959), and converted to the chloride according to S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak, and W. G. Young, *J. Amer. Chem. Soc.*, **80**, 5965 (1958).