The right-handed α-helix of poly-L-tyrosine was found to be more stable than the left-handed α-helix by 1.7 kcal/residue. In view of complications, resulting from the presence of the tyrosyl chromophore, in the interpretation of experimental ORD data for poly-L-tyrosine,[12,13] the calculations reported here provide additional evidence that this polymer exists in the right-handed α-helical form when the tyrosyl side chains are un-ionized.

[12] G. D. Fasman, E. Bodenheimer, and C. Lindblow, *Biochemistry*, 3, 1665 (1965).

[13] Y. H. Pao, R. Longworth, and R. L. Kornegay, *Biopolymers*, 3, 519 (1964).

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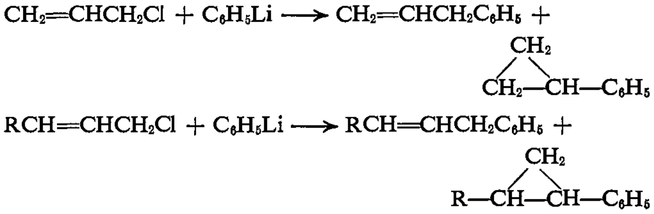
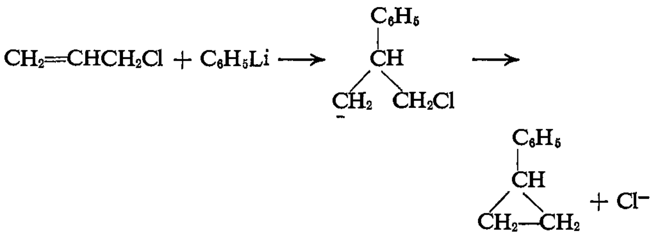
A Carbene Mechanism for the Formation of Phenylcyclopropane from Allyl Chloride and Phenyllithium

Sir:

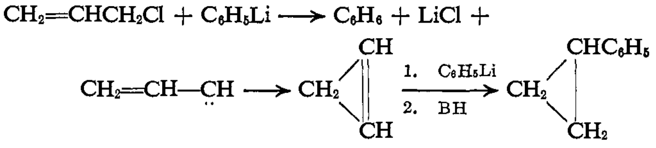
It has recently been reported[1] that the reaction of allyl chloride with phenyllithium yielded phenylcyclopropane in addition to the expected major product, allylbenzene. Other allylic chlorides underwent similar transformations. The mechanism proposed[1] for cyclopropane



formation involved addition of phenyllithium at the β-carbon atom followed by ring closure with expulsion of chloride ion.

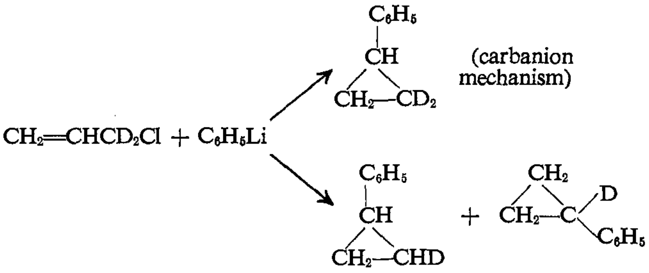


The literature reveals few examples of the addition of organolithium reagents to an unactivated double bond.[2] Because of this, we feel that a different mechanism is most likely, and the following scheme seems plausible.



Organolithium-catalyzed α elimination of an allylic halide to an alkenyl carbene[3] and subsequent cyclopropene formation is a well-established process;[5] while the addition of phenyllithium to a cyclopropene has not been observed, other nucleophiles are known to add to the double bond of a three-membered ring.[6]

As a means of differentiating between the two mechanisms, we investigated the reaction of phenyllithium with allyl-1,1-d_2 chloride. Were the carbanion mechanism operative, phenylcyclopropane-2,2-d_2 would be the product; if, on the other hand, the carbene mechanism were correct, the product would consist of an approximately equal mixture of phenylcyclopropane-2-d_1 and phenylcyclopropane-1-d_1.



Acrylyl chloride was reduced with lithium aluminum deuteride,[7] yielding allyl-1,1-d_2 alcohol[8] which was converted without rearrangement into allyl-1,1-d_2 chloride[9] by the action of thionyl chloride and tri-*n*-butylamine.[10] The reaction of allyl-1,1-d_2 chloride with phenyllithium in refluxing ether for 5 hr yielded allylbenzene and phenylcyclopropane in 55–62 and 0.9–1.1%, respectively, of the theoretical yields based upon allyl chloride.[11]

The following observations are consistent with the α-elimination mechanism and contrary to predictions based upon the carbanion mechanism.

(1) Phenylcyclopropane from allyl-1,1-d_2 chloride was approximately 90% monodeuterated, 7% dideuterated, and 3% undeuterated.[12] The integrated areas

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[1] (a) S. Wawzonek, B. Studnicka, H. J. Bluhm, and R. E. Kallio, *J. Am. 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).

[2] (a) *Cf.* J. E. Mulvaney and Z. G. Garlund, *ibid.*, 30, 917 (1965). (b) An intramolecular addition of a Grignard reagent to an isolated double bond has recently been reported: H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Letters*, 4297 (1966).

[3] We use the term carbene for simplicity, being fully aware of current thinking that divalent carbon species are not intermediates in α eliminations.[4]

[4] (a) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, 87, 4270 (1965); (b) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964); (c) M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, 87, 2293 (1965).

[5] G. L. Closs and L. E. Closs, *ibid.*, **83**, 2015 (1961); **85**, 99 (1963).

[6] R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

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

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

[9] The sample contained 2.00 deuterium atoms at C_1 as established by nmr analysis and greater than 1.90 deuterium atoms by mass spectral analysis.

[10] S. H. Sharmon, F. F. Caserio, J. C. Leak, and W. G. Young, *J. Am. Chem. Soc.*, 80, 5965 (1958).

[11] The yields with undeuterated allyl chloride under identical conditions were 29–37 and 8–10%, respectively; total hydrocarbon yields from deuterated material of as high as 85% have been obtained using excess phenyllithium, but this leads to the extensive isomerization of allylbenzene to β-methylstyrene which interferes with our method of isolating phenylcyclopropane.

[12] We are currently reinvestigating the products formed from allyl-1,1-d_2 chloride in an attempt to determine the deuterium content of phenylcyclopropane more accurately. We suspect that the small amount of dideuterated phenylcyclopropane is due not to the carbanion mechanism but rather to abstraction of a deuteron from allylbenzene-d_2.[13]

[13] D. E. Applequist and M. A. Lintner (*J. Org. Chem.*, 31, 3062 (1966)) have shown that quenching of the allyl chloride–phenyllithium reaction mixture with deuterium oxide does not lead to incorporation of the isotope into phenylcyclopropane. We have observed the identical result but, since all of our data point to the α-elimination mechanism, we believe that 2-phenylcyclopropyllithium

of the nmr absorptions for the benzylic hydrogen and the nonbenzylic ring protons were in the ratio 1:8.[14,15] Allylbenzene from the deuterated chloride was 94% dideuterated and 6% monodeuterated; 24% of the material contained deuterium at C_1 and 76% at C_3, thereby indicating that the S_N2' process takes place to a greater extent than the S_N2 for this system.

(2) From product yields in five experiments using both deuterated and undeuterated allyl chloride, it is clear that a substantial kinetic isotope effect exists, with the undeuterated material yielding phenylcyclopropane at the greater rate. This is strong evidence that a carbon–hydrogen bond is broken in the rate-determining transition state.

(3) Preliminary experiments have indicated that phenyllithium does, indeed, add to synthetic cyclopropene,[17] yielding phenylcyclopropane as the major product.

The experiments described above establish the α-elimination mechanism for cyclopropane formation. Work is continuing to determine the generality of this reaction with other substrates and other bases; we are also pursuing an investigation of the factors that influence the relative amounts of S_N2 and S_N2' processes for allylic halides.

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is neutralized by proton abstraction from the major product, allylbenzene. Although 24% of the allylbenzene contains deuterium at the allylic position, a kinetic isotope effect favoring abstraction of a proton from the remaining 76% would lead to the formation of only a small amount of dideuterated phenylcyclopropane. Experiments are now in progress to determine if allylbenzene is, indeed, the proton source for the cyclopropyllithium.

(14) By the carbanion mechanism, the ratio should be 1:2; by the carbene mechanism, 1:7.

(15) The discrepancy between the observed value and that expected by the carbene mechanism may well be due to experimental errors arising from the small amount of material, from the problems inherent in integrating a weak nmr spectrum, and from the presence of both mono- and dideuterated materials in the sample. Since the observed ratio is in the direction expected[16] from a secondary deuterium isotope effect on the addition of phenyllithium to cyclopropene-1-d_1, we hope that further refinement of our data will establish whether this ratio is significantly different from 1:7.

(16) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 1861 (1961).

(17) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

(18) National Defense Education Act Fellow.

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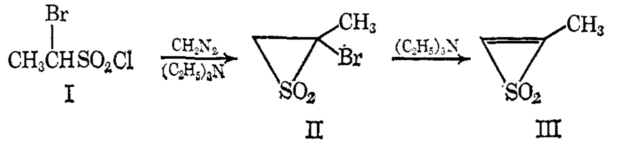
A New Synthesis of Vinylene Sulfones. Application to the Monomethyl Derivative

Sir:

We recently reported[1] the synthesis of 2,3-diphenylvinylene sulfone[2] and demonstrated the striking stability of this compound relative to its dihydro derivative. However the question as to whether this stability is in some part a reflection of dπ–pπ interaction is complicated by the presence of the phenyl substituents attached to the carbon–carbon double bond. We now wish to report a new method for the synthesis of vinylene sulfones and its successful application to an aliphatic example, the monomethyl derivative III. Treating 1,1-dibromoethane with sodium sulfite gave the sodium salt of α-bromoethanesulfonic acid which, with phosphorus pentachloride, was converted in 64% yield to α-bromoethanesulfonyl chloride[3] [I, bp 40° (0.5 mm); infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.24, 8.42, 8.59, 8.69 μ (SO_2); nmr ($CDCl_3$): δ 2.21 (3 H, doublet), 5.42 (1 H, quartet)]. Treating the sulfonyl chloride I with diazomethane in ether at 7–8° in the presence of triethylamine according to the method of Opitz and Fischer[4] gave in 64% yield 2-bromo-2-methylethylene sulfone[3] [II, mp 57–58° dec; infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.50, 8.67, 8.96 μ (SO_2); nmr ($CDCl_3$): δ 2.27 (3 H, singlet), 3.41 (2 H, singlet)]. The structure of II was confirmed by fragmentation to sulfur dioxide and 2-bromopropene upon gentle warming. Dehydrobromination of II by means of triethylamine at 3° over a period of 72 hr gave in 50% yield methylvinylene sulfone[3] [III, mp 59–60°; infrared: $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.22 (C=C) and 7.82, 8.42 μ (SO_2)]. In the accessible ultraviolet region the vinylene sulfone shows only end absorption with the extinction coefficient rising from 434 at 220 mμ to 932 at 210 mμ. The general shape of the curve is similar to that reported for other aliphatic α,β-unsaturated sulfones.[5]



I II III

Compound III appears to be stable indefinitely at room temperature but on heating to about 90° undergoes decomposition to give methylacetylene and sulfur dioxide.[6] Particularly interesting is the nmr spectrum ($CDCl_3$) of III which shows a doublet at δ 2.50 (3 H, methyl, J = 1.1 cps) and a quartet at δ 9.04 (1 H, vinyl, J = 1.1 cps). These positions are comparable to those observed by Breslow and Altman[7] for methylcyclopropenone (δ 2.40 and 8.70).[8]

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(1) L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, 87, 5804 (1965).

(2) Thiirene 1,1-dioxide according to *Chemical Abstracts* nomenclature.

(3) All new compounds gave correct elemental analyses and molecular weights (vapor osmometry) and consistent spectral data.

(4) G. Opitz and K. Fischer, *Z. Naturforsch.*, **18b**, 775 (1963); *Angew. Chem.*, 77, 41 (1965).

(5) E. S. Waight, *J. Chem. Soc.*, 2440 (1952).

(6) It has not yet been possible to synthesize the corresponding 2,3-dihydro derivative for direct comparison of its stability with that of III. However, a number of simple alkyl derivatives of ethylene sulfone have been described by Opitz and Fischer,[4] and these appear to be relatively unstable at room temperature. The precursor II undergoes decomposition on standing at room temperature in chloroform solution over a period of 1–2 days. In the crystalline state II rapidly loses weight on standing in the open at room temperature. A sample sealed in a small glass vial completely liquefied over a period of 8–10 hr. The liquid was shown to be 2-bromopropene.

(7) R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, 88, 504 (1966).

(8) Attempts to determine a "ring-current" shift[9,10] for the 2-methyl group did not give any meaningful results because of the lack of suitable model compounds.

(9) Compare (a) J. A. Elvidge, *Chem. Commun.*, 160 (1965); (b) R. J. Abraham and W. A. Thomas, *J. Chem. Soc., Sect. B*, 127 (1966). For a pungent criticism of the whole matter relating to "ring-current" shifts see J. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

(10) Apart from any similarity in electronic structure it would be expected that the methyl and vinyl absorptions of methylvinylene sulfone would be downfield from those of methylcyclopropenone. This is apparent from a comparison of simple ketones with the analogous sulfones. A comprehensive study of the latter has been published [P. Biscarini, F. Taddei, and C. Zauli, *Boll. Sci. Chim. Ind. Bologna*, **21**, 169 (1963)].