α-Elimination and Substitution in the Reaction of Allyl Chloride with Phenyllithium. The Stereochemistry of the Addition of Phenyllithium to Cyclopropene[1]

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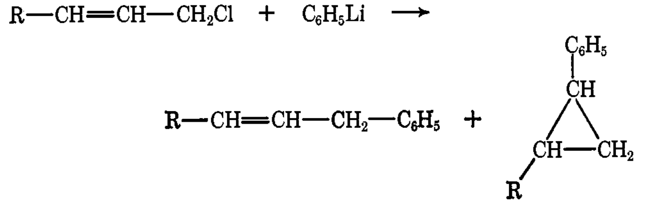
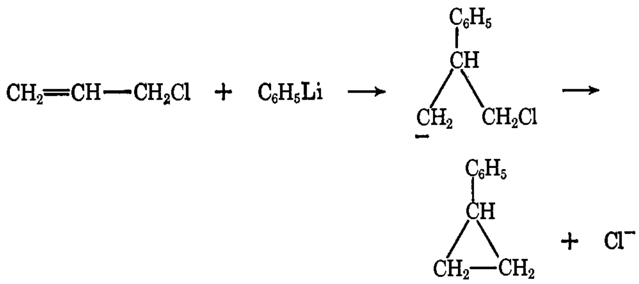
Abstract: Allyl chloride reacts with phenyllithium to produce allylbenzene and phenylcyclopropane. The mechanism of this reaction has been elucidated by determining the distribution of the isotopic label in the products from allyl-1,1-d_2 chloride and allyl-1-^{14}C chloride. These data, along with the kinetic isotope effect for phenylcyclopropane formation, are consistent with the sequence α-elimination to vinylcarbene, cyclization to cyclopropene, and addition of phenyllithium to the double bond. Allylbenzene is formed primarily (76.3%) by an S_N2' process. The addition of phenyllithium across the double bond of authentic cyclopropene proceeds with better than 99% stereospecificity to *cis*-2-phenylcyclopropyllithium.

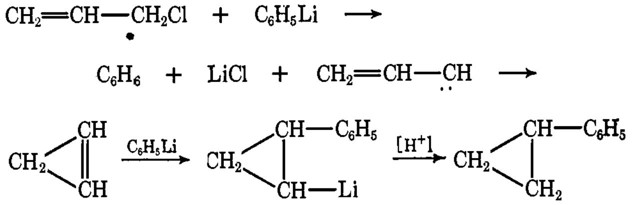
The reaction of phenyllithium with allyl chloride (R = H) and γ-substituted derivatives [R = CH_3 or $CH_2C(CH_3)_2CH_2C(CH_3)_3$] yields substitution products and phenyl-substituted cyclopropanes.[3] We became interested in this reaction since the tentatively proposed[3] mechanism for cyclopropane formation (Scheme I) postulates addition of phenyllithium to an isolated double bond, a reaction with little precedent.[4]



Scheme I



Scheme II



An attractive alternative (Scheme II) involves α-elimination yielding vinylcarbene[5,6] followed by cyclization to cyclopropene;[5,8] although the addition of an organolithium reagent across a cyclopropene double bond has not been observed, various nitrogen, oxygen, and sulfur bases are known to add.[9]

As our initial studies on the mechanism were nearing completion,[1a] Applequist and Lintner[10] independently proposed the mechanism outlined in Scheme II; since they observed that quenching of the reaction mixture with deuterium oxide leads to no incorporation of the isotope into phenylcyclopropane, they concluded that 2-phenylcyclopropyllithium cannot be an intermediate and, therefore, rejected the α-elimination mechanism. Although we have observed the identical result, all of our other data are in agreement with Scheme II; a likely explanation for this apparently anomalous result will be presented.

Our approach for differentiating between the mechanisms of Schemes I and II was to use isotopically

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[1] Two preliminary accounts of this work have appeared: (a) R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **88**, 5681 (1966); (b) J. G. Welch and R. M. Magid, *ibid.*, **89**, 5300 (1967).

[2] National Defense Education Act Fellow.

[3] (a) S. Wawzonek, B. Studnicka, H. J. Bluhm, and R. E. Kallio, *J. Amer. Chem. Soc.*, 87, 2069 (1965); (b) S. Wawzonek, H. J. Bluhm, B. Studnicka, R. E. Kallio, and E. J. McKenna, *J. Org. Chem.*, 30, 3028 (1965).

[4] (a) *Cf.* J. E. Mulvaney and Z. G. Garlund, *ibid.*, **30**, 917 (1965). (b) P. D. Bartlett, S. Friedman, and M. Stiles, *J. Amer. Chem. Soc.*, **75**, 1771 (1953). (c) Intramolecular addition of a Grignard reagent to an unactivated double bond has been observed: H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966). (d) One example of the reverse reaction, cleavage of the β,γ-carbon–carbon bond of a Grignard reagent, has recently been reported: G. Fraenkel and J. W. Cooper, *ibid.*, 599 (1968).

[5] The reaction of allyl chloride with sodium amide yields cyclopropene, presumably *via* vinylcarbene: G. L. Closs and K. D. Krantz, *J. Org. Chem.*, 31, 638 (1966).

[6] We use the term carbene and draw divalent carbon structures for simplicity, being fully aware of the overwhelming evidence against the intermediacy of free carbenes in α-eliminations.[7]

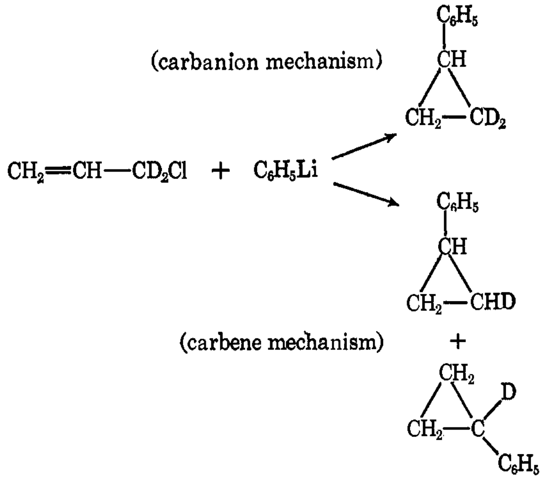
[7] (a) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964); (b) M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965); (c) G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965); (d) W. Kirmse and G. Wächterhäuser, *Tetrahedron*, **22**, 73 (1966); (e) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966); (f) G. L. Closs, "Abstracts of the Twentieth National Organic Symposium of the American Chemical Society," Burlington, Vt., June 18–22, 1967; (g) for an example of an α-elimination in which a free carbene does appear to be involved, see D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967).

[8] Alkenylcarbenes, produced in a variety of ways, invariably yield cyclopropenes: (a) G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003, 2015 (1961); **85**, 99 (1963); (b) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963); (c) F. Fisher and D. A. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).

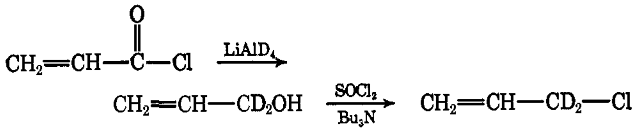
[9] (a) G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966); (b) T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Amer. Chem. Soc.*, **87**, 3026 (1965); (c) T. C. Shields and P. D. Gardner, *ibid.*, **89**, 5425 (1967); (d) T. C. Shields, B. A. Loving, and P. D. Gardner, *Chem. Commun.*, 556 (1967); (e) the reverse reaction, expulsion of diphenylmethylsodium from 2-diphenylmethylcyclopropylsodium, has been postulated: A. Maercker and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 1742 (1966).

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

labeled allyl chloride. Although we have since repeated these experiments with carbon-14-labeled material, our first study utilized allyl-1,1-d_2 chloride. Were the carbanion mechanism (Scheme I) operative, phenylcyclopropane-2,2-d_2 would be the product; if, on the other hand, the carbene mechanism (Scheme II) were correct, approximately equal amounts of phenylcyclopropane-2-d_1 and phenylcyclopropane-1-d_1 would be formed. From this reaction, we also hoped to gain insight into the mode of formation of the coupling product, allylbenzene.



The Reaction of Allyl-1,1-d_2 Chloride with Phenyllithium. Reduction[11] of acrylyl chloride with lithium aluminum deuteride yields allyl-1,1-d_2 alcohol[12] which is converted without allylic rearrangement into allyl-1,1-d_2 chloride[13,14] by thionyl chloride and tri-*n*-butylamine.[15]



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow{LiAlD_4} CH_2{=}CH{-}CD_2OH \xrightarrow[Bu_3N]{SOCl_2} CH_2{=}CH{-}CD_2{-}Cl$$

Reaction of allyl-1,1-d_2 chloride with phenyllithium in refluxing ether for 5 hr yields allylbenzene and phenylcyclopropane in 74–78 and 2.4–2.8%, respectively (two runs), of the theoretical yield (based upon phenyllithium and assuming that 2 mol of phenyllithium is required per mole of phenylcyclopropane); the yields with ordinary allyl chloride under identical conditions are 38–48 and 21–26%, respectively (three runs).[16]

Mass spectral analysis[17,18a] of phenylcyclopropane isolated from one of the reactions with allyl-1,1-d_2 chloride showed the presence of 90% of monodeuterated, 7% of dideuterated, and 3% of undeuterated material; determination of total deuterium content by nmr integration indicated the presence of *ca.* 1.2 deuterium atoms/molecule. Mass spectral determination[14,18b] of deuterium in phenylcyclopropane from another run, however, gave 58% d_1, 39% d_2, and 3% d_0. Benzene, isolated from this reaction, was shown[14] to contain deuterium, as expected for the α-elimination mechanism. The first set of numbers is in substantial agreement with the prediction of monodeuterated material based upon Scheme II, but the second set is far removed. Since all of our other data strongly support the carbene mechanism, we conclude that 2-phenylcyclopropyllithium-d_1 *is* formed, but does not survive the reaction conditions and is protonated and/or deuterated before work-up. Two sources of deuterium, allyl-1,1-d_2 chloride and 3-phenylpropene-3,3-d_2, are present in large excess, as are two potential proton donors, ether and 3-phenylpropene-1,1-d_2. Should this interpretation be correct, it would also explain why deuterated phenylcyclopropane is not observed from deuterium oxide quenching of the reaction of unlabeled allyl chloride with phenyllithium.[10] Although the configurational stability of cyclopropyl anions is established,[19] cyclopropyllithium reagents can be appreciably neutralized by as weak a proton donor as ether or tetrahydrofuran.[19a,f] It is, therefore, not unreasonable to expect their neutralization by the much stronger carbon acids, allyl chloride and allylbenzene. Since *cis*-2-phenylcyclopropyllithium is the known intermediate in this reaction (see below), we have examined its stability toward the several carbon acids. In fact, *cis*-2-phenylcyclopropyllithium is partially neutralized (5–15%) by ether after 5 hr, substantially neutralized (70–80%) by allylbenzene after 4 hr, and completely neutralized by allyl chloride in less than 1 hr, all in refluxing ether. Another possible cause of departure from the expected values is proton–deuteron exchange of cyclopropene (see below).

While the amount of isotopic label is inconclusive, these experiments do provide two concrete results in support of the α-elimination mechanism. The integrated areas of the nmr absorptions for the benzylic and the nonbenzylic ring protons are in the ratio 1:8 in the sample that is 90% monodeuterated phenylcyclopropane and 1:6–8 in other samples. The mechanism of Scheme I would lead to areas in the ratio 1:2 while that of Scheme II would give 1:7. Our result, subject to the usual errors attending electronic integration of the spectrum from a very small sample, means that about 50% of the deuterium is on the benzylic carbon.[20–22] This is possible *only* by the α-elimination

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[11] R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, 24, 297 (1959).

[12] The sample contained 1.95 deuterium atoms at C_1 as established by nmr analysis.

[13] The sample contained 2.00 deuterium atoms at C_1 as established by nmr analysis and greater than 1.98 deuterium atoms by mass spectral measurements.[14]

[14] Kindly performed by Dr. E. G. Carlson and Mr. M. J. O'Neil, Shell Oil Co., Houston Research Laboratory, Deer Park, Texas.

[15] S. H. Sharman, F. C. Caserio, J. C. Leak, and W. G. Young, *J. Amer. Chem. Soc.*, 80, 5965 (1958).

[16] (a) Each of these experiments employed a mole ratio of allyl chloride or allyl-1,1-d_2 chloride to phenyllithium of 1.3:1.0. (b) When equimolar amounts of deuterated material and phenyllithium are used, the yields of allylbenzene and phenylcyclopropane are 83 and 3.6%, respectively.

[17] Kindly performed by Dr. Thomas Aczel and Mr. G. R. Taylor, Esso Research and Engineering Co., Baytown, Texas.

[18] (a) The mass spectral data allow, at best, only rough estimates of the relative abundance of the various deuterated species. (b) Depending upon assumptions made concerning isotope effects upon fragmentation, the positional distribution of deuterium, and the fragments responsible for each peak, one obtains a range of values: 40–68% d_1, 32–42% d_2, 0–18% d_0.

[19] (a) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964); (b) H. M. Walborsky and A. E. Young, *ibid.*, **86**, 3288 (1964); (c) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *ibid.*, **84**, 2465 (1962); (d) F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4838 (1962); (e) D. A. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961); (f) D. Seyferth and H. M. Cohen, *J. Organometal. Chem.*, **1**, 15 (1963).

[20] The discrepancy between the observed value (1:8) and that expected for random addition of phenyllithium to cyclopropene-1-d_1 is in the direction expected for a secondary deuterium isotope effect, whether the nature of the effect is due to changes in hybridization[21] or to the destabilizing inductive effect of a deuterium on a carbanion.[22]

[21] (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 1861 (1961); (b) A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 3836 (1964); (c) A. J. Kresge and Y. Chiang, *ibid.*, **89**, 4411 (1967).

[22] A. Streitwieser, Jr., and D. E. van Sickle, *ibid.*, **84**, 254 (1962).

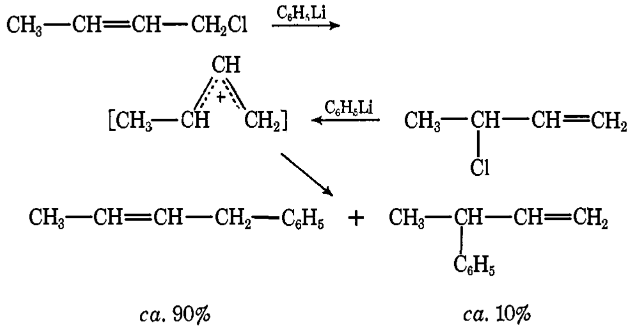
route. We are confident that deuterium is not introduced at the benzylic position by base-catalyzed exchange, since deuterium oxide hydrolysis of a solution of phenyllithium and phenylcyclopropane which had been refluxed for 5 hr gives completely undeuterated phenylcyclopropane.

Probably the most compelling evidence for the carbene mechanism to come from the deuterium study is the previously mentioned difference in product yields between undeuterated and deuterated allyl chloride. Under identical experimental conditions, the reaction of allyl-1,1-d_2 chloride with phenyllithium yields substantially less phenylcyclopropane and more allylbenzene than does that of undeuterated material. This is consistent with Scheme II since phenylcyclopropane formation requires carbon-hydrogen bond rupture. We cannot assign a precise value to the kinetic isotope effect for the α-elimination since in no experiment do we account for all of the reagents. We can, however, assign a range of values for pairs of deuterated and undeuterated reactions by making extreme assumptions about the fate of phenyllithium not accounted for by the two hydrocarbon products. In one such calculation, the kinetic isotope effect for phenylcyclopropane formation is $k_H/k_D = 4.29\text{–}11.8$.[23]

On the basis of some preliminary experiments, we now find that we can account for more of the reagents than in the cases cited earlier. When a stream of argon is swept through the reaction flask during the addition of phenyllithium to allyl chloride[16a] and into a solution of cyclopentadiene in pentane, the known[24] Diels-Alder adduct with cyclopropene is formed; upon hydrolysis of the reaction mixture, substantially more cyclopropene is generated and is trapped by the diene. The yields based upon phenyllithium (as before) are allylbenzene (22%), phenylcyclopropane (14%), cyclopropene before hydrolysis (*ca.* 1.5%),[25] cyclopropene after hydrolysis (27%).[25,26] Allylbenzene and phenylcyclopropane are formed in the same ratio as in our other experiments, but in lower yield (possibly because allyl chloride is being swept out of the reaction vessel). We can affirm our original postulate in that cyclopropene *is* formed in the reaction, but that most of it is converted into its lithium salt by abstraction of an olefinic proton.[8,9a] To the extent that this lithium salt can abstract a proton/deuteron from one of the carbon acids present in the solution, another explanation is available for the lack of agreement of the deuterium content of phenylcyclopropane with Scheme II. We are currently investigating the possibility of using this reaction for an improved synthesis of cyclopropene.

Allylbenzene, the major product from the reaction of allyl-1,1-d_2 chloride, is better than 98% dideuterated (by both nmr and mass spectral[14] analysis).[27,28] The distribution of deuterium (by nmr integration) shows that the major portion of allylbenzene arises by substitution with rearrangement. That the SN2′ process[29] predominates is not unexpected,[30] although it stands in contrast to the observations of Cristol, *et al.*,[31] who suggested that α-methylallyl chloride and γ-methylallyl chloride react with phenyllithium in ether by an ionization mechanism to yield identical mixtures of the phenyl-substituted alkenes.[32] It might be argued that the observed distribution of deuterium in allylbenzene results from an isotope effect upon either an ionization[31] or direct substitution process. This would, however, require a secondary isotope effect greater than the largest one known,[33] and, furthermore, is in the direction opposite to that expected for either type of mechanism.

$$CH_2{=}CH{-}CD_2{-}Cl + C_6H_5Li \longrightarrow \underset{23\text{–}25\%}{CH_2{=}CH{-}CD_2{-}C_6H_5} + \underset{75\text{–}77\%}{C_6H_5{-}CH_2{-}CH{=}CD_2}$$



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(23) The data used for this calculation are as follows. Reaction of 133 mmol of allyl chloride with 102 mmol of phenyllithium yields 49.2 mmol of allylbenzene and 13.0 mmol of phenylcyclopropane; reaction of 115 mmol of allyl-1,1-d_2 chloride with 115 mmol of phenyllithium[16b] yields 95.0 mmol of allylbenzene and 2.11 mmol of phenylcyclopropane. The minimum isotope effect is obtained by assuming that *all* of the phenyllithium not accounted for by products *is* promoting α-elimination, but that the resulting carbene undergoes other reactions and/or cyclopropene so produced is not trapped by phenyllithium. The maximum isotope effect is obtained by assuming that *none* of the unaccounted-for phenyllithium is giving α-elimination. In the protium case, of the 102 mmol of phenyllithium, we can account for 49.2 mmol (allylbenzene) and 2(13.0) mmol (phenylcyclopropane); 26.8 mmol is not accounted for. In the deuterium case, of the 115 mmol of phenyllithium, 15.8 mmol is unexplained. For the calculation of the minimum isotope effect, 39.8 mmol of phenyllithium is used to promote α-elimination from allyl chloride and 17.9 mmol from allyl-1,1-d_2 chloride. Then, for allyl chloride, the ratio of the rate constant for α-elimination $(k_e^H)_{min}$ to that for substitution (k_s^H) is $(k_e^H/k_s^H)_{min} = 39.8/49.2$; for allyl-1,1-$d_2$ chloride $(k_e^D/k_s^D)_{min} = 17.9/95.0$. Assuming that there is no isotope effect on the substitution reaction (*i.e.*, $k_s^H = k_s^D$), $(k_e^H/k_e^D)_{min} = (39.8/49.2)(95.0/17.9) = 4.29$. For the maximum isotope effect, $(k_e^H/k_s^H)_{max} = 13.0/49.2$ and $(k_e^D/k_s^D)_{max} = 2.11/95.0$; then $(k_e^H/k_e^D)_{max} = 11.8$. Similar calculations using other pairs of reactions give values of k_e^H/k_e^D ranging from 2.35 to 16.8.

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

(25) The yield of cyclopropene is calculated assuming quantitative trapping by cyclopentadiene.

(26) The yield of cyclopropene after hydrolysis is calculated assuming that 2 molar equiv of phenyllithium is required.

(27) Since allylbenzene is dideuterated, we can rule out its being formed by capture of the carbene $CH_2{=}CH\ddot{C}D$ by phenyllithium followed by protonation; while it is possible that the resulting phenylallylic anion would be neutralized by deuteron abstraction from another species in solution, it is more likely that deuteration and/or protonation would occur at the terminal carbon[28] giving β-methylstyrene.

(28) (a) Allylbenzene is converted into β-methylstyrene by phenyllithium in ether. (b) Potassium *t*-butoxide in either *t*-butyl alcohol or dimethyl sulfoxide effects the same transformation: S. W. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5791 (1966).

(29) (a) We use the mechanistic labels SN2′ and SN2 merely to indicate substitution with and without rearrangement, respectively; evidence discussed in this paper makes it likely that the process is, in fact, a direct substitution and not an SN1 process. (b) Allylic substitution in a polar aprotic solvent is expected to proceed by a bimolecular process: D. G. Lesnini, P. D. Buckley, and R. M. Noyes, *J. Amer. Chem. Soc.*, **90**, 668 (1968).

(30) R. H. de Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(31) S. J. Cristol, W. C. Overhults, and J. S. Meek, *J. Amer. Chem. Soc.*, **73**, 813 (1951).

(32) 1-Phenyl-2-methylcyclopropane (of unspecified stereochemistry) is also formed from γ-methylallyl chloride,[3] although it was not found by Cristol, *et al.*[31]

(33) The secondary isotope effect on the solvolysis of a cyclohexyl brosylate containing a β-deuterium atom is $k_H/k_D = 1.44$: V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **86**, 945 (1964); the 76:24 distribution we have found, rather than 50:50, would require an inverse isotope effect of *ca.* 3.2, or *ca.* 2.1 per deuterium atom.

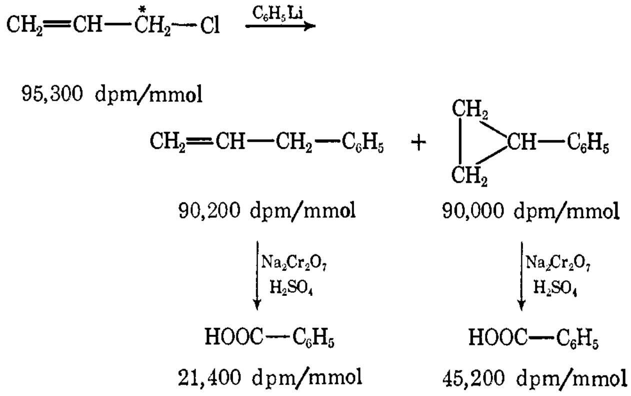
To illustrate, were the substitution to proceed by SN1 reaction to the ion pair $[CH_2{=}CHC^+D_2 \leftrightarrow C^+H_2CH{=}CD_2]Cl^-$, two factors might influence the position of attack by phenyllithium. First, attack at the deuterium-bearing carbon produces a change in its hybridization from sp^2 to sp^3 (of which only a small amount will be felt in the transition state which must resemble the carbonium ion) while attack at the other carbon leads to no such change at the deuterated end; whether the reasons are steric[34] or inductive,[21,22,35] all such reactions (*i.e.*, sp^2 going to sp^3) proceed faster at carbon bonded to deuterium. Second, phenyllithium might be expected to attack that carbon having the greater positive charge; the electron-releasing inductive effect of deuterium[35,36] should produce an unequal distribution such that more than 50% of the charge is on the deuterated carbon. The ionization mechanism, by either argument, leads to the expectation that $CH_2{=}CHCD_2C_6H_5$ will be the major component, contrary to our observation.

Were the reaction to proceed by direct displacement, as we believe, the isotope effect upon SN2 attack on allyl-1,1-d_2 chloride (relative to undeuterated allyl chloride) would be very close to unity[35b,37] while SN2′ attack would occur more slowly owing to the change in hybridization of carbon bonded to deuterium from sp^3 to sp^2. Thus, the ratio of SN2′/SN2 calculated from the data on allyl-1,1-d_2 chloride is, if anything, somewhat *smaller* than if there were no isotope effect.[38]

Bordwell, *et al.*,[39] have cautioned against the use of the SN2′ label unless it has been shown that the substitution with rearrangement does not proceed either by SNi′ to a more reactive species followed by rapid SN2 or by formation of an ion pair followed by rapid attack by the nucleophile. The first possibility can be dismissed since any equilibrium of allyl-1,1-d_2 chloride and allyl-3,3-d_2 chloride will favor the former[21,22,34,35] and both chlorides should undergo SN2 reaction at about the same rate.[35b,37] The second can also be ruled out by the arguments presented above against an ionization process, and by the general lack of any evidence for the nucleophilic interception of an ion pair in an aprotic solvent faster than its collapse to starting material.[29b]

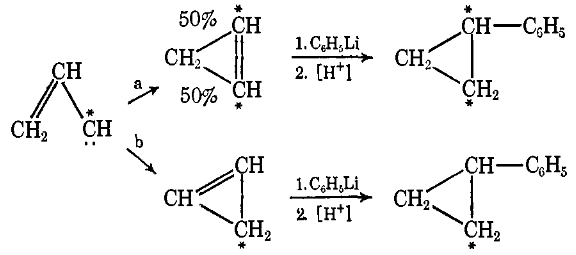
We are currently reexamining the reactions of the α- and γ-methyl compounds[31] to determine if a contradiction with our study does, in fact, exist. Although a change in mechanism from direct displacement to ionization is possible with the additional methyl group, it is also conceivable that γ-methylallyl chloride gives primarily the unrearranged product and α-methylallyl chloride reacts with predominant rearrangement due to steric hindrance by the methyl on the SN2′ and SN2 reactions, respectively.

The Reaction of Allyl-1-^{14}C Chloride with Phenyllithium. In order to resolve the ambiguities in the deuterium experiments, we have studied the distribution of radioactive carbon in the products derived from allyl-1-^{14}C chloride.[40,41] We can assign much more accurate values to the position of a radioactive isotope since liquid scintillation analysis gives activities to better than 1%. Allylbenzene and phenylcyclopropane from allyl-1-^{14}C chloride and phenyllithium were oxidized (by sodium dichromate in sulfuric acid) to benzoic acid with the results shown below.[42] By these measurements, 50.2% of the radioactivity is at the benzylic carbon of phenylcyclopropane, in excellent agreement with the prediction of Scheme II. Allylbenzene is formed by predominant (76.3%) SN2′ reaction.



This experiment, furthermore, demonstrates that the formation of cyclopropenes from alkenylcarbenes occurs by intramolecular addition to the double bond (Scheme III, path a) and not by carbon–hydrogen insertion (Scheme III, path b). In view of the known cyclization of vinylcarbenes bearing two alkyl substituents on the terminal carbon,[8] path a was certainly to be expected, but until now, path b could not be excluded for the less substituted cases.

Scheme III



The Stereochemistry of the Addition of Phenyllithium to Cyclopropene. Scheme II postulates the addition of phenyllithium across the double bond of cyclopropene. Since the only reported reaction of cyclopropenes with organolithium reagents is abstraction of an olefinic

(34) (a) L. S. Bartell, *J. Amer. Chem. Soc.*, **83**, 3567 (1961); (b) H. C. Brown andG. J. McDonald, *ibid.*, **88**, 2514 (1966); (c) H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. McDonald, *ibid.*, **88**, 2520 (1966).

(35) (a) A. Streitwieser, Jr., and H. S. Klein, *ibid.*, **86**, 5170 (1964); (b) B. Östman, *ibid.*, **87**, 3163 (1965); (c) T. C. Jones and E. R. Thornton, *ibid.*, **89**, 4863 (1967).

(36) (a) A. J. Kresge and R. J. Preto, *ibid.*, **89**, 5510 (1967); (b) H. Simons and D. Palm, *Angew. Chem. Intern. Ed. Engl.*, **5**, 920 (1966).

(37) (a) H. Simon and D. Palm, *Chem. Ber.*, **92**, 2701 (1959); (b) V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, 74, 5285 (1952).

(38) We have another reason for expecting that the amount of SN2′ reaction may be greater than 76%; no matter what proportion of $CH_2{=}CHCD_2C_6H_5$ and $C_6H_5CH_2CH{=}CD_2$ had been initially formed, the latter (the SN2′ product) would be more rapidly transformed into β-methylstyrene.

(39) F. G. Bordwell, R. W. Hemwall, and D. A. Schexnayder, *J. Amer. Chem. Soc.*, **89**, 7144 (1967).

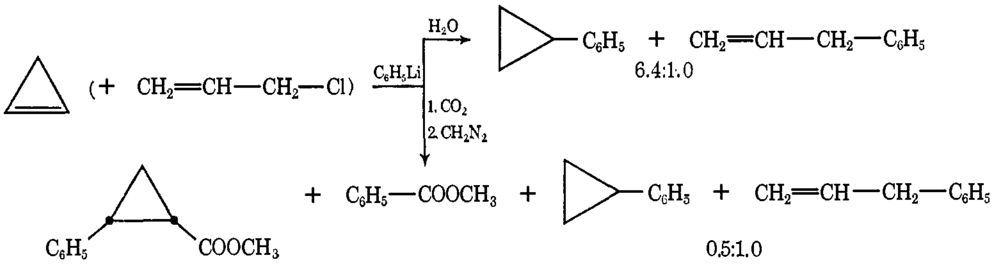
(40) This is prepared[15] from allyl-1-^{14}C alcohol; we thank Mallinckrodt Nuclear for a generous sample of the labeled alcohol.

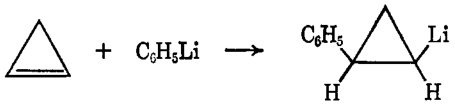
(41) Allyl-1-^{14}C alcohol (96,800 dpm/mmol) is converted into allyl-1-^{14}C chloride (95,300 dpm/mmol) which upon ozonolysis[15] yields formaldehyde with less than 0.2% of the radioactivity (dimedone derivative, 170 dpm/mmol).

(42) No carbon skeletal rearrangement occurs during the oxidation. This is demonstrated by the conversion of styrene-α-^{14}C (289,000 dpm/mmol) in two steps into 1-phenylcyclopropane-1-^{14}C (277,000 dpm/mmol) which upon oxidation yields benzoic acid with no loss of radioactivity (278,000 dpm/mmol).

proton,[8,9a] we have investigated the reaction of phenyllithium with an authentic sample of cyclopropene.[43,44] In fact, the only volatile products formed upon quenching of the reaction mixture with water are phenylcyclopropane and allylbenzene in an over-all yield of 2.5% and in the mole ratio 20:1; allylbenzene undoubtedly arises by the reaction of phenyllithium with a small amount of allyl chloride carried over with cyclopropene. By far the major portion of phenylcyclopropane must occur by the reaction of phenyllithium with cyclopropene itself; only a small amount can come from the reaction with allyl chloride since the mole ratio of phenylcyclopropane to allylbenzene when allyl chloride is added to phenyllithium is 0.35:1.

In a separate experiment, the cyclopropene–phenyllithium reaction mixture was poured over freshly crushed Dry Ice. An aliquot removed before carbonation and quenched with water yielded phenylcyclopropane and allylbenzene in a mole ratio of 6.4:1. The neutral fraction after carbonation contained only trace amounts of these two hydrocarbons in a mole ratio of 0.5:1; therefore, better than 90% of the cyclopropyllithium present in the mixture *did* react with carbon dioxide. The aqueous fraction, upon acidification and esterification with diazomethane, yielded only methyl benzoate and methyl *cis*-2-phenylcyclopropanecarboxylate; the presence of as little as 0.5% of the *trans* ester would have been detected. Therefore, the addition of phenyllithium to cyclopropene proceeds with better than 99% stereospecificity to *cis*-2-phenylcyclopropyllithium. Since both *cis*- and *trans*-1-bromo-2-phenylcyclopropanes are converted stereospecifically into the ester of retained configuration (*n*-butyllithium followed by carbonation and esterification with diazomethane), we conclude that none of the *trans*-lithio compound is formed in the *addition* reaction. We are confident that *cis*-2-phenylcyclopropyllithium comes *only* from the addition since a solution of phenyllithium and phenylcyclopropane yields only benzoic acid after carbonation.





This *cis* stereospecificity is in accord with the commonly accepted mechanism for the reaction of carbonyl compounds with organolithium reagents.[45] In view of the well-known tendency of organolithium reagents to exist as aggregates in solution but to undergo reactions in a more reactive, less associated form,[46,47] we are uncertain about the composition of the transition state. Kinetic studies currently in progress should indicate which of the two likely possibilities (a four-membered transition state with monomeric phenyllithium or a six-membered one with the dimer) is correct.[48] The possibility that this reaction is radical rather than ionic in nature should not be dismissed,[49] although under normal circumstances, the cyclopropyl radical will not maintain configurational stability.[50]

Experimental Section

Analytical glpc work was performed on either a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector) or a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector) and utilized the following columns: A, Ucon 50HB260 (20%) on Chromosorb P, $^1/_8$ in. × 6 ft; B, SE-30 (7%) on Chromosorb W (acid washed) DMCS, $^1/_8$ in. × 10 ft; C, Ucon 50HB260 (20%) on Chromosorb P, $^1/_8$ in. × 10 ft; D, SE-30 (20%) on Chromosorb P, 0.25 in. × 5 ft; E, Ucon 50-HB260 (20%) on Chromosorb P, 0.25 in. × 5 ft; F, FFAP (15%) on Chromosorb W, 0.25 in. × 5 ft. Preparative glpc work was done on the Varian instrument above with the following columns: D, above; N, SE-30 (30%) on Chromosorb P, $^3/_8$ in. × 20 ft; P, Carbowax 20M (15%) on Chromosorb P, $^3/_8$ in. × 20 ft; Q, SE-30 (30%) on Chromosorb P, $^3/_8$ in. × 10 ft. All yields were calculated by quantitative glpc using a Disc Integrator.

Nmr spectra were recorded on Varian Associates A-60 and A-56/60A[51] spectrometers. Measurements of radioactivity were made on a Packard 3000 Series Tri-Carb liquid scintillation spectrometer system.

All reactions involving either lithium or lithium reagents were run under an inert atmosphere.

Materials. Phenyllithium was prepared in the usual way and was standardized by the Gilman method.[52] Methyllithium in ether was obtained from either Foote Mineral Co. or Alfa Inorganics, Inc. Authentic samples of allylbenzene, β-methylstyrene, and *trans*-2-phenylcyclopropanecarboxylic acid were obtained from Aldrich Chemical Co. Phenylcyclopropane was prepared from styrene by the Simmons–Smith reaction.[53] 1-Phenylcyclopropane-1-^{14}C was prepared from styrene-α-^{14}C (Mallinckrodt Nuclear) in

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(43) Cyclopropene was prepared[44] by the tetramethylethylenediamine-promoted reaction of methyllithium with allyl chloride.

(44) We thank Professor L. Friedman for suggesting this modification of the Closs and Krantz cyclopropene synthesis.[5] We have been unable to effect better than a 2.5% conversion but the reaction is much cleaner than the literature[5] synthesis.

(45) C. G. Swain and L. Kent, *J. Amer. Chem. Soc.*, **72**, 518 (1950).

(46) (a) C. G. Screttas and J. F. Eastham, *ibid.*, **88**, 5668 (1966); (b) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 2174 (1966); (c) R. Waack and P. West, *J. Organometal. Chem.*, **5**, 188 (1966); (d) S. G. Smith, *Tetrahedron Lett.*, 6075 (1966).

(47) For studies of phenyllithium and related compounds, see (a) H. J. S. Winkler and H. Winkler, *J. Amer. Chem. Soc.*, **88**, 964, 969 (1966); (b) P. West and R. Waack, *ibid.*, **89**, 4395 (1967).

(48) The casual use of such data to determine the degree of association of the reactive species has recently been criticized: T. L. Brown, *J. Organometal. Chem.*, **5**, 191 (1966).

(49) (a) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 5517 (1967). (b) H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967). (c) The N,N,N′,N′-tetramethyl-*o*-phenylenediamine-catalyzed addition of ethyllithium to anthracene may proceed by a radical reaction: H. E. Zieger and D. Schaeffer, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(50) (a) H. M. Walborsky and C-J. Chen, *J. Amer. Chem. Soc.*, **89**, 5499 (1967); (b) H. M. Walborsky, C-J. Chen, and J. L. Webb, *Tetrahedron Lett.*, 3551 (1964).

(51) We wish to acknowledge the assistance of the National Science Foundation in the purchase of this instrument.

(52) H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

(53) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

two steps by addition of dibromocarbene[54] followed by reduction of the *gem*-dibromocyclopropane with chromium(II) sulfate.[55] Isomerically pure samples (greater than 95%) of *cis*- and *trans*-1-bromo-2-phenylcyclopropane were obtained by preparative glpc (column D) of the reaction mixture from the partial reduction of 1,1-dibromo-2-phenylcyclopropane with methylmagnesium iodide.[56] Lithium aluminum deuteride (minimum isotopic purity of 98%) was obtained from both Bio-Rad Laboratories and Alfa Inorganics, Inc.

Reaction of Allyl Chloride with Phenyllithium. An 18-ml portion of *ca.* 0.8 *M* phenyllithium (*ca.* 15 mmol) in ether was added over 30 min to 1.50 g (19.7 mmol) of allyl chloride in 10 ml of ether. The reaction mixture was stirred at gentle reflux for 5 hr, hydrolyzed with 5 ml of 1 *N* hydrochloric acid, washed with saturated sodium chloride solution, and dried (magnesium sulfate). Quantitative glpc analysis (column A) showed that 0.67 g (38%) of allylbenzene and 0.19 g (21%) of phenylcyclopropane were formed.

In a series of reactions with unlabeled allyl chloride using both inverse and normal additions, the total yield of products ranged from *ca.* 50 to 70% with the ratio of phenylcyclopropane to allylbenzene consistently remaining in the range 1:3 to 1:4. When greater than 1 equiv of phenyllithium was used, β-methylstyrene was also produced in yields of from 1 to 10%.

The above reaction was repeated, but was quenched with deuterium oxide. Nmr analysis of phenylcyclopropane isolated by preparative glpc (column N) showed that there was no incorporation of deuterium.

Reaction of Allyl-1,1-d_2 Chloride with Phenyllithium. The phenyllithium reaction was repeated with allyl-1,1-d_2 chloride (isotopic purity greater than 99% as determined by nmr and mass spectral analyses). Product yields in two of these reactions were 74–78% for allylbenzene and 2.4–2.8% for phenylcyclopropane.

Samples of allylbenzene were isolated from several of these reactions by preparative glpc (column N or P); nmr analysis indicated the presence of 1.93–2.09 deuterium atoms/molecule and showed that 23–25% of the deuterium was at the 1 position while 75–77% was at the 3 position. Mass spectral analysis showed that the sample was greater than 98% dideuterated.

Similar isolation of phenylcyclopropane and nmr analysis indicated the presence of 0.5–1.5 deuterium atoms/molecule, depending upon the individual sample; the quantity of deuterated material available for nmr integration was limited because of the substantial isotope effect on α-elimination. The ratio of integrated peak areas for the benzylic to nonbenzylic ring protons ranged from 1:6 to 1:8. Mass spectral analysis of phenylcyclopropane from one reaction showed it to be 90% d_1, 7% d_2, and 3% d_0; analysis of the product from another reaction, however, indicated that it was 58% d_1, 39% d_2, and 3% d_0. Benzene was isolated from one reaction; mass spectral analysis showed that it was 24% d_1 and 76% d_0.

Reaction of Allyl-1-^{14}C Chloride with Phenyllithium. A 250-ml portion of *ca.* 0.75 *M* phenyllithium (0.19 mol) in ether was added over 1.5 hr to 20 g (0.26 mol) of allyl-1-^{14}C chloride (95,300 dpm/mmol) in 100 ml of ether. The reaction mixture was refluxed for 2 hr and was worked up as above. Quantitative glpc analysis (column C) showed that 5.48 g (24%) of allylbenzene and 2.19 g (19%) of phenylcyclopropane were formed. Liquid scintillation analysis of the purified products yielded activities of 90,200 dpm/mmol for allylbenzene and 90,000 dpm/mmol for phenylcyclopropane.

Stability of *cis*-2-Phenylcyclopropyllithium toward Carbon Acids. A. Toward Ether. A solution of 34 mmol of *n*-butyllithium in 21 ml of hexane and 100 ml of ether was treated with 2.0 g (10 mmol) of *cis*-1-bromo-2-phenylcyclopropane. The resulting mixture was stirred at reflux for 5 hr and was hydrolyzed with deuterium oxide. The ethereal layer was washed with saturated sodium chloride solution, dried (magnesium sulfate), and concentrated to *ca.* 5 ml. Glpc analysis (columns B and C) indicated that greater than 95% of the bromo compound had reacted. Preparative glpc (column N) afforded *ca.* 350 mg (*ca.* 35%) of pure phenylcyclopropane; integration of the nmr spectrum showed that presence of 0.85–0.95 deuterium atom/molecule, exclusively at the nonbenzylic ring position.

B. Toward Allylbenzene. A solution of 34 mmol of *n*-butyllithium in 21 ml of hexane and 300 ml of ether was treated with 2.0 g (10 mmol) of *cis*-1-bromo-2-phenylcyclopropane. The mixture was brought to reflux and 30.0 g (250 mmol) of allylbenzene was added. The solution was stirred at reflux for 4 hr and was worked up with deuterium oxide as above. Glpc analysis (columns B and C) indicated the presence of allylbenzene, phenylcyclopropane, and β-methylstyrene in a mole ratio of *ca.* 40:1:0.3. The mixture was diluted with 50 ml of acetone and was treated with 200 ml of saturated aqueous potassium permanganate and then with solid potassium permanganate until glpc analysis indicated that all of the olefins were destroyed. The manganese dioxide was reduced by treatment with concentrated hydrochloric acid and solid sodium bisulfite. The resulting mixture was worked up and purified by preparative glpc (column N) affording *ca.* 100 mg (*ca.* 9%) of pure phenylcyclopropane; integration of the nmr spectrum showed the presence of 0.2–0.3 deuterium atom/molecule at the nonbenzylic ring position.

C. Toward Allyl Chloride. A solution of 40 mmol of *n*-butyllithium in 25 ml of hexane and 300 ml of ether was treated with 2.0 g (10 mmol) of *cis*-1-bromo-2-phenylcyclopropane. The mixture was brought to reflux and upon addition of 32 g (400 mmol) of allyl chloride a vigorous reaction occurred. The mixture was stirred at reflux for 1 hr and was worked up with deuterium oxide in the normal manner. Integration of the nmr spectrum of isolated phenylcyclopropane (*ca.* 30% yield) showed that no deuterium was incorporated into the molecule.

Oxidation of Radioactive Phenylcyclopropane. A mixture of 7.4 g (25 mmol) of sodium dichromate, 17 ml of concentrated sulfuric acid, 0.91 g (7.7 mmol) of phenylcyclopropane (90,000 dpm/mmol), and 90 ml of water was stirred at gentle reflux for 13 hr. The mixture was extracted with ether; the combined extracts were washed with 5 ml of saturated sodium chloride solution and extracted with 5% sodium hydroxide solution. The combined basic extracts were boiled to drive off ether and were acidified while hot with concentrated hydrochloric acid yielding 0.61 g (70%) of benzoic acid as white flakes, mp 119–122°. The crude product was dissolved in base, filtered, and acidified while hot; 0.48 g (51%) of pure benzoic acid, mp 122–123°, crystallized out. Liquid scintillation analysis gave an activity of 45,200 dpm/mmol (50.2% of the activity in phenylcyclopropane).

Phenylcyclopropane (277,000 dpm/mmol) synthesized from styrene-α-^{14}C was oxidized by the same procedure. Liquid scintillation analysis of the resulting purified benzoic acid yielded an activity of 278,000 dpm/mmol (100% retention of activity).

Oxidation of Radioactive Allylbenzene. Using the same procedure as above but on twice the scale, 2.0 g (15.5 mmol) of allylbenzene (90,200 dpm/mmol) yielded 1.32 g (70%) of purified benzoic acid, mp 122–123°. Liquid scintillation analysis gave an activity of 21,400 dpm/mmol (23.7% retention of the original activity).

Preparation of *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene, the Diels–Alder Adduct of Cyclopropene and Cyclopentadiene.[44] A four-necked flask was fitted with addition funnel, mechanical stirrer, 7-in. Allihn condenser filled with glass helices (cooled with ice water), and rubber septum with syringe needle through which argon was admitted. The condenser was connected *via* a cold trap maintained at *ca.* −20° to a gas washing bottle which contained 66 g (1.0 mol) of cyclopentadiene in 150 ml of pentane. The reaction flask was charged with 23 g (0.3 mol) of allyl chloride, 35 g (0.3 mol) of tetramethylethylenediamine, and 100 ml of ether. While a slow stream of argon was passed through the system, the solution was brought to reflux and 0.3 mol of methyllithium in 120 ml of ether was added over 3.5 hr. With argon still sweeping the system, the reaction was quenched with water. Glpc analysis (columns D and B) of the pentane solution indicated the presence of the known[24] Diels–Alder adduct of cyclopropene and cyclopentadiene (*ca.* 1%); identification was made by a comparison of glpc retention times with authentic material prepared by the method of Closs and Krantz.[5]

Reaction of Cyclopropene with Phenyllithium. The same apparatus and quantities of reagents as above were used, except that the gas washing bottle was replaced by a three-necked Morton flask containing 0.11 mol of phenyllithium in 130 ml of ether and equipped with a high-speed Morton stirrer, reflux condenser, and glass tube through which gases generated in the four-necked flask could enter the solution. Normal work-up of the phenyllithium reaction mixture and glpc analysis gave 0.89 g (2.5%) of phenylcyclopropane and a much smaller amount of allylbenzene (mole ratio of the products 20:1).

Carbonation of the Reaction Mixture from Cyclopropene and Phenyllithium. 2-Phenylcyclopropyllithium was produced as de-

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(54) W. J. Dale and P. E. Swarzentruber, *J. Org. Chem.*, 24, 955 (1959).

(55) H. Nozaki, T. Aratani, and R. Noyori, *Tetrahedron*, 23, 3645 1967).

(56) D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1702 (1966).

scribed above from 0.3 mol of allyl chloride. An aliquot from the reaction mixture was hydrolyzed; glpc analysis gave a ratio of phenylcyclopropane to allylbenzene of 6.4:1. The bulk of the phenyllithium solution was slowly poured under a cover of argon into a 600-ml beaker which was about one-third full of freshly crushed Dry Ice (covered with 200 ml of ether and *ca.* 10 ml of phenyllithium solution (*ca.* 0.7 *M*) to ensure dryness). The resulting mixture was allowed to warm to room temperature with occasional stirring and was acidified with *ca.* 300 ml of 1 *N* hydrochloric acid. The aqueous phase was separated and extracted with ether. The combined extracts were washed with 10% sodium hydroxide solution and dried; glpc analysis (column E) showed a very small amount of a 1:2 mixture of phenylcyclopropane to allylbenzene.

The combined basic extracts were acidified with concentrated hydrochloric acid and extracted with ether. The ethereal extracts were dried (magnesium sulfate) and treated with excess diazomethane in ether;[57] glpc analysis (columns D and F) indicated the presence of a large amount of methyl benzoate and about a 1% yield of methyl *cis*-2-phenylcyclopropanecarboxylate; the presence of as little as 0.5% of the *trans* ester (relative to the *cis* ester) would have been detected. Concentration of the solution and preparative glpc (column Q) yielded a pure sample of methyl *cis*-2-phenylcyclopropanecarboxylate; the structure was confirmed by comparison of its nmr spectrum and glpc retention times with an authentic sample.

Trapping of Cyclopropene Produced in the Reaction of Allyl Chloride and Phenyllithium. A slow stream of argon was passed through a flask containing 38 g (0.5 mol) of allyl chloride in 100 ml of ether and into a gas washing bottle (cooled in an ice bath) containing 25 ml of cyclopentadiene and 250 μl of anisole (as an internal standard) in 150 ml of pentane. About 0.30 mol of phenyllithium in 500 ml of ether was added over 40 min to the allyl chloride solution, generating enough heat to give vigorous reflux; the solution was refluxed for an additional 20 min. Glpc analysis (column B) of an aliquot withdrawn from the pentane solution gave a peak area ratio of the Diels–Alder adduct, tricyclooctene, to anisole of *ca.* 5:1. After hydrolysis of the phenyllithium reaction mixture, still under a stream of argon, glpc analysis of a new aliquot from the pentane solution gave a ratio of tricyclooctene to anisole of *ca.* 44:1. Quantitative glpc analysis showed that 4.35 g (27%) of the Diels–Alder adduct was formed. The pentane solution was concentrated and vacuum distilled giving a 15% isolated yield of tricyclooctene whose structure was confirmed by nmr.

Work-up of the phenyllithium reaction mixture in the normal manner and glpc analysis indicated the presence of 7.9 g (22%) of allylbenzene and 2.5 g (14%) of phenylcyclopropane.

Stereospecific Syntheses of Methyl *cis*-2-Phenylcyclopropanecarboxylate and Methyl *trans*-2-Phenylcyclopropanecarboxylate. A stirred solution of 250 mg (1.3 mmol) of *cis*-1-bromo-2-phenylcyclopropane (greater than 95% isomeric purity) in 30 ml of ether was treated with *ca.* 4.8 mmol of *n*-butyllithium in 3 ml of hexane and the resulting yellow solution was stirred for 25 min at room temperature. A 10-ml aliquot was syringed under a cover of argon into a beaker containing freshly crushed Dry Ice (covered by 20 ml of ether and *ca.* 1 ml of *n*-butyllithium solution). After the mixture had come to room temperature, 10 ml of ether and 10 ml of water were added. The aqueous layer was extracted with ether and the combined extracts were dried (magnesium sulfate); glpc analysis (column D) showed the presence of phenylcyclopropane (*ca.* 0.5%). The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether; the extracts were dried (magnesium sulfate) and treated with excess diazomethane[57] in ether. Glpc analysis (column D) indicated that methyl *cis*-2-phenylcyclopropanecarboxylate was formed (48%). A sample was purified by preparative glpc (column Q) and its structure was confirmed by nmr analysis.

By the same procedure, 248 mg (1.3 mmol) of *trans*-1-bromo-2-phenylcyclopropane (greater than 95% isomeric purity) afforded phenylcyclopropane (10%) and methyl *trans*-2-phenylcyclopropanecarboxylate (19%). The structure of the ester was confirmed by comparison with an authentic sample prepared from the *trans* acid diazomethane.[57]

Stability of Phenylcyclopropane to Phenyllithium. A solution of 110 mg (0.95 mmol) of phenylcyclopropane and 25 ml of 0.87 *M* phenyllithium (22 mmol) in ether was stirred at room temperature for 1 hr and was then poured over freshly crushed Dry Ice and worked up as above. Glpc analysis (column D) of the ethereal solution showed the presence of phenylcyclopropane (78 mg, 71% recovery) and benzene. The aqueous phase after acidification with concentrated hydrochloric acid, extraction with ether, and esterification with diazomethane[57] yielded methyl benzoate as the only ester. In a similar experiment, a solution of phenylcyclopropane and phenyllithium was refluxed for 5 hr and was hydrolyzed with deuterium oxide. Phenylcyclopropane was isolated from the reaction mixture (80% recovery by preparative glpc on column N); nmr analysis gave no indication of deuterium incorporation.

Isomerization of Allylbenzene to β-Methylstyrene with Phenyllithium. A mixture of 3.0 g (25 mmol) of allylbenzene in 10 ml of ether and *ca.* 30 mmol of phenyllithium in 50 ml of ether was refluxed for 7 hr. After work-up in the normal manner, glpc analysis (column A) indicated the presence of allylbenzene and β-methylstyrene in a ratio of 52:48. A portion of the β-methylstyrene was isolated by preparative glpc (column N) and its structure was confirmed by its nmr spectrum.

Acknowledgment. We wish to thank the Robert A. Welch Foundation for partial support of this research.

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(57) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 166, footnote 3.