Tetrahedron Letters No.46, pp. 3459-3464, 1964. Pergamon Press Ltd.
Printed in Great Britain.

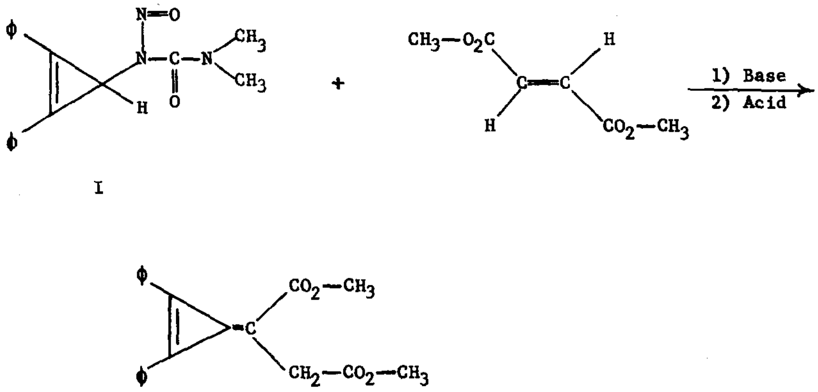
ATTEMPTS TO GENERATE A CYCLOPROPENYLIDENE. II. ISOLATION OF A SPIROPENTENE

W. M. Jones[1] and Mary E. Stowe

Department of Chemistry, University of Florida, Gainesville, Florida

(Received 2 September 1964; in revised form 2 October 1964)

We have recently reported[2] our finding that the reaction of N,N-dimethyl-N'-nitroso-N'-(2,3-diphenyl-2-cyclopropenyl)urea (I) with base in the presence of excess dimethyl fumarate followed by acid work-up gives the methylenecyclopropene[3] II according to the following equation.



I

II

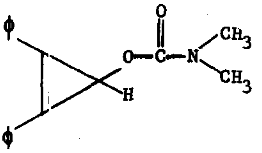
---

[1] Alfred P. Sloan Fellow.

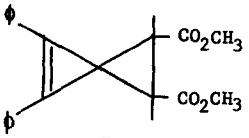
[2] W. M. Jones and J. M. Denham, J. Am. Chem. Soc., 86, 944 (1964).

[3] For other examples of methylenecyclopropene syntheses, see: M. A. Battiste, ibid., 86, 942 (1964); A. S. Kende, ibid., 85, 1882 (1963).

At this time we would like to report the isolation of two intermediates in the reaction; N,N-dimethyl-O-2,3-diphenyl-2-cyclopropenyl carbamate III and the spiropentene IV.



III



IV

The carbamate (III), which probably arises *via* loss of nitrogen from the diazocarbamate[4] was isolated by heating a relatively concentrated solution of the nitrosourea in heptane (0.5 g. in 15 ml.) until one mole of gas had been evolved (*ca.* 20 min.). Cooling the resulting mixture gave an orange solid that was recrystallized to give a white product, m.p. 96.5-97° dec. (C, 77.22; H, 6.04; N, 4.82).

The carbamate is very sensitive to moisture.[5] Its infrared spectrum shows maxima at 5.52 microns indicating a cyclopropene ring[6] and at 5.91 microns which is consistent with a carbamate carbonyl.[7] Its ultraviolet spectrum is typical of a 1,2-diphenylcyclopropene[6] having maxima in CH_2Cl_2

---

[4] *Cf.* R. Huisgen and H. Reimlinger, *Ann.*, **599**, 161 (1956); E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955); E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1179 (1961); A. Streitwieser and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957).

[5] As appears to be typical of cyclopropenes singly bonded to oxygen containing functional groups (See R. Breslow, J. Lockhart and H. W. Chang, *ibid.*, **83**, 2375 (1961); R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).) the carbamate undergoes facile hydrolysis to give as the principle product the symmetrical diphenylcyclopropenyl ether.

[6] R. Breslow, H. Hover and H. W. Chang, *ibid.*, **84**, 3168 (1962).

[7] K. Nakanishi, Infrared Absorption Spectroscopy, Holden Day, Inc., San Francisco, Calif., 1962, p. 47.

at 227 (23,200), 232 sh. (21,800), 289 sh. (27,350), 304 (36,000) and 320 (27,400) millimicrons. The n.m.r. spectrum in $DCCl_3$ showed peaks at tau = 2.19 and 2.60 (multiplets), 4.80, 7.07 and 7.50. The spectrum changed rapidly with time, ultimately giving a spectrum that consisted of thirteen peaks, most of which were multiplets. Treatment of the carbamate with potassium t-butoxide in heptane in the presence of dimethyl fumarate followed by treatment with acid gave the methylenecyclopropene II, thus confirming the assumption that this is an intermediate in the reaction.

The intermediacy of the spiropentene in this reaction was suspected rather early in our investigations due to changes in the ultraviolet spectrum between 250 and 400 millimicrons (the spectral region below 250 millimicrons was blanked out by absorption of the dimethyl fumarate). In the first few minutes of reaction the spectrum changed from that of the nitrosourea to the carbamate (Fig. 1). Upon addition of base and further heating, the maxima in the 300 millimicron region slowly disappeared and were replaced by a rather broad maximum centered at 328 millimicrons (Fig. 1). Treatment of an aliquot of the heptane solution of the reaction mixture with concentrated HCl followed by dilution with water then gave a deep yellow solution that had the spectrum of the methylenecyclopropene II.[2] It was therefore evident that the reaction had more than one distinct intermediate. Separation of the second intermediate could not be effected by chromatography because all adsorbents that we tried effected virtually instantaneous conversion to the methylenecyclopropene. Separation was finally effected by allowing a concentrated heptane reaction mixture to cool in the refrigerator and then carefully separating the spiropentene from the dimethyl fumarate with tweezers. Recrystallization of this material from heptane gave a nearly colorless solid that gave a satisfactory analysis for

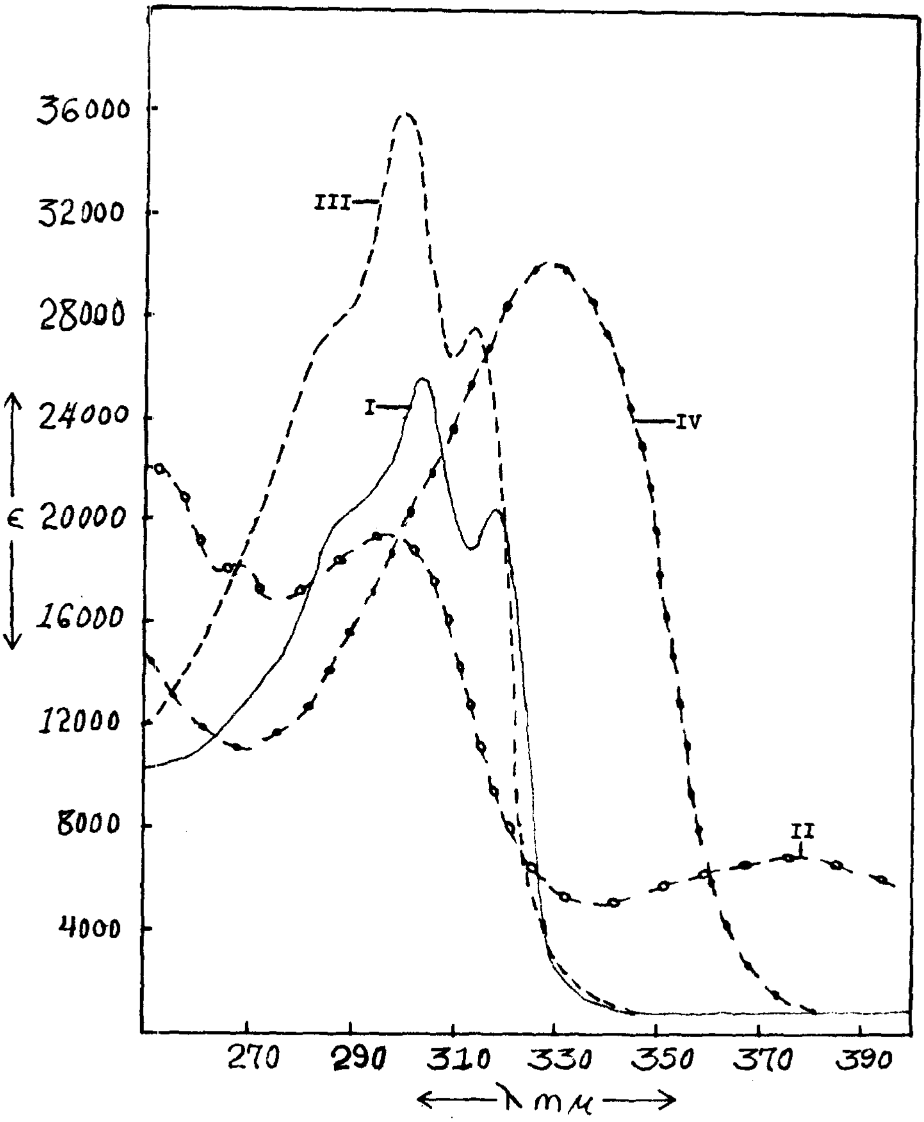


Figure 1.--Ultraviolet absorption spectra of nitrosourea I (solid line); carbamate III (dashed line); spiropentene IV (closed circles); methylenecyclopropene II (open circles).

the spiropentene (C, 75.35; H, 5.45) although it did not give a sharp melting point. In fact, the melting range varied from 100-128° to 117-128° depending on the rate of heating. The ultraviolet spectrum of the melt showed that the melting behavior was due to conversion to the methylenecyclopropene II.

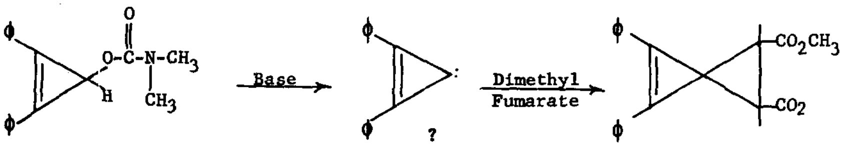
The spiropentene structure was deduced from the following observations. The analysis and the mass spectrum (M. W. 334 ± 2) of the intermediate shows that it is an isomer of the methylenecyclopropene. Its conversion to the methylenecyclopropene clearly shows that the diphenylcyclopropene ring is still intact. This, then, leaves relatively few reasonable structures for this intermediate. Of the possible structures, all but the spiropentene have a carbon-carbon double bond with one hydrogen on it. These possibilities are all excluded by the n.m.r. spectrum which shows resonances at tau = 2.16 (phenyl multiplet), 2.59 (phenyl multiplet), 6.34 (ester methyls) and 6.92 (spiropentene hydrogens) ppm with relative areas of 10:6.6:1.9. There is no absorption in the vinyl region. Further evidence for the spiropentene structure obtains from the infrared spectrum that shows a weak cyclopropene peak at 5.58 microns,[6] a single carbonyl absorption at 5.82 microns and no carbon-carbon double bond absorption.

The ultraviolet spectrum of the spiropentene has maxima in CH_3CN at 234 (35,600), 240 sh. (31,660) and at 328 (30,100) millimicrons. The bathochromic shift of the diphenylcyclopropene absorption to 328 millimicrons is interesting because it suggests conjugation between the *pi* system of the diphenylcyclopropene and the saturated ring of the spiropentene.[8]

---

[8] For a recent rather comprehensive review of the thoroughly investigated phenomenon of cyclopropane conjugation as well as an interesting discussion of the stereoelectronic requirements for cyclopropane conjugation, see A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

The formation of the spiropentene in this reaction is interesting, not only because it is an example of a new highly strained ring system, but the conditions required for its formation are suggestive of a cyclopropenylidene intermediate. This possibility is under further investigation.



Acknowledgment.--The authors are most grateful to the U. S. Army Research Office (Durham) and to the National Science Foundation for their generous support of this work. They are also indebted to Dr. M. B. Fallgatter for running the mass spectra, to Dr. M. A. Battiste for his helpful discussions and to Prof. M. J. S. Dewar for suggesting an explanation for the unusual ultraviolet spectrum of the spiropentene.