CYCLOPROPYLIDENE: THE ORIGIN OF 1,1-DIPHENYLALLENE IN THE REACTION

OF N-NITROSO-N-(2,2-DIPHENYL)CYCLOPROPYL UREA WITH LITHIUM ETHOXIDE

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IN the course of an examination of the reaction of N-nitroso-N-(2,2-di-phenyl)-cyclopropyl urea (I) with lithium ethoxide we have observed as the predominant product 1,1-diphenylallene. This observation was certainly not
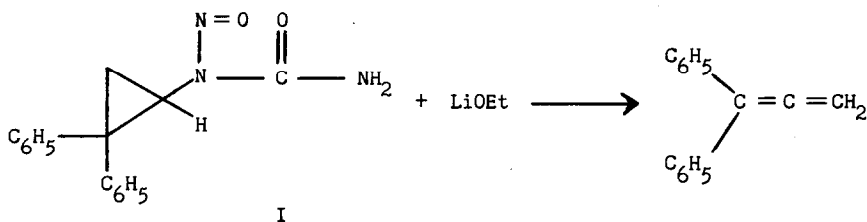

surprising in view of the fact that allene has been found to be the predominant product in several formally analogous reactions,[1-6] all of which can be represented by the following equation.
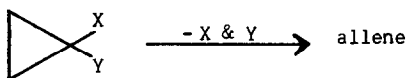
[1] W. von E. Doering and P.M. LaFlamme, Tetrahedron 2, 75 (1958).

[2] W.R. Moore and H.R. Ward, J. Org. Chem. 25, 2073 (1960).

[3] T.J. Logan, Tetrahedron Letters 173 (1961).

[4] L. Skattebol, Tetrahedron Letters 167 (1961).

[5] H. Schechter, Abstracts of Papers presented at A.C.S. Meeting, Washington, D.C., pp. 15-O (1962).

[6] K. Bayes, J. Amer. Chem. Soc. 83, 3712 (1961).

To date, however, there has been presented no compelling evidence for
the source of allene. Doering and LaFlamme[1] suggested a variety of possible
intermediates from which allene formation might occur in the reaction of
1,1-dibromocyclopropane with magnesium or sodium and convincingly narrowed
the possibilities down to collapse of either the bromocarbanion or the
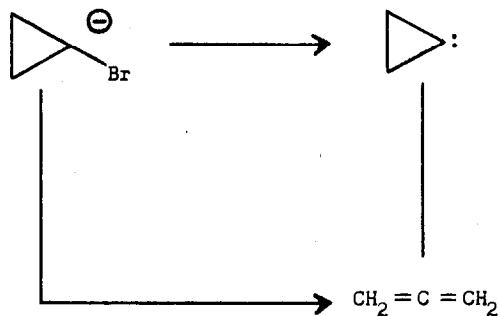
carbene. However, they were not able to assess the relative importance of
these two modes.

The purpose of this communication is to present certain observations
that we have made which are most readily explained by assuming that the
formation of 1,1-diphenylallene from the action of lithium ethoxide on
N-nitroso-N-(2,2-diphenyl)cyclopropyl urea results from at least <u>two differ-
ent precursors</u>.

Evidence for these conclusions was obtained in the following way.
Consider the following reaction scheme.[7,8]

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[7] In the arguments that follow, for the sake of simplicity, the diazocyclo-
propane and the carbene are assumed to be distinct intermediates. However,
it must be pointed out that the diazocyclopropane has never been isolated
and we have no real proof that the free carbene is ever formed. Thus, our
results could be equally well accommodated by a concerted decomposition of
the nitrosourea or the diazocyclopropane (or both) combined with reaction
of the carbene with the olefin; or, even possibly a concerted decompo-
sition of the nitrosourea followed by direct reaction of the diazocyclo-
propane with olefin to give the spiropentane. However, whatever the
actual nature of the distinct intermediates, the results reported are most
readily accommodated by a scheme involving two different intermediates;
only one of which is capable of reacting with olefin to give a spiropentane.

[8] Capture of the cyclopropylidene with <u>cis</u>- and <u>trans</u>-2-butene has been pre-
viously reported.[9] The structure of 1,1-diphenylallene was proved by its
infrared spectrum[10] and by partial reduction to a product which was identi-
cal with an authentic sample of 1,1-diphenyl-1-propene.

nitrosourea (I)

+

lithium ethoxide

$R = C_6H_5$
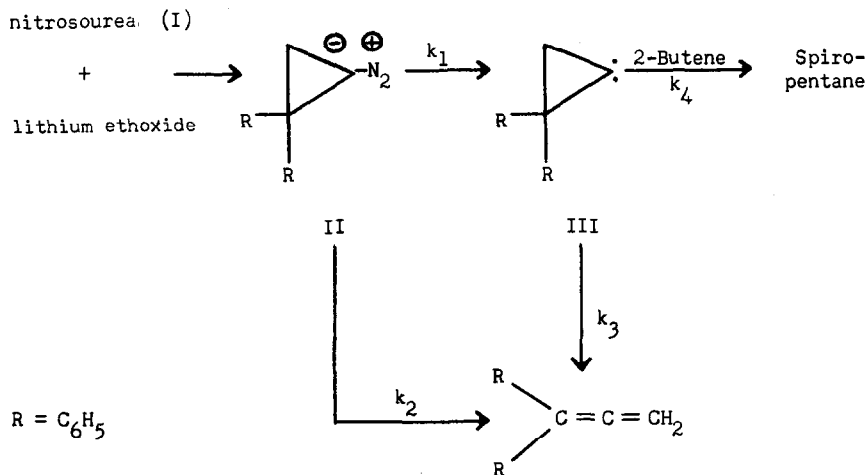
Employing a steady state treatment and assuming the butene concentration does not change appreciably during the reaction, it can be shown that the ratio of spiropentane to allene can be expressed by the general equation (1).

$$\frac{\text{spiropentane}}{\text{allene}} = \frac{k_1 k_4 \text{ (butene)}}{k_1 k_3 + k_2 k_3 + k_2 k_4 \text{ (butene)}} \tag{1}$$

If the sole source of allene is cyclopropylidene (III) (i.e. $k_2 = 0$) then equation (1) reduces to (2) and a plot of the ratio of spiropentane to allene versus the concentration of butene should give a straight line with slope k_4/k_3.

$$\frac{\text{spiropentane}}{\text{allene}} = \frac{k_4}{k_3} \text{ (butene)} \tag{2}$$

On the other hand, if the sole source of allene is a concerted decomposition of the diazocyclopropane (i.e. $k_3 = 0$) then equation (1) reduces to

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[9] W.M. Jones, _J. Amer. Chem. Soc._ **82**, 6200 (1960).

[10] T.L. Jacobs, R. Akawie and R.G. Cooper, _J. Amer. 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).

(3) and it is seen that the ratio of spiropentane to allene would be independent of the concentration of the olefin.

$$\frac{\text{spiropentane}}{\text{allene}} = \frac{k_1}{k_2} \qquad (3)$$

Finally, of course, if k_2 and k_3 are competitive and the allene has two distinct precursors (pictured here as the diazocyclopropane and the cyclopropylidene), then the ratio of spiropentane to allene should be expressed by equation (1).

Analytical techniques were therefore developed for determining absolute concentrations of 1,1-diphenylallene and the spiropentane which has been found[9] to result from the addition of 2,2-diphenylcyclopropylidene to trans-2-butene.[11] The results of a series of reactions of the nitroso-urea with lithium ethoxide at varying concentrations of trans-2-butene are shown in Table 1. It is at once seen that the ratio of spiropentane to allene is not constant; thus excluding a concerted decomposition of the diazocyclopropane as the sole source of allene. Furthermore, a plot of the ratio of spiropentane to allene versus the concentration of butene is shown in Fig. 1. These points obviously do not give a straight line. Thus the carbene as the sole precursor of the allene becomes an unlikely possibility.

Finally, it was found that the experimental observations could be quite well accommodated by equation (1) which conveniently simplified to (4) by dividing the numerator and the denominator by $k_2 k_4$. Values of 0.52 for k_1/k_2 and 3.06 for $k_3 k_4$ were then obtained from the slope and an intercept of a least squares plot of spiropentane/(allene)(butene) versus spiro-

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[11] Gas chromatography was used to determine the concentration of the spiropentane. Methyl-alpha-methyl cinnamate was used as an internal standard. The tendency of 1,1-diphenylallene to polymerize[4] under even very mild thermal conditions made gas chromatography an unreliable analytical tool for determining its concentration. However, it was found that the ultraviolet absorption of the allene at 250 mμ could be used quite successfully since the allene appears to be stable at low temperatures and low concentrations.

TABLE 1[a]

trans-2-Butene, moles/1.	Spiropentane / Allene
1.14	0.113
1.14	0.103
1.14	0.098
2.27	0.157
2.27	0.168
3.41	0.236
4.51	0.268
6.81	0.339
6.81	0.286
7.95	0.318
11.35	0.362
11.35	0.362

[a] Obtained from a reaction series using 1.00 g (0.00356 mole) of the nitrosourea and 0.278 g of lithium ethoxide [prepared by the method of T.L. Brown, D.W. Dickerhoof and D.A. Bafus, J. Amer. Chem. Soc. 84, 1371 (1962)] in a total of 25.0 ml of varying molar concentrations of trans-2-butene in Reagent Grade n-heptane at 0°. The spiropentane and allene formation accounted for 85-88 per cent of the starting nitrosourea ; independent of the olefin concentration.

pentane/allene. When these values were substituted into equation (4) the calculated curve shown in Fig. 1 was obtained. Thus, although the observed

$$\frac{\text{spiropentane}}{\text{allene}} = \frac{\frac{k_1}{k_2}(\text{butene})}{\frac{k_1 k_3}{k_2 k_4} + \frac{k_3}{k_4} + (\text{butene})} \qquad (4)$$

curvature might possibly result from a reaction mechanism that we have not considered or, even possibly, from solvent effects, the coincidence of the curve calculated from equation (1) and the observed curve is quite striking and certainly suggests that the allene does indeed have two different precursors.
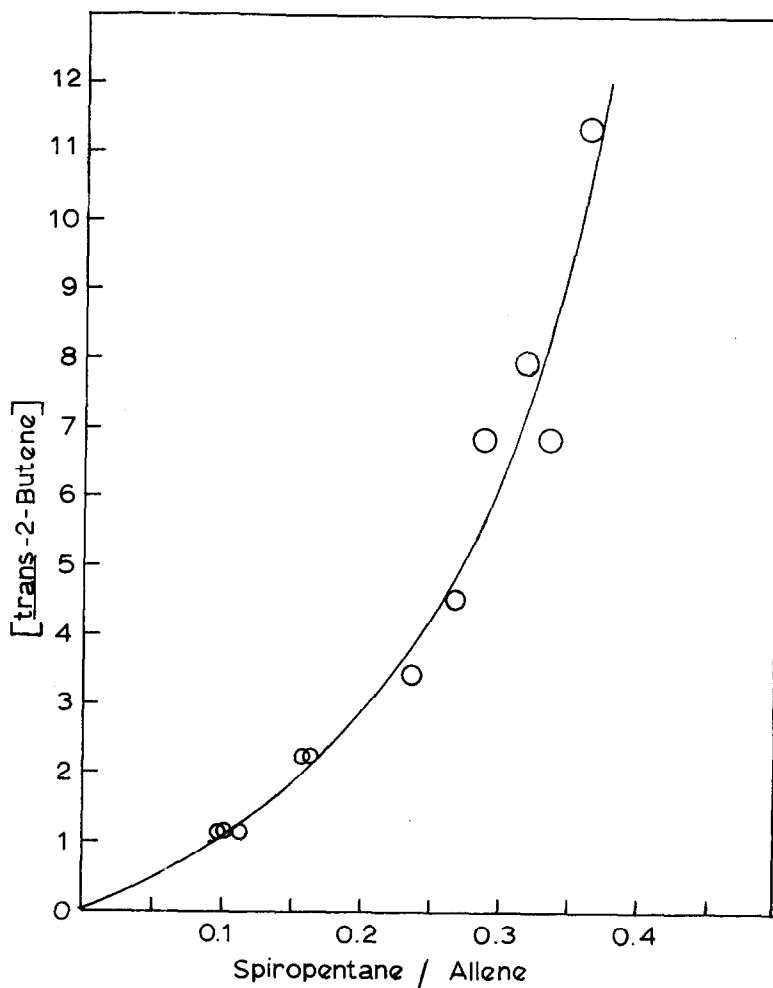
FIG. 1

Curve calculated from equation (4) (solid line):
O, experimental results.