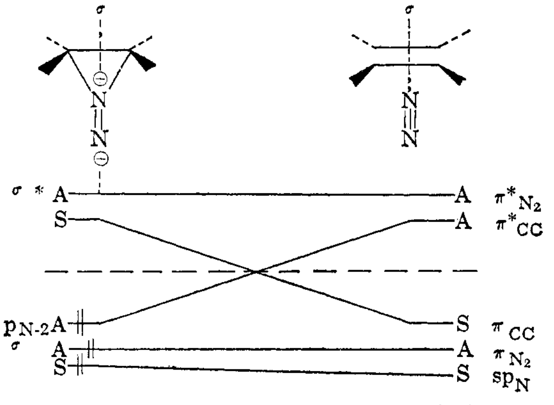
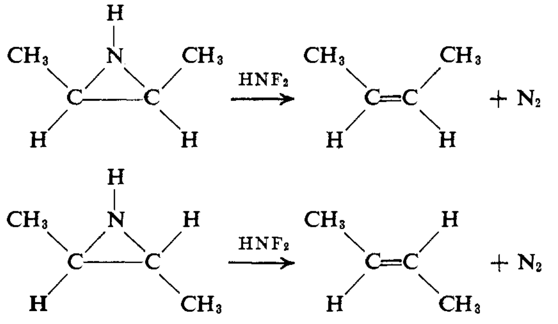
Lemal, Dartmouth College, is

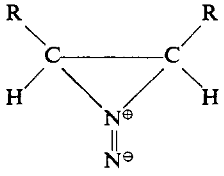


Treatment of *cis*- and *trans*-2,3-butenimines[4] with difluoramine at 0° has been found to give olefin of the same configuration as the aziridine. The product composition was determined by means of infrared and vapor phase chromatographic analysis. In both cases stereochemistry was retained to the extent of 96% or more.



The known[5] stereospecific elimination of nitrous oxide from N-nitrosoaziridines has been cited as an example of the application of the orbital symmetry theory,[3] and it has also been suggested that the stability of N-nitroso-3-pyrroline[6] confirms the theory's predictive power. However, in order to construct the orbital correlation diagrams for these nitroso compounds, the plane of the N=O π bond must be rotated so that it is orthogonal to the orbital of the unshared electrons on the amino nitrogen. A number of studies[7] have shown that there must be considerable N=N double bond character in the ground state of nitrosamines, indicating considerable overlap of these orbitals. The transition state leading to elimination may not resemble the ground state, however, but there are no data available to bear on this point. It would appear that more rehybridization would be required from the orthogonal transition state, suggesting that it would be of higher energy.

If the postulated intermediate, **1**, is the species involved in the elimination under study,[8] then its decomposition and the stereospecific decomposition of episulfones[9] constitute exceptions to the applicability of the Hoffmann-Woodward theory. At this point it



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seems reasonable to adopt the view that the theory as presently constituted is not in fact applicable to three-membered rings and that the apparent correspondence with it of the nitrous oxide elimination is a red herring.[10] In any case the exceptions now outnumber the applications.[11]

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[4] We are grateful to Professor G. K. Helmkamp, University of California, Riverside, Calif., for generous samples of both isomers of the aziridine.

(5) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(6) S. D. McGregor and D. M. Lemal, *J. Am. Chem. Soc.*, **88**, 2858 (1966).

(7) For a summary of leading references, see G. J. Karabatsos and R. A. Teller, *ibid.*, **86**, 4373 (1964).

(8) In order to establish this point securely, Dr. D. M. Lemal is attempting to prepare the corresponding N-(toluenesulfonylamino) derivative in order to subject it to base-catalyzed decomposition.

(9) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966); N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

(10) Alternatively the reaction could be nonconcerted as predicted by theory, but two-step processes could produce a stereochemical result identical with that of a concerted reaction.

(11) Recently it has been reported [G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, 32, 459 (1967)] that the elimination of SO from the 2-butene episulfoxides is nonstereospecific. Such a result is predicted by the Woodward-Hoffmann theory.

(12) Alfred P. Sloan Fellow, 1966–present.

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The Geometric Stability of 1,3-Diphenylallyllithium

Sir:

It has been established that allylic anions,[1] cations,[2] and radicals,[3] when generated as transient intermediates, resist rotation about their partial double bonds long enough to maintain the geometry imposed by their progenitors. It is of obvious interest to learn if this result is applicable to long-lived allylic species, and we now report results on anions generated from *cis*- and *trans*-1,3-diphenylpropene (*cis*- and *trans*-I).[4]

Addition of 1.1 equiv of butyllithium in hexane to either *cis*- or *trans*-I in THF and subsequent quenching of the resulting magenta solution with D_2O affords a 97:3 mixture of *trans*-:*cis*-I-3*d*. To study the geometrical lability of the anionoid intermediate, we have examined the nmr spectrum of purified 1,3-diphenylallyllithium from *cis*- and *trans*-I and have concluded that we are dealing with a largely delocalized, anionoid species which requires an extraordinarily low $\Delta G^{\ddagger}$ for rotation about bonds which simple Hückel theory predicts to have considerable double bond character.

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(1) D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

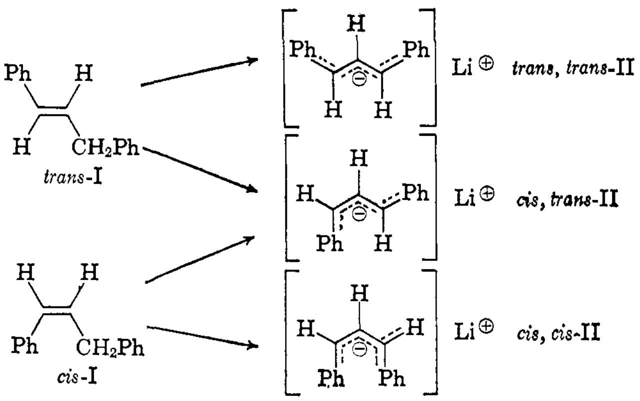
(2) W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376 (1960).

(3) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(4) *cis*- and *trans*-I were prepared by a modified Wittig reaction and were separated by gas phase partition chromatography. Each isomer was >95% pure and their spectral properties agreed with those of authentic samples kindly supplied by G. W. Griffin and R. C. Petterson (*cf.* G. W. Griffin, *et al.*, *ibid.*, **87**, 1410 (1965).

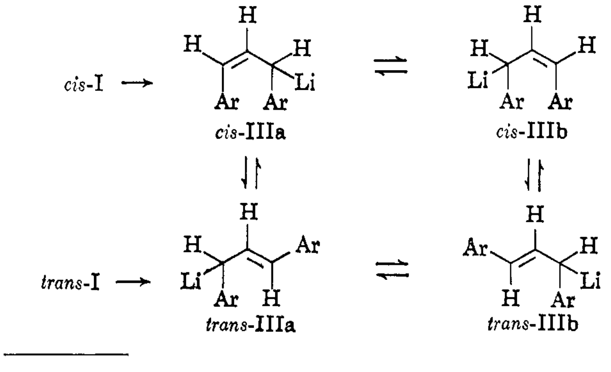
The nmr spectrum obtained from either *cis*- or *trans*-I (Figure 1) is consistent only with *trans,trans*-1,3-diphenylallyllithium (*trans,trans*-II) as the predominate species and eliminates all but traces of the other geometrical isomers (*cis,trans* and *cis,cis*) of II. The magnetically equivalent α protons (2 H doublet at δ 4.6) and the central β proton (1 H triplet centered at δ 7.2) constitute an AB_2 type (J_{A-B} = 13 cps) which accommodates either *trans,trans*- or *cis,cis*-II but rules out *cis,trans*-II in which nonequivalence of the α protons requires the more complex ABC-type pattern. We can decide in favor of *trans,trans*-II on the basis of the chemical shift of the β proton; only this isomer can readily attain a completely coplanar, strain-free conformation, and the unusually low-field resonance of the β proton is best explained by the diamagnetic deshielding influence of the vicinal, coplanar phenyl groups in *trans,trans*-II.

Scheme I



The fact that both *cis*- and *trans*-I give rise to the same intermediate is novel, or significant, only to the extent that it can be regarded as a delocalized carbanionic species (*cf.* Scheme I). On the other hand, if this intermediate is an essentially covalent (sp^3 hybridized) organolithium compound which can rapidly tautomerize to yield an equilibrated distribution of products[5] (*cf.* Scheme II), then the identity of the products from *cis*- and *trans*-I is a trivial result, reflecting only the anticipated difference in the thermodynamic stabilities of *trans*-III (a and b) over *cis*-III (a and b). Therefore, the significance of the present findings is directly dependent on our capacity to assess the ionic character of this carbon–lithium bond.

Scheme II



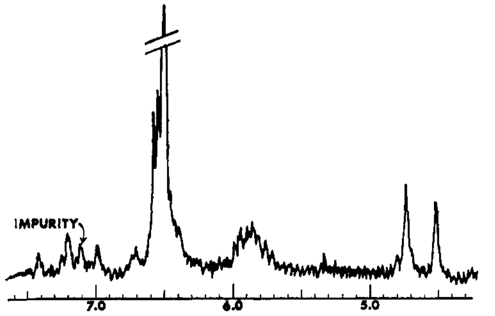


Figure 1. Nuclear magnetic resonance spectrum of 1,3-diphenylallyllithium in THF-d_8 at 38° and 60 Mc/sec with TMS as internal standard.

The upfield shift of the phenyl resonances of the anionoid species (Figure 1) clearly indicates that considerable negative charge is delocalized into the phenyl rings and especially to the *para* position. The eight-proton multiplet centered at δ 6.5 and the two-proton multiplet at δ 5.9 are, respectively, very similar to the *ortho–meta* and *para* resonances of diphenylmethyllithium[6] and the 1- and 3-phenyls of 1,2,3,4-tetraphenylcyclobutenyllithium.[7] In view of the amount of charge delocalization, it is likely that all of these are largely ionic species in THF, and ^{13}C nmr data support an essentially sp^2-hybridized α-carbon atom in diphenylmethyllithium.[8]

Since the negative charge in 1,3-diphenylallyllithium is delocalized into the phenyl rings, it must be similarly distributed over the allylic carbons, leading to partial double bonding and a rotational barrier. Hückel molecular orbital calculations predict a bond order of 0.66 for the 1,3-diphenylallyl anion, which, assuming a proportionality between bond order and bond energy, would amount to a 27-kcal rotational barrier.[9] Thus, the finding that the anionoid intermediate (most probably *cis,trans*-II), initially formed from *cis*-I with butyllithium, undergoes ready geometrical isomerization, even when prepared and examined at −30°, is unexpected.[10] Though these results are not necessarily extrapolatable to other stable allylic systems, it does suggest that the finding of rapid rotation about the C–C bonds of an allyl group is not sufficient cause for the *a priori* elimination of a delocalized anionoid species.[5a]

An alternative mechanistic possibility, that geometrical isomerism occurs by way of complex equilibria involving rapid exchange between ionic and covalent species, is not readily explorable with the present system but is being actively investigated with related systems.

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(5) Roberts and co-workers have interpreted their nmr studies of allylic Grignard reagents on the basis of rapidly interconverting covalent tautomers: (a) J. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959); (b) J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961); (c) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *ibid.*, **84**, 2010 (1962); (d) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, 185 (1962).

(6) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(7) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *ibid.*, **87**, 3019 (1965).

(8) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *ibid.*, **88**, 1272 (1966).

(9) Based on a 40-kcal energy difference between a single and a double bond.

(10) Additional experimental evidence has been obtained which rules out isomerization *via* either radical anions or rapid intramolecular proton transfer during formation of the lithium compound.

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