

Experimental¹⁶

Dipole Moment Measurements.—The dielectric constants were measured in benzene solutions at 25° with a heterodyne beat type apparatus¹⁷ similar to that described by Chien,¹⁸ modified by the addition of a 1000-cycle filter. The dipole moments were calculated as described by Halverstadt and Kumler.¹⁹ The molecular refractivities were obtained by summation

(16) The authors wish to thank Mr. H. Talts for running the infrared and n.m.r. spectra.

(17) L. F. Reed, M.S. Thesis, Polytechnic Institute of Brooklyn, 1960.

(18) J. Y. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

of the bond refractivities values given by Vogel, *et al.*²⁰ The infrared spectra were run as potassium bromide pellets and n.m.r. spectra were carried out as saturated solutions in deuteriochloroform with tetramethylsilane as an internal standard.

Acknowledgment.—We wish to acknowledge gratefully the support of this work by the National Science Foundation, Grant Number NSF G-17448.

(19) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2933 (1942).

(20) A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind. (London)*, 358 (1950).

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The Cyclopropylidene¹: Generation and Reactions

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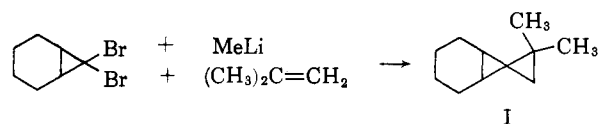
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A study of the reaction of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea with various bases has been carried out. The most effective base was found to be lithium ethoxide (presumably as its alcoholate). In the absence of carbene acceptors the reaction leads to a high yield (up to 96%) of 1,1-diphenylallene. Reaction of the nitroso-urea with base in the presence of acceptor olefins leads to a mixture of 1,1-diphenylallene and the spiropentane (*ca.* 20%) that would be expected to result from addition of 2,2-diphenylcyclopropylidene to the olefin. The spiropentane structures were proved by their spectral properties and, in one case, by alternate synthesis. Evidence is presented for initial formation of 2,2-diphenyldiazocyclopropane followed by its spontaneous collapse to 1,1-diphenylallene and 2,2-diphenylcyclopropylidene. The carbene can apparently either collapse to give the allene or react with the olefin to give the spiropentane. Competition reactions were run with various olefins and it was found that the results could be accommodated by an electrophilic carbene in which the two aryl groups create a dominating steric effect when opposed to alkyl groups on the acceptor olefin. Reaction of the cyclopropylidene with *cis*- and *trans*-2-butene is stereospecific.

Unsuccessful attempts to capture the cyclopropylidene have been reported by several investigators. For example, Moore and Ward³ first reported the fact that the reaction of 1,1-dibromocyclopropanes with methyl- or butyllithium in cyclohexene gives allenes, but none of the spiropentanes that would result from addition of the anticipated⁴ cyclopropylidene to the carbon-carbon double bond. Similar failures to trap this intermediate have also been reported by Logan,⁵ who examined the reaction of 1,1-dichloro-2-alkylcyclopropanes with magnesium metal in the presence of alkyl or aryl halides, and by Skattebol,⁶ who studied the reaction of a variety of dihalocyclopropanes with alkyllithiums. Again, both of these investigators found the predominant products to be allenes.

The production of allenes in reactions of this type is certainly not surprising in view of the fact that as early as 1958, Doering and LaFlamme⁷ reported that the reaction of dibromocyclopropanes with magnesium or sodium yielded allenes as the predominant products. Furthermore, Doering and LaFlamme suggested a variety of possible intermediates from which allene formation might occur in these reactions and convincingly narrowed the possibilities down to collapse of either the bromocarbene or the carbene. However, they were not able to assess the relative importance of these two modes of reaction. The problem of prevent-

ing the collapse to allene of either the halo carbene or the cyclopropylidene was very cleverly solved by Moore and Ward,³ who examined the reaction of 7,7-dibromonorcarane with methyllithium. In this system, the cyclopropane is fused to a six-membered ring which would certainly inhibit formation of the allene (1,2-cycloheptadiene) and, indeed, Moore and Ward have isolated a variety of products which are typical of carbene intermediates. For example, reaction with isobutylene gave spiropentane (I).⁸



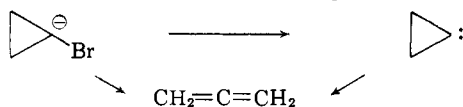
At the same time that Moore and Ward were examining the dibromonorcarane system, we began a study of the generation and decomposition of selected diazocyclopropanes. The purpose of this paper is to report some of the results of our investigations on 2,2-diphenyldiazocyclopropane.

As a convenient starting material we selected 2,2-diphenylcyclopropanecarboxylic acid, a compound which can be readily obtained from the reaction of diphenyldiazomethane with methyl acrylate.⁹ Conversion of this acid to the corresponding nitroso-urea was cleanly effected by the reactions shown in the flow sheet.

The nitroso-urea was then treated with a variety of bases in attempts to generate 2,2-diphenyldiazocyclopropane. However, under all conditions where any reaction occurred, spontaneous nitrogen evolution was observed and, except for transient yellow colors, in no case was a solution obtained that had the typical color of a diazoalkane. When the reaction was effected in saturated hydrocarbon solvents, it was found that the

(8) For another example of the formation of a spiropentane from reaction of a *gem*-dibromocyclopropane with methyllithium, see L. Skattebol, *Chem. Ind. (London)*, 2146 (1962).

(9) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955).



(1) For the preliminary communication on this work, see W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960).

(2) Alfred P. Sloan Fellow, 1963-1965.

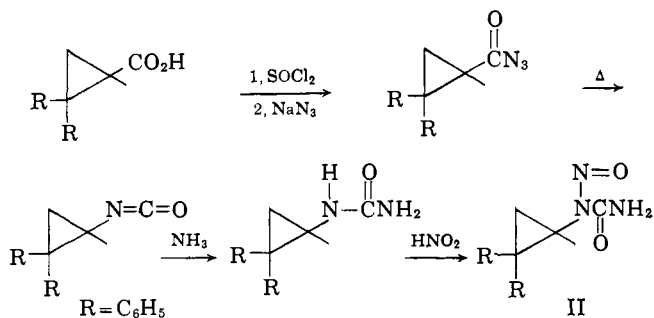
(3) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962).

(4) For references related to the production of carbenes from the reaction of polyhalomethylenes with alkyllithium reagents, see: G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

(5) T. J. Logan, *Tetrahedron Letters*, 173 (1961).

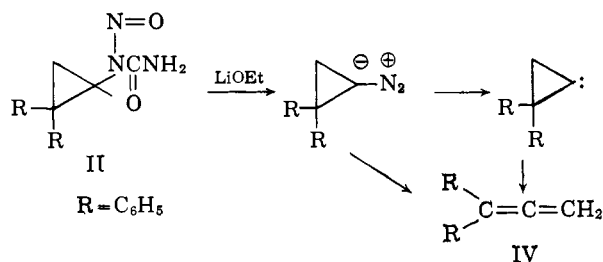
(6) L. Skattebol, *ibid.*, 167 (1961).

(7) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

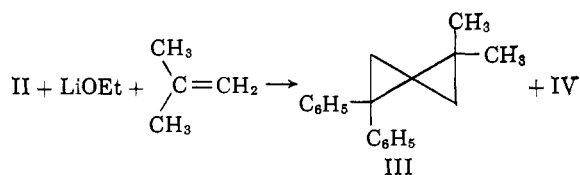


principal product was 1,1-diphenylallene (as high as 96% yield but usually about 90%).¹⁰

From these preliminary observations it was recognized that the diazocyclopropane was probably being formed but was apparently quite unstable, collapsing either in a concerted manner or *via* the carbene to the allene.



The nitrosourea was therefore treated with base in the presence of acceptor olefins (usually as the solvent) and found to give, in addition to appreciable quantities of the allene, the spirocyclopropane products anticipated from reaction of the carbene with the double bond. Although many different bases have been found to be effective in this reaction, we have found that by far the



cleanest product results from the reaction of the nitrosourea with unsublimed, air-dried lithium ethoxide (a white powder that contains about one mole of what is probably ethanol). In a typical reaction, the nitrosourea was stirred with an equimolar amount of lithium ethoxide (alcoholate) in isobutylene until nitrogen evolution ceased (generally about 90% of theoretical). Elution chromatography of the hydrocarbon-soluble product gave 18% of the spirocyclopropane III; g.l.p.c. analysis of the crude reaction product showed 22% of the spirocyclopropane to be present. The generality of this reaction for the synthesis of hydrocarbon spirocyclopropanes was shown by effecting the reaction in the presence of a variety of acceptor olefins (see Table III in the Experimental section). In each case, the other major product was 1,1-diphenylallene. Generally, the total yield of hydrocarbon products was 85–90%.

The spirocyclopropane structures were initially suggested for the adducts as a result of analyses, molecular weights (on the adducts arising from reaction with *cis*- and *trans*-2-butene), negative chemical tests for unsaturation, and the fact that the ultraviolet spectra of all adducts were found to be virtually identical with the spectra of typical diphenylcyclopropane model com-

pounds. In addition to the above-mentioned tests, the following spectral and chemical data present compelling evidence for the spirocyclopropane structures.

Infrared Spectra.—The infrared spectra of all adducts show no absorption between 5.8 and 6.5 μ except for the typical phenyl absorption which appears around 6.3 μ . Furthermore, all adducts show a moderately strong, sharp absorption at $9.88 \pm 0.03 \mu$. The significance of this absorption deserves some attention. Contrary to earlier reports,¹¹ recent evidence has appeared which suggests that there is not a truly reliable characteristic infrared absorption in the 10- μ region for the cyclopropane ring.¹² However, Wilcox and Craig¹³ have very recently reported their observation that several 7-spirocyclopropane derivatives of [2.2.1]-bicyclic systems all show a band at $9.91 \pm 0.03 \mu$, an absorption that they feel is quite characteristic of this type of compound. The fact that the spirocyclopropanes of Wilcox and Craig¹³ experience exocyclic strain similar to the cyclopropane rings of spirocyclopropanes suggest the possibility that the absorption at 9.91 μ might be generally characteristic of strained cyclopropane rings.¹⁴

The near-infrared spectra of some of the spirocyclopropanes were also examined. It was found that, as would be expected for cyclopropane rings,¹⁵ in every case examined an absorption was found at about 1.65 μ .

Nuclear Magnetic Resonance Spectra.—The presence of two cyclopropane rings in the hydrocarbon products is clearly indicated by the magnitudes of the geminal coupling constants of the ring hydrogens in the addition products of *trans*-2-butene and isobutylene. In the former case, the hydrogens on the ring containing the phenyls are slightly nonequivalent, and the coupling constant between them is obtainable as 4.1 c.p.s. For the latter compound, the hydrogens on the ring containing methyl substituents are made nonequivalent by the difference in their relationship to the phenyl groups, and the coupling constant is 4.5 c.p.s. These values of *J* are quite close to the value of 5.0 c.p.s. reported by Applequist¹⁶ for chlorospirocyclopropane and deviate considerably from the values of 12 to 13 found for several cyclobutanes.^{17,18}

Further support for the presence of a three-membered ring is given by the chemical shifts of the ring hydrogens. Those on the ring containing the phenyl groups all appear in the region 8.48–8.63 τ ; those on the portion of the molecule derived from the olefin have τ -values above 9 units. The resonances of the latter hydrogens are not always resolvable in the spectra, but the broad peaks, running up to 9.5 τ in the adducts of cyclohexene, *cis*-2-butene, and *trans*-2-butene, can only be explained as due to the distinctive high-field shift observed for cyclopropyl hydrogens as compared to hydrogens in rings of larger sizes. It is interesting that in the 2-butene adducts, in which methyl groups are attached to cyclopropyl carbons which also bear hydrogens, the methyl resonances appear as singlets. Coupling of the methyl hydrogens with the ring hydrogens would

(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 28.

(12) See C. F. H. Allen, T. J. David, W. J. Humphlett, and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957); A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959).

(13) C. F. Wilcox, Jr., and R. R. Craig, *ibid.*, **83**, 3866 (1961).

(14) For another example, see ref. 7.

(15) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); D. T. Warner, *J. Org. Chem.*, **24**, 1536 (1959); P. G. Gassman, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 27-O.

(16) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

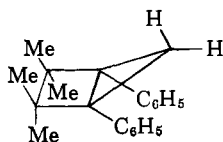
(17) J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2212 (1962).

(18) E. Lustig, *J. Chem. Phys.*, **37**, 2725 (1962).

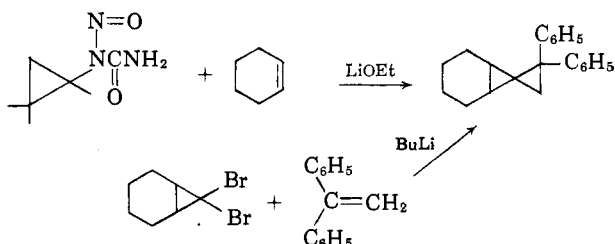
(10) Schechter has reported that unsubstituted diazocyclopropane undergoes decomposition to allene; H. Schechter, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 15-O.

be expected, but the near equality of chemical shifts of the two types of hydrogens causes the spectrum to show no evidence of coupling. The hydrogens β to the phenyl groups correspond in chemical shift quite closely to the ring hydrogens in cyclopropanes containing two phenyl groups on one carbon atom.

Finally, there are symmetry arguments which lead to the exclusion of possible structures that could not be excluded by other considerations. For example, the following structure for the 2,3-dimethyl-2-butene adduct is not excluded by chemical properties or the infrared spectrum but becomes unlikely since the two cyclopropyl ring hydrogens in this molecule would be nonequivalent, whereas the n.m.r. spectrum shows only one sharp peak for these hydrogens.



Alternate Synthesis.—Finally, as quite compelling evidence for the structure of at least one of the products, the adduct isolated from the reaction of the nitroso-urea with base in the presence of cyclohexene was alternately synthesized by the method of Moore and Ward.³ The two products had identical melting points, showed no depression upon admixture, and had



identical g.l.p.c. retention times and identical infrared spectra.

TABLE I
N.M.R. CHEMICAL SHIFTS^a OF SPIROPENTANES

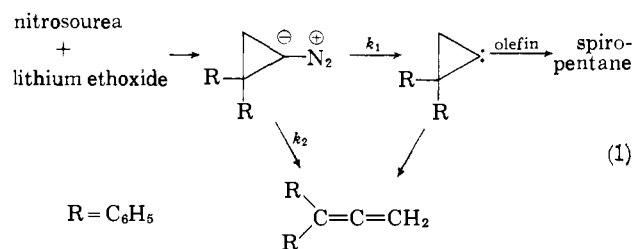
| Acceptor olefin | Phenyl | Chemical shifts (τ -values) | | |
|------------------------|-------------------|-----------------------------------|-------------------------------|------------------|
| | | H on ring bearing phenyls | H on ring derived from olefin | Methyl hydrogens |
| <i>trans</i> -2-Butene | 2.84 ^b | 8.55 | c | c |
| Butene | 3.01 ^b | 8.63 | | |
| Isobutylene | 2.75 (sharp) | 8.48 | 9.31 | 8.74 |
| | 3.0 (broad) | | (doublet) 9.54 | 9.00 |
| <i>cis</i> -2-Butene | 2.89 (sharp) | 8.63 ^d | 9.0 | 8.97 |
| | | | (multiplet) | |
| 2,3-Dimethyl-2-butene | 2.91 (sharp) | 8.52 | ... | 8.90 |
| | | | | 9.07 |
| Cyclohexene | 2.90 (broad) | 8.56 | 8.65 ^e | ... |
| | 2.94 (broad) | | | |

^a τ -Values from tetramethylsilane. ^b Broadens on dilution. ^c Overlapping multiplet. ^d In our preliminary communication¹ this peak was erroneously reported as a quartet. ^e Broad band, 8.0 to 9.5.

The Nature of the Intermediate.—Despite the fact that there is little doubt that the adducts have the spirocyclic structures, this, in itself, cannot be taken as proof that the cyclopropylidene has been formed as a real entity. However, there are several factors that certainly suggest the actual intermediacy of the carbene.

Of initial significance is the fact that the allene formed apparently has at least two distinct precursors, only one of which can react with an olefin to give a spirocyclic structure.

The following scheme has been suggested to explain these results. The evidence for the reaction involving two distinct precursors was described in detail and will not be dealt with here.



However, there was not presented compelling evidence for the precise nature of the allene precursors and, although the diazocyclopropane and carbene are intuitively attractive intermediates, the data presented could conceivably be explained by other pairs of possible allene precursors. Of the possible candidates for these two species, there are at least two different spirocyclic precursors that should be considered; the carbene and the diazocyclopropane. That the latter is an unlikely possibility is apparent for several reasons. First, the reaction of diazoalkanes with olefins unactivated by electron-withdrawing groups is rare and generally involves strained double bonds.²⁰ Furthermore, in those cases where reaction with non-activated double bonds has been observed, the pyrazoline has been isolated as a stable product.²¹

The other possible method by which the diazocyclopropane could react directly with the double bond to give a spirocyclic product would involve formation of some type of 1-pyrazoline precursor (possibly a zwitterion) which could lose nitrogen before ring closure. To our knowledge, there is no precedent for such a reaction.^{22,23}

Finally, by far the most compelling evidence for the two allene precursors being the diazocyclopropane and the carbene arises from the reaction of the nitroso-urea with lithium ethoxide in the presence of diethyl fumarate. Of initial significance was the fact that, in the presence of diethyl fumarate, there was no detectable nitrogen evolution and 1,1-diphenylallene was formed in only trace amounts. This leads to the conclusion that the diethyl fumarate must interrupt the reaction prior to formation of the second allene precursor. Furthermore, from the product ratio studies previously reported, it is known that the ratio of k_1/k_2 in eq. 1 is about 0.5. In other words, only about one-third of the initial allene precursor goes to the second allene precursor. However, there was isolated from the reaction in the presence of diethyl fumarate a 47.5% yield of the pyrazoline that would be expected from reaction of the diazocyclopropane with the ester. It therefore becomes obvious that the first allene precursor must be a nucleophilic species and, furthermore, must be capable of giving the pyrazoline with diethyl fumarate. In other words, the diazocyclo-

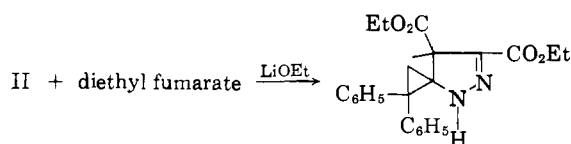
(19) W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, **20**, 927 (1962).

(20) Cf. H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 77-78.

(21) The 1-pyrazoline that would be formed by reaction of the diazocyclopropane with an unactivated double bond would be expected to be quite stable since it would simply be an unactivated five-membered azo ring. For comparison, azoisopropane (*i*-PrN=N-*i*-Pr) is an extremely stable material exhibiting an activation energy of 41 kcal. per mole for its decomposition. See H. C. Ramsperger, *J. Am. Chem. Soc.*, **60**, 714 (1928).

(22) Many cases of spontaneous nitrogen evolution from low temperature reactions of specific diazo compounds with activated olefins have been reported. However, even in these cases the cyclopropane apparently is preceded by the pyrazoline which, in the cases where this special phenomenon is observed, would be expected to be quite unstable. See L. Horner and E. Lingnau, *Ann.*, **587**, 93 (1954); R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(23) Unpublished results of T. H. Glenn.



propane is the most likely first allene precursor. This, then, leaves the cyclopropylidene as the most likely candidate for the second allene precursor and the intermediate that reacts with olefins to give spiro-pentanes.

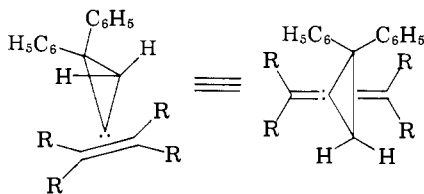
More direct evidence for the carbene as a distinct intermediate was obtained by competitive reactions with various olefins. This is a test that has been applied in many instances to determine the electrophilicity or nucleophilicity of carbenes. In most instances, the carbene behaves as an electrophile, thus leading to the prediction that the more nucleophilic the double bond, the faster the reaction.²⁴ The results of our investigation are summarized in Table II and are compared with a study of an unsymmetrical carbene, the chlorocarbene.²⁵

TABLE II
RELATIVE RATES OF ADDITION OF 2,2-DIPHENYLCYCLO-
PROPYLIDENE AND CHLOROCARBENE TO OLEFINS

| Olefin | (<i>k/k₀</i>)cyclo- propylidene ^a | (<i>k/k₀</i>)CHCl ^b |
|------------------------|--|---|
| 2,3-Dimethyl-2-butene | 0.41 | 2.80 |
| Isobutylene | 1.00 | 1.00 |
| <i>trans</i> -2-Butene | 0.42 | 0.45 |
| <i>cis</i> -2-Butene | 1.15 | .91 |
| Cyclohexene | 1.23 | .60 |
| 1-Pentene | | .23 |
| 1-Butene | 0.22 | |

^a Measured in competition with cyclohexene. ^b These data taken from Closs and Schwartz.²⁵

The data do not follow the order that would be predicted by strictly electronic considerations for either an electrophilic or a nucleophilic species. However, they do follow the order predicted for an unsymmetrical *electrophilic* species that exhibits a dominating steric effect^{26,27} when the two phenyl rings on the cyclopropylidene are opposed to one or more alkyl groups. For example, addition to isobutylene occurs more rapidly than addition to *trans*-2-butene.



In each of these cases, one of the incoming phenyl rings is opposed to one methyl group and the predicted electronic order obtains. On the other hand, addition to isobutylene is faster than to 2,3-dimethyl-2-butene. In the latter case, both of the phenyl rings are opposed to alkyl groups and the steric effect prevails.²⁸ Cyclo-

(24) Cf. W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956). For an example of a nucleophilic carbene reaction, see H. W. Wanzlick and E. Schikora, *Ber.*, **94**, 2389 (1961).

(25) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960).

(26) For examples of other unsymmetrical carbenes in which steric effects operate, see G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960); E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); U. Schöllkopf and G. J. Lehmann, *Tetrahedron Letters*, **4**, 165 (1962).

(27) For at least one example of an unsymmetrical carbene in which steric effects apparently do not operate, see G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962).

(28) W. R. Moore, H. R. Ward, and R. F. Merritt (*ibid.*, **83**, 2019 (1961)) have reported that the cyclopropylidene derived from 7,7-dibromonor-

hexene and *cis*-2-butene were found to be particularly reactive, a result that would be predicted for a reaction in which the two phenyl rings of the cyclopropylidene can approach unopposed to any alkyl groups.²⁹ Finally, 1-butene was found to be the least reactive of all the olefins studied despite the fact that the two phenyls could approach unopposed to any alkyl groups. This, again, suggests that the intermediate is an electrophilic species.

Another common characteristic of carbenes is their tendency to insert into carbon-hydrogen bonds.³⁰ Products resulting from the insertion of the cyclopropylidene were therefore sought. Such products were not detected when the nitrosoarea was treated with base in hydrocarbon solvents. Attempts to isolate insertion products from reaction of the nitrosoarea with base in the more reactive diethyl ether³¹ have failed. However, the gas chromatogram of the crude reaction mixture shows several new peaks with retention times that are consistent with insertion products. Further work on this phase of the reaction is presently underway.

Finally, since the intermediate in the reaction of the nitrosoarea with base is apparently the carbene, we felt that it would be interesting to apply Skell's³² chemical test for the multiplicity of the electrons. Reactions of the cyclopropylidene was therefore effected with *cis*- and *trans*-2-butene and, within experimental error, the reaction was stereospecific.³³ This suggests that insofar as Skell's chemical test for the multiplicity of electrons is general, at the instant of reaction with the olefin the cyclopropylidene is in the singlet form.³⁴

Finally, the apparent extreme thermal instability of the diazocyclopropane deserves some mention. In contrast to most simple diazoalkanes (including diazocyclobutane),³⁵ diazocyclopropane decomposes spontaneously even at temperatures as low as -20° . One obvious reason for this rapid loss of nitrogen is the concerted collapse of the diazocyclopropane to the allene. However, the loss of nitrogen from the ring to give the carbene must also be quite rapid to compete with the concerted decomposition to the allene. As a possible explanation for this reactivity we would like to suggest that ring strain holds the nitrogen of the diazocyclopropane out of the plane of the ring. This, in turn, decreases the double bond character of the carbon-nitrogen bond by effectively reducing the contribution of canonical form V to the diazocyclopropane hybrid.

carane does not add to 2,3-dimethyl-2-butene and have attributed this to steric hindrance.

(29) Reaction with cyclohexene and *cis*-2-butene could give products in which the two phenyl rings are either *cis* or *trans* to the alkyl portion of the original olefins. In both cases, only one product could be isolated and the gas chromatogram of the crude reaction mixtures showed single spiro-pentane peaks. It is most likely that both isomers were formed but not separated on our column.

(30) For a good review of this subject, see W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(31) W. von E. Doering, L. H. Knox, and M. Jones, Jr., *J. Org. Chem.*, **24**, 136 (1959).

(32) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); R. M. Etter, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959); P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960).

(33) The product from the reaction of the carbene with *trans*-2-butene was devoid of any of the *cis*-2-butene product. However, the product from the reaction with *cis*-2-butene showed a small shoulder on the *cis* adduct g.l.p.c. peak (less than 10%) with a retention time the same as the *trans* adduct. This was at first disturbing. However, chromatographic analysis of the *cis*-2-butene (Matheson, C.P. grade) used for the experiments showed two peaks, the smaller of which had the same retention time as *trans*-2-butene. We were not able to determine accurately the amount of this material, but it appeared to be on the order of 15% of the mixture.

(34) Consistent with this is the observation of Moore and his group²⁸ that the reaction of 7,7-dibromonorcarane with alkyllithium in the presence of *cis*- and *trans*-2-butene is stereospecific.

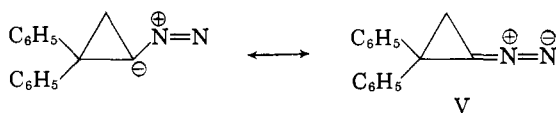
(35) D. E. Applequist and D. E. McGreer, *J. Am. Chem. Soc.*, **82**, 1965 (1960).

TABLE III
 THE PROPERTIES OF 2,2-DIPHENYLCYCLOPROPYLIDENE ADDUCTS

| Acceptor | M.p., °C. | Yield, % (g.l.p.c.) | Retention times, ^c min. | Infrared absorption, μ | Near- infrared absorption, μ | Analyses, % | | | |
|------------------------|------------------------|------------------------|--|-------------------------------|--|-------------|------|-------|------|
| | | | | | | Calcd. | | Found | |
| | | | | | | C | H | C | H |
| 2,3-Dimethyl-2-butene | 69.5–70.0 ^a | 16 | 26.3 | 9.88 | 1.648 | 91.25 | 8.75 | 91.25 | 8.90 |
| Isobutylene | 47.5–48.0 ^a | 22 | 26.6 | 9.86 | 1.648 | 91.88 | 8.12 | 91.99 | 8.08 |
| <i>trans</i> -2-Butene | 51.5–52.0 ^a | 23 | 17.0 | 9.86 | 1.648 | 91.88 | 8.12 | 92.05 | 7.91 |
| <i>cis</i> -2-Butene | 31.0–32.0 ^a | 22 | 17.1 ^d | 9.86 | 1.647 | 91.88 | 8.12 | 92.06 | 7.76 |
| Cyclohexene | 82.0–82.5 ^b | 21 | 49 | 9.91 | 1.654 | 91.92 | 8.08 | 91.84 | 8.06 |
| 1-Butene | Oil | 9 | 20.4 | 9.84 | | 91.88 | 8.12 | 91.60 | 8.33 |

^a Recrystallized from 95% ethanol. ^b Recrystallized from ethyl acetate. ^c For g.l.p.c. conditions, see "Analyses for Spiropentanes and 1,1-Diphenylallene" in the Experimental section. ^d The gas chromatogram of this reaction mixture showed a second peak at 20.1 min. which is probably due to the *cis* isomer. This material occurred in such a small yield that no attempt was made to isolate and characterize it.

This, of course, would lower the activation energy for loss of the nitrogen.



Experimental³⁶

Materials.—Cyclohexene (Eastman Kodak Co. White Label) was purified by fractional distillation before use. Isobutylene, *trans*-2-butene, *cis*-2-butene, and 1-butene (all Matheson, C.P. grade) were used without further purification. *n*-Heptane (Phillips Hydrocarbons, research grade) was used without further purification as was 2,3-dimethyl-2-butene, which was obtained from K & K Laboratories. Butyllithium in hexane was used as obtained from the Foote Mineral Co.

Analyses for Spiropentanes and 1,1-Diphenylallene.—Gas-liquid phase chromatographic analyses were carried out at 250° using an Aerograph A-350 vapor fractometer containing a 10 × 0.25 in. column charged with G.E. SF-96(50) silicone fluid on 60–100 mesh firebrick.

Absolute amounts of the various spiropentanes were determined by employing an internal standard (α -methyl methylcinnamate). Owing to the tendency of 1,1-diphenylallene to polymerize, g.l.p.c. could not be used for its analysis. The ultraviolet absorption of the allene at 250 $m\mu$ (ϵ 12,030) was used to determine its concentration.

N-(2,2-Diphenylcyclopropyl)-urea.—In a typical preparation, 18 ml. (0.25 mole) of thionyl chloride was added to 30.0 g. (0.126 mole) of 2,2-diphenylcyclopropanecarboxylic acid.⁹ The mixture was refluxed for 2 hr. after which all traces of thionyl chloride were removed by distillation under reduced pressure. To the residual acid chloride was added 250 ml. of dry acetone. The mixture was stirred and cooled in an ice bath. To the cold solution was rapidly added 8.2 g. (0.126 mole) of sodium azide dissolved in a minimum amount of water. The mixture was stirred with cooling for 1 hr. after which it was poured into water and extracted with ether. The ether layer was dried over magnesium sulfate (it is crucial that the ether layer be quite dry). The dry ether solution of the acid azide was added dropwise to 400 ml. of dry refluxing benzene. After the addition was complete the benzene solution was refluxed until nitrogen evolution ceased. The benzene solution was then cooled in an ice bath and anhydrous ammonia passed through the cold solution for 2 hr. For best results the ammonia should be passed into the solution quite rapidly for the first 15 min. The urea precipitated from the cold benzene solution as a white solid. Recrystallization from a mixture of ethanol and water gave 16 g. (over-all yield of 50%) of the pure urea, m.p. 134–135°.

Anal. Calcd. for C₁₆H₁₆N₂O: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.98; H, 6.44; N, 11.07.

N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea.—Sixteen grams (0.0635 mole) of N-(2,2-diphenylcyclopropyl)-urea was dissolved in 60 ml. of a mixture of 70% glacial acetic acid and 30% acetic anhydride. The mixture was cooled in an ice bath. To the cold, stirred solution was added dropwise over a 30-min. period 4.42 g. of sodium nitrite (0.064 mole) dissolved in 20 ml. of water. To this solution was added 40 ml. of water. The nitrosourea precipitated from the solution during the addition of the water. The precipitate was removed by filtration and washed well with water followed by a little ether. Recrystallization from a mixture of chloroform and petroleum ether gave 9.0 g. (50%) of a very light yellow solid, m.p. 114–115° dec.

(36) Melting points are uncorrected. Nuclear magnetic resonance spectra were determined in carbon tetrachloride solution employing a Varian 4300-2 high-resolution spectrometer operating at 56.4 Mc.

Anal. Calcd. for C₁₆H₁₆N₂O₂: C, 68.31; H, 5.37; N, 14.94. Found: C, 68.42; H, 5.53; N, 14.88.

Lithium Ethoxide.—To 100 ml. of absolute ethanol in a flask equipped with an efficient condenser was added lithium wire (3.5 g., 0.05 g.-atom). After the initial reaction subsided, the mixture was refluxed for 8 hr. The excess ethanol was then removed by evaporation under reduced pressure to give a white amorphous solid. Air drying yielded a finely divided solid weighing about 42 g. This solid is presumed to be lithium ethoxide monoalcoholate since treatment with sodium hydride evolved a volume of hydrogen consistent with such a formulation. Removal of ethanol from the solid may be accomplished using sublimation techniques. Attempted sublimation at 240° and 2 mm. gave a small amount of sublimed material which had retained its ethanol. However, the bulk of the material did not sublime but lost its ethanol, leaving behind a white solid which ignited upon exposure to the atmosphere.

The preparation of lithium ethoxide as reported by Brown, Dickerhoof, and Bafus³⁷ was also used. However, the ethoxide so obtained showed no advantages to that obtained by simply dissolving lithium in ethanol.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea with Lithium Ethoxide in Isobutylene.—To 1.0 g. (3.6 mmoles) of the nitrosourea in a flask equipped with a Dry Ice cold finger condenser was added 25 ml. of isobutylene. The stirred mixture was cooled to –35° and 0.35 g. (3.6 mmoles assuming the material is the alcoholate) of lithium ethoxide was added. The reaction mixture was vigorously stirred and allowed to warm to –15° and maintained near this temperature throughout the reaction. Upon reaching –15°, nitrogen evolution began and continued for ca. 30 min. to give a total of about 90% of the quantitative amount. Stirring and cooling were continued for one additional hour after which the reaction mixture was filtered. The residual solid was washed with reagent grade *n*-heptane and the extracts combined with the filtrate. Aliquots of the filtrate were analyzed for spiropentane (22%) by g.l.p.c. and for 1,1-diphenylallene³⁸ (65%) by the ultraviolet. The remainder of the filtrate was evaporated to a yellow oil from which the spiropentane was isolated by chromatography on activated alumina (ca. 60 g. of alumina per g. of mixture) using petroleum ether as the eluting solvent. The spiropentane came off of the column very quickly, followed rather closely by the allene. Recrystallization of the spiropentane from 95% ethanol gave 0.16 g. (19%) of white needles, m.p. 47.5–48.0°.

Anal. Calcd. for C₁₉H₂₀: C, 91.88; H, 8.12. Found: C, 91.99; H, 8.08. The results of similar experiments in the presence of a variety of olefins are given in Table III.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were run in solution in carbon tetrachloride, with tetramethylsilane as internal reference, using a Varian DP-60 instrument. Chemical shifts were determined by measurement of side-banded spectra, using the average of repetitive scans and continuously monitoring the oscillator frequency with an electronic counter. Values of the shifts were converted to those for infinite dilution by extrapolating the results obtained on the original solution, usually a saturated solution, and on solutions with concentrations of 50 and 25% of the concentration of the original solution.

Competitive Reactions with Various Olefins.—To a cooled (ice bath), stirred mixture of 10 ml. each of cyclohexene and the competing olefin containing 0.50 g. (0.0018 mole) of N-nitroso-

(37) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

(38) 1,1-Diphenylallene was identified by its infrared spectrum, which showed strong absorptions at 5.19 and 11.70 $m\mu$ (cf. T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Am. Chem. Soc.*, **72**, 1272 (1950); J. H. Wotiz, *ibid.*, **73**, 692, 5503 (1951); **74**, 1960 (1952); J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957)). Further identification was obtained by partial reduction to 1,1-diphenyl-1-propene, which was compared with an authentic sample and found to be identical in every way.

N-(2,2-diphenylcyclopropyl)-urea was added 0.19 g. (ca. 0.0019 mole) of lithium ethoxide alcoholate. Nitrogen evolution began immediately and was essentially complete in 10 min. Stirring and cooling were continued for an additional 30 min. at which time the reaction mixture was filtered and the filtrate evaporated to give an oily residue that was analyzed by g.l.p.c.

Alternate Synthesis of 1,1-Diphenyl-4,5-tetramethylenespiropentane.—7,7-Dibromonorcarane³⁹ (14.0 g., 0.056 mole) and 10.0 g. (0.056 mole) of 1,1-diphenylethylene⁴⁰ were dissolved in 15 ml. of dry ether, and the mixture was cooled to 0°. Butyllithium in hexane (3.56 g., 0.056 mole) was added dropwise to the stirred and cooled mixture over a 45-min. period. After the addition was complete the reaction mixture was stirred for an additional 2 hr. at room temperature and filtered. The filtrate was washed with water and dried over magnesium sulfate. The dried solution was taken to near dryness and a small portion (0.25 ml.) was separated by gas chromatography to give about 10 mg. of the desired spiro-pentane. Recrystallization from ethyl acetate gave pure material, m.p. 82.0–82.5°; no depression on admixture with the material obtained from the reaction of the nitroso-urea with lithium ethoxide in cyclohexane. The infrared spectra of the two materials were also identical.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea with Lithium Ethoxide in *n*-Heptane.—To a stirred mixture of the nitroso-urea (1.00 g., 3.56 mmoles) in 25 ml. of reagent grade *n*-heptane at 0° was added lithium ethoxide alcoholate (0.35 g., ca. 3.6 mmoles). After 5 min. stirring, nitrogen evolution began and was 95% complete after 60 min. Stirring and cooling were continued for one additional hour after which the reaction mixture was filtered. The residue was washed thoroughly with reagent grade *n*-heptane and the filtrates combined. The filtrate was analyzed for 1,1-diphenylallene and found to contain 96% of that calculated.

The allene is a colorless oil when it is first formed or immediately after it is eluted from alumina (if it is kept cold). However, it apparently polymerizes rather rapidly when it is kept as the liquid at room temperature.⁶ The structure of the allene was deduced from its infrared spectrum⁴¹ and by partial reduction to

(39) W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(40) Prepared by the method of C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 226.

a product which was identical in every way with an authentic sample of 1,1-diphenyl-1-propene.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea with Lithium Ethoxide in Ethyl Ether.—To 2.00 g. (0.0071 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea and 25 ml. of pure anhydrous ethyl ether stirred at 0° was added 0.70 g. (0.0071 mole) of lithium ethoxide alcoholate. Nitrogen evolution began immediately and continued for approximately 40 min. After a total of 2 hr. stirring and cooling the reaction mixture was filtered; the solid obtained was washed with anhydrous ethyl ether and the washing added to the filtrate. Evaporation of the filtrate gave a yellow oil which was chromatographed over alumina using pentane as the eluent. The oil obtained by this chromatography was shown by g.l.p.c. to be a complex mixture and at least three major components of this mixture are unique to the reaction in ethyl ether; they are not produced by this reaction when run in saturated hydrocarbon solvents. Attempted purification and isolation of the various components by preparative scale g.l.p.c. was not successful.

Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea by Lithium Ethoxide in Diethyl Fumarate.—To 1.00 g. (0.00356 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea in 20 ml. of diethyl fumarate (Eastman Organic Chemicals) at 0° was added 0.35 g. (0.0036 mole) of lithium ethoxide alcoholate. The mixture was stirred and cooled for 1 hr. at the end of which no nitrogen had evolved and a white solid had precipitated. Isolation of the solid by filtration was followed by thorough washing with pentane. (The filtrate was shown by g.l.p.c. to contain both benzophenone and a trace of 1,1-diphenylallene.) The isolated solid was then stirred with cold, dilute hydrochloric acid, filtered, washed with water, and dried. Recrystallization from methanol gave the pyrazoline in 47.5% yield, m.p. 147–149°, λ_{\max} 320 m μ (ϵ 10,900); 3.00, 5.76, 5.99, 6.52 μ .

Anal. Calcd. for C₂₃H₂₄N₂O₄: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.20; H, 6.30; N, 6.88.

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(41) T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Am. Chem. Soc.*, **72**, 1272 (1950); J. H. Wotiz, *ibid.*, **73**, 692, 5503 (1951); **74**, 1960 (1952); J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

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Isotope Effects on Acidity of Deuterated Formic, Acetic, Pivalic, and Benzoic Acids¹

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Conductivity measurements give the following results for $pK_D - pK_H$: DCOOH, 0.030 \pm 0.004; CD₃COOH, 0.014 \pm 0.002; C₆D₅COOH, 0.010 \pm 0.002; 2,6-C₆H₃D₂COOH, 0.003 \pm 0.001. The treatment of these isotope effects as "normal" inductive effects is discussed.

Introduction

During the past few years, many phenomena have been reported in which deuterium acts as an apparent electron-donating inductive substituent relative to hydrogen.³ Examples include the nuclear quadrupole coupling constants of deuterated methyl halides in which deuterium is effectively more electropositive than hydrogen⁴ and the n.m.r. chemical shifts in deuterated fluorocarbons.⁵ These effects seem clearly to be due to the anharmonicity of C–H vibrations and the greater amplitude of C–H compared to C–D vibrations. Of especial importance in organic chemistry are the experimental findings that the magnitude of such isotope effects is sufficient to cause significant changes in equilibrium acidities. DCOOH,^{6–8} CD₃COOH,^{3,9,10} and

C₆H₅CD₂COOH^{3,10,11} are reported to be 6–12% weaker acids than the corresponding protium acids.

In the normal treatment of isotope effects on equilibrium constants, changes in zero point energies on the vibrational partition functions are of primary importance. Bell and Crooks¹² have shown that the use of experimental values of all of the vibration frequencies of HCOOH, HCO₂[–], DCOOH, and DCO₂[–] gives a calculated isotope effect in such a treatment, $\Delta pK = 0.037$, which is close to Bell and Miller's carefully measured experimental value,⁸ 0.035. The use of all of the experimental values automatically includes some anharmonicity influences and is clearly superior to methods which involve only a few of the molecular vibrations or

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(2) (a) Alfred P. Sloan Fellow, 1958–1962. (b) National Science Foundation Cooperative Graduate Fellow, 1959–1961; University of California Fellow, 1961–1962.

(3) For a complete summary, see E. A. Halevi in "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963.

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