

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

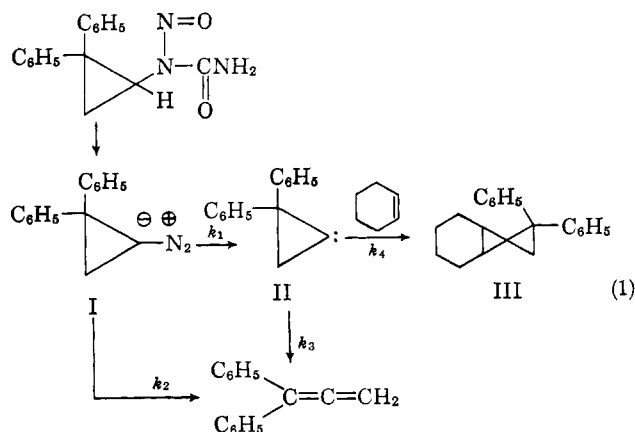
The Generation of 2,2-Diphenyldiazocyclopropane and 2,2-Diphenylcyclopropylidene from the Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea¹

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The thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea in nonpolar solvents has been investigated. In refluxing *n*-heptane, up to 95% of 1,1-diphenylallene is formed. In refluxing cyclohexene, a mixture of 65% of 1,1-diphenylallene and 22% of spiropentane III is formed. In diethyl fumarate, the thermal decomposition of the nitrosourea gives 44% of pyrazoline IV. The ratio of spiropentane to allene resulting from the thermal decomposition in varying mixtures of cyclohexene and *n*-heptane was determined and was found to be consistent with a reaction scheme in which the allene has at least two distinct precursors, only one of which adds to the cyclohexene to give the spiropentane. The yield of pyrazoline IV suggests that one of these intermediates is 2,2-diphenyldiazocyclopropane and the other is 2,2-diphenylcyclopropylidene.

The reaction of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea with base (lithium ethoxide alcoholate) has been rather thoroughly investigated in these laboratories³ and it has been demonstrated that this reaction leads initially to 2,2-diphenyldiazocyclopropane that spontaneously decomposes to give 1,1-diphenylallene and 2,2-diphenylcyclopropylidene. We would now like to report our finding that the thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea in *n*-heptane at 82° gives rise to a high yield of 1,1-diphenylallene, while thermal decomposition of this nitrosourea in refluxing cyclohexene gives a mixture of the allene and the corresponding spiropentane adduct. Furthermore, we have obtained evidence that suggests the following path for these conversions.



In addition to a convenient method for the synthesis of both the allene and the spiropentane, these results represent the first reported case of the direct formation of a carbene from the thermal decomposition of a nitroso precursor^{4,5} and the first reported method for generating a diazocyclopropane under nonbasic conditions.⁶

(1) A portion of this work was taken from a thesis submitted by M. H. Grasley in partial fulfillment of the requirements for the degree Doctor of Philosophy at the University of Florida.

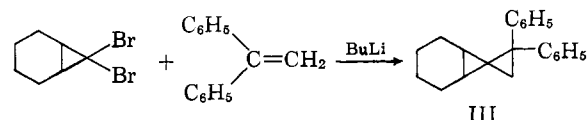
(2) Alfred P. Sloan Fellow, 1963-1965.

(3) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

(4) The thermal decomposition of N-nitrosoamides of alkylamines has been thoroughly studied and it has been found that these decompositions lead to either the corresponding diazoalkane or alkyl diazonium ion, depending upon the relative stabilities of the potential cations. For thorough discussions on this subject, see: E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1174, 1179 (1961); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957); A. R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956).

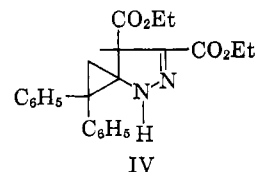
(5) The thermal decomposition of alkylnitrosoamides has received very little attention. One reported instance of such a decomposition was carried out by Huisgen and Reimlinger⁴ on N-methyl-N-nitrosourea. It was found that this decomposition was complicated by migration of the nitroso group followed by loss of nitrogen to give methyl isocyanate. If this type of migration takes place in our system, it is only to a small extent.

N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea was obtained by the method previously reported.^{3,7} Decompositions were effected in a bath heated by refluxing *t*-butyl alcohol (b.p. 82°). At this temperature, decomposition is complete in about 10 min. The yield of allene in the absence of acceptor olefin ranged from 80-95%. In cyclohexene as solvent, the yield of isolated spiropentane III was 17% (21.9% g.l.p.c.). The structure of the spiropentane was proved by analysis, spectral properties,⁸ and alternate synthesis by the method of Moore and Ward.^{3,9}



Direct evidence for the cyclopropylidene II as an intermediate in the thermal decomposition of the nitrosourea resides in the formation of the spiropentane. Thus, as has been pointed out previously,³ it is highly unlikely that a diazocyclopropane would react directly with an unactivated olefin to give the spiropentane under conditions as mild as those used in this study.

Direct evidence for the diazocyclopropane I as a distinct intermediate was obtained by effecting the thermal decomposition in diethyl fumarate. Under these conditions it was found that virtually no gas evolution occurred, no detectable allene was formed, and the diazocyclopropane was trapped as pyrazoline IV which was isolated in 44% yield.



Evidence supporting the dual path to 1,1-diphenylallene (eq. 1) was obtained by employing the same type of analysis that has been applied to the base-induced reaction.¹⁰ In this method, the spiropentane:allene ratio is determined at varying concentrations of the ac-

(6) The generation of the diazocyclopropane under thermal conditions takes on special significance in light of the instability of this intermediate. Thus, 2,2-diphenyldiazocyclopropane decomposes spontaneously at the lowest temperature at which we have been able to generate it (-15°) and its mere presence has been surmised by the occurrence of transient colors and trapping with suitable acceptors.^{3,7} The instability of the diazo compound has not only precluded its isolation but the fact that formation required base prevented its use in reactions involving base-sensitive reagents. Having eliminated this latter restriction, we feel that we are now in a position to explore more fully the chemistry of diazocyclopropanes.

(7) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960).

(8) For a complete discussion of the spectral properties of spiropentanes, see ref. 3.

(9) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

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

ceptor olefin. Analysis of eq. 1, assuming a steady state for the carbene concentration and constant olefin concentration¹¹ during the reaction, gives different relationships between the spiropentane:allene ratio and the concentration of the olefin depending upon the relative magnitudes of the various rate constants. For example, if k_2 is negligibly small, the spiropentane:allene ratio is proportional to the olefin concentration. If k_3 equals zero, the spiropentane:allene ratio is independent of the concentration of the olefin. However, if neither k_2 nor k_3 equals zero, the spiropentane:allene ratio is

$$\frac{\text{spiropentane}}{\text{allene}} = \frac{(k_1/k_2)(\text{cyclohexene})}{(k_1k_3/k_2k_4) + (k_3/k_4) + (\text{cyclohexene})} \quad (2)$$

described by eq. 2. The results of a series of decompositions in varying mixtures of cyclohexene and *n*-heptane are given in Table I. Figure 1 shows a plot of these results and this plot is compared with a curve calculated from eq. 2 in which k_1/k_2 and k_3/k_4 are set equal to 0.61 and 7.2, respectively.¹²

TABLE I^a

Cyclohexene, moles/l.	Spiropentane/allene ^b	Cyclohexene, moles/l.	Spiropentane/allene ^b
0.91	0.047:0.047	5.49	0.210:0.194
1.83	0.072:0.071	7.35	0.254:0.248
3.66	0.134:0.144	9.22	0.286:0.274

^a Data obtained from a reaction series using 1.0 mmole of the nitroso-urea in a total of 50 ml. of varying molar concentrations of cyclohexene in reagent grade *n*-heptane at 82°. The spiropentane and allene formed accounted for 75–81% of the starting nitroso-ureas, independent of the olefin concentration. ^b Data given for duplicate runs.

The coincidence of the calculated and observed curves support the suggested reaction scheme involving two distinct allene precursors, only one of which can react with an olefin to give a spiropentane.¹³

Furthermore, if this conclusion is valid and can be extrapolated to diethyl fumarate solvent, then the thermal decomposition in diethyl fumarate becomes compelling evidence for the diazocyclopropane as the initial allene precursor. This arises from the fact that no gas evolution was observed, no allene was detected, and the pyrazoline (IV) was actually isolated in over 38% yield. If the ratio of k_1/k_2 is 0.61, the maximum amount of pyrazoline that could arise from the second allene precursor is 38%. The pyrazoline must then arise from the first precursor which, in turn, is most likely the diazocyclopropane.

Finally, if the diazocyclopropane is the initial allene precursor, then the second precursor which also must be capable of forming a spiropentane with an olefin is certainly most likely the cyclopropylidene.

(11) In all runs, the olefin is in large molar excess.

(12) In the previously reported¹⁰ decomposition of the nitroso-urea with lithium ethoxide at 0°, the ratio of k_1/k_2 and k_3/k_4 (0.52 and 3.06, respectively) were obtained from the slope and an intercept of a least squares plot of spiropentane/(allene)(olefin) vs. spiropentane/allene. Magnification of error is inherent in such a treatment, and in the present system this treatment did not allow us to arrive at rate constant ratios with any degree of certainty. However, it was recognized that if the thermal decomposition and the base-induced decomposition proceed through the same initial intermediate, and if it is further assumed that the frequency factors for the two modes of decomposition of the diazo compound are the same, the ratio of k_1/k_2 for the higher temperature run can be readily calculated from the lower temperature reaction by use of the Arrhenius equation. This leads to a ratio of 0.61 for k_1/k_2 which, when substituted into eq. 2, gives a value of 7.2 for the ratio of k_3/k_4 . The theoretical curve using these values is given in Fig. 1. Although these results do not require it, they do suggest that the base-induced reaction and the thermal reaction have a common intermediate.

(13) It should be pointed out that the dual path to allene is not the only possible explanation for the curvature of the plot of spiropentane:allene vs. olefin. For example, this could simply be a solvent effect arising from the fact that these experiments involved a change in solvent from pure heptane to pure cyclohexene. Although such a possibility cannot be excluded, we feel that it is rather unlikely since it would require a coincidental fitting of the experimental curve to eq. 2.

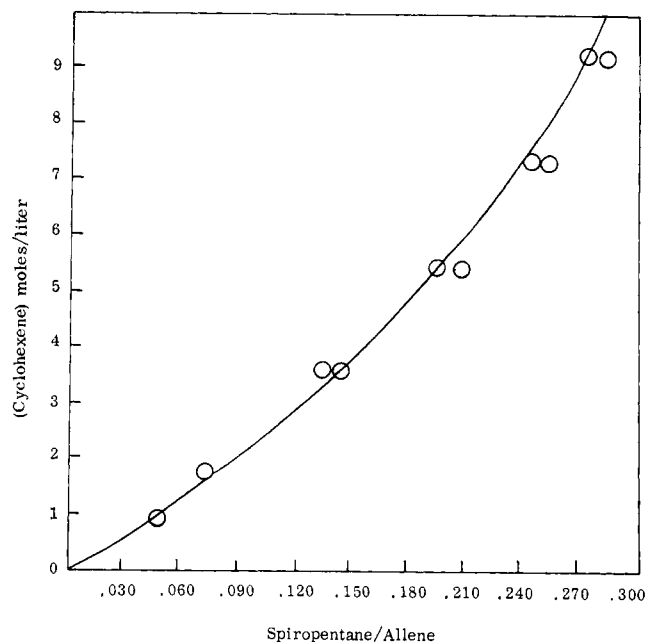


Fig. 1.—Curve calculated from eq. 2 (solid line); O, experimental results.

If therefore appears that, in contrast to the complex course previously reported⁵ for the thermal decomposition of *N*-methyl-*N*-nitroso-urea, the thermal decomposition of *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)-urea proceeds cleanly to 2,2-diphenyldiazocyclopropane that can lose nitrogen to give 2,2-diphenylcyclopropylidene or, possibly, collapse in a concerted manner to 1,1-diphenylallene. Since the rather clean and straightforward course of this reaction most likely results from the fact that it involves a small, strained ring, we are presently investigating other strained ring systems.

Experimental

***N*-Nitroso-*N*-(2,2-diphenylcyclopropyl)-urea.**—The nitroso-urea was prepared by the previously described³ method.

Thermal Decomposition of *N*-Nitroso-*N*-(2,2-diphenylcyclopropyl)-urea in *n*-Heptane.—A stirred mixture of 1.00 g. (3.56 mmoles) of the nitroso-urea and 25 ml. of *n*-heptane was heated to 80° and held for 30 min. During the heating, gas evolution began around 60° and continued for 20 min. During the period of heating about 1.5 equivalents of gas was evolved. Gas evolution in this reaction is consistently greater than 1 mole per mole of nitroso-urea. Presumably this is a result of gases other than nitrogen being produced by the urea portion of the molecule. After the 30-min. period the reaction mixture was cooled to room temperature and diluted with *n*-heptane for 1,1-diphenylallene analysis. Analysis by means of its ultraviolet absorption at 250 mμ (ϵ 12,030) showed a yield of 95%. Evaporation to dryness gave 1,1-diphenylallene that was identical with an authentic sample.³

Thermal Decomposition of *N*-Nitroso-*N*-(2,2-diphenylcyclopropyl)-urea in Cyclohexene.—A stirred mixture of 1.00 g. (3.56 mmoles) of the nitroso-urea and 25 ml. of cyclohexene was brought to reflux and held for 30 min. At the end of this period gas evolution had ceased and the original yellow solution had lost its color. After cooling to room temperature, aliquots of the mixture were analyzed for the spiropentane³ (using g.l.p.c. with methyl- α -methyl cinnamate as an internal standard) and for 1,1-diphenylallene (by its ultraviolet absorption at 250 mμ, ϵ 12,030). The yield of spiropentane was 21.9% and the yield of 1,1-diphenylallene was 65%. The spiropentane was isolated by chromatography over alumina and was found to be identical in every way with authentic material.³

Thermal Decomposition of *N*-Nitroso-*N*-(2,2-diphenylcyclopropyl)-urea in Diethyl Fumarate.—To 25 ml. of diethyl fumarate (Eastman Organic Chemicals) was added 3.00 g. (0.0107 mole) of the nitroso-urea. The mixture was stirred and heated at 75° for 2 hr. During this period virtually no gas evolution was observed and a white precipitate separated. The mixture was cooled to room temperature and filtered to give 0.14 g. of white solid that was shown by mixture m.p. and infrared to be urea, m.p. 133–133.5°.

To the filtrate was added 20 ml. of pentane and the mixture was cooled to 0° to give 1.85 g. (44%) of pyrazoline IV, m.p. 147–149°. This material was identical in every way with the pyrazoline synthesized by reaction of the nitrosourea with lithium ethoxide in diethyl fumarate.³

Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea in Varying Concentrations of Cyclohexene.—Decompositions were effected in a reaction flask that contained a magnetic stirring bar and was held at 82° by refluxing *t*-butyl alcohol in an outer jacket. Before use, Eastman cyclohexene was distilled from lithium aluminum hydride and Phillips pure grade heptane was distilled through a column packed with metal turnings. Prior to the addition of the solvents, the vessel was brought to temperature and thoroughly flushed with dry nitrogen. The appropriate volumes of cyclohexene and *n*-heptane were pipetted into the reaction vessel to give a total volume (25°) of 50 ml. In calculating the concentration of the cyclohexene, corrections were employed for the change in density of cyclohexene upon heating to 77.6°¹⁴ and the change in density of *n*-heptane upon heating to 80°.¹⁵ To the hot stirred mixture was then added a weighed pellet (ca. 1.0 mmole) of the nitrosourea.¹⁶ The reaction was allowed to proceed for 10 min. during which time gas evolution was measured. In general, about 1.5 equivalents of

gas was evolved. A mark on the side of the reaction vessel and the absence of refluxing solvent in the condenser in the gas collection line established that the volume of the solvent underwent no significant change during the course of the reaction. At the end of 10 min., the reaction mixture was transferred by a pipet to a 100-ml. volumetric flask. The reaction vessel was rinsed with heptane and the washings were added to the volumetric flask. The solution was then made up to 100 ml. with heptane and stored in the refrigerator.¹⁶

The absolute amount of 1,1-diphenylallene was determined with a Beckman Model DU spectrophotometer employing the absorbance at 250 m μ . The absolute amount of the spiropentane was determined by removing the hydrocarbon solvent from the reaction product and adding a known weight of methyl- α -methyl cinnamate (internal standard) to the residue. Analyses were carried out by g.l.p.c. using a 10-ft. column (1/8 in. inside diameter) packed with 5% by weight of Apiezon L on 60–80 mesh Gas Chrom Z using a column temperature of 230° and a flame ionization detector. Integrated areas were used for the calculations and were compared with standard mixtures of spiropentane and ester. In all cases, the total yield of spiropentane plus allene ranged between 75 and 81%.

Acknowledgment.—The authors are most grateful to the National Science Foundation for support of this work.

(16) 1,1-Diphenylallene tends to polymerize upon standing.¹⁷ This polymerization is greatly accelerated when the liquid allene is warmed. However, it was found that under our reaction conditions (dilute solution, short heating periods) the allene is stable.

(17) L. Skattebol, *Tetrahedron Letters*, 167 (1961).

(14) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp. 65, 162; J. Timmerman, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950, pp. 60, 205.

(15) The total yield of spiropentane and 1,1-diphenylallene was found to vary with the batch of nitrosourea. For this reason, all of the runs using solvent mixtures were made from the same initial batch of starting material.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GA.]

Organic Peroxides. III. The Behavior of Cyclohexaneformyl Peroxide in the Presence of Excess Stable Radicals. The Simultaneous Determination of Kinetics and Free Radical Efficiencies in the Thermal Decompositions of Free Radical Initiators¹

BY ROBERT C. LAMB² AND JAS. GRADY PACIFICI³

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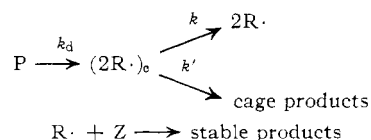
The first-order rate constants and free radical efficiencies in the thermal decompositions of cyclohexaneformyl peroxide in benzene in the temperature range 30–50° were determined spectrophotometrically by measuring the fading of galvinoxyl, which was present in excess. Experiments in which α,γ -bis-(diphenylene)- β -phenylallyl (BDPA) and DPPH were used as scavengers in benzene at 45° gave results similar to those obtained in the galvinoxyl experiments. All of the experiments indicate a low free radical efficiency (24% or less) for the decomposition of cyclohexaneformyl peroxide in benzene. The volatile products formed in the decomposition of cyclohexaneformyl peroxide in benzene containing excess galvinoxyl are ester, acid, bicyclohexyl, cyclohexane, and cyclohexene.⁴ On the basis of the slight dependence of the free radical efficiencies upon temperature, it is argued that these products are formed in cage reactions of radicals, rather than in rearrangement reactions of the peroxide.

Introduction

A new modification of an old method for determining free radical efficiencies was suggested recently.⁵ The method consists of using an excess⁶ of a stable free radical as a scavenger for reactive free radicals formed in the decomposition of an initiator. The use of an excess of scavenger enables one to determine the free

radical efficiency of the initiator and the first-order rate constant of its decomposition in the same experiment.

The (oversimplified)⁷ mechanistic scheme used in this work may be described as



where P = peroxide, $(2R\cdot)_c$ = solvent cage containing a pair of reactive radicals, $R\cdot$ = reactive radical, and Z = stable radical used as scavenger. Assuming the steady state in $R\cdot$ and $(2R\cdot)_c$, one obtains

$$-dZ/dt = 2k_d f P, \text{ where } f = k/(k + k')$$

which may be integrated with proper limits to give the two eq. 1 and 2

$$\ln(Z - Z_\infty)/(Z_0 - Z_\infty) = -k_d t \quad (1)$$

$$f = (Z_0 - Z_\infty)/2P_0 \quad (2)$$

(7) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961), and literature cited therein.

(1) Supported by the Petroleum Research Fund administered by the American Chemical Society, Grant PRF-869-A-4. This paper was read at the Southeastern Regional Meeting of the American Chemical Society in Charlotte, N. C., Nov. 15, 1963. Paper I in this series is given as ref. 5. Paper II: R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

(2) To whom correspondence should be addressed.

(3) PRF Predoctoral Fellow, 1962–1963.

(4) It has been reported by Hart and Wyman that the only products of decomposition of cyclohexaneformyl peroxide in carbon tetrachloride at 70° are cyclohexyl chloride and ester. Apparently, the peroxide behaves quite differently in the two solvents; cf. H. Hart and D. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

(5) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *ibid.*, **84**, 2635 (1962).

(6) The word *excess*, as used in this paper, means that enough stable radical is used so that some remains after *all* the initiator has decomposed. In most of the experiments, the ratio of the molar concentrations of stable radical to peroxide (Z_0/P_0) is less than one, inasmuch as the free radical efficiency of cyclohexaneformyl peroxide is low.