were refluxed with potassium metal for several hours and distilled. Refluxing and distillation were repeated three times.

Epr Spectra. All epr measurements were made with a Varian 4502 spectrometer with 100-kc modulation.

Absorption Spectra. A Cary Model 14 recording spectrophotometer was used. In the determination of low-temperature spectra, a Pyrex dewar was used.

Preparation of Diradicals. Bis(pyridinium iodide) (0.12 g), 3% sodium amalgam (1.0 g) (excess), and a stirring bar were sealed into the reaction flask. After pumping down to $\sim 10^{-6}$ mm, degassed acetonitrile (about 20 ml) was introduced by using a vacuum line. The reaction mixture was stirred for about 1 hr at $0 \sim -30°$. The mixture gradually became greenish blue in color. After about 1 week at room temperature, the solvent was removed and residue extracted with degassed isopentane–3-methylpentane, 9:1 (PMP). Extraction was performed two or three times. In the cases of the diradicals **3** and **4**, a slightly greenish blue solution of the diradicals were obtained. The PMP solution of diradical **5** was almost colorless. The concentrations of the diradical solutions obtained were $\sim 10^{-4}$ *M*, because the diradicals were only slightly soluble in PMP.

Determination of Concentration of Diradicals. The PMP solvent (4.5 ml) of the diradical **3** solution was replaced by degassed acetonitrile (6.4 ml). The absorption spectrum of the acetonitrile solution as well as that of PMP solution was carefully determined. Methylviologen dichloride (2 mg) was added to the acetonitrile solution. The solution gradually became blue and the absorption maximum at 6050 Å associated with methylviologen cation radical increased. Absorbance at 6050 Å reached a maximum (1.6) in 5 days. From reported data on methylviologen cation radical (ϵ_{6050} 10060),[14] the concentration of the diradical solution **3** was determined to 2.26×10^{-4}. Determinations of concentrations were performed for the diradicals **4** and **5** by the same method.

Determination of Relative Spin Concentration. The epr spectrum of a PMP solution of diradical **3** of known concentration (8×10^{-4} *M* from absorption spectrum) was measured by the overmodulation method. The epr spectra of dilute solutions of the diradicals **4** (2×10^{-4} *M*) and **5** ($\sim 1 \times 10^{-4}$ *M*) were also determined with the same modulation frequency and almost the same signal gain of spectrometer as in the case of diradical **3**. The epr spectrum of a very dilute solution ($\sim 5 \times 10^{-5}$) of 1-methyl-4-carbomethoxypyridinyl radical was measured under the same conditions. The epr tubes chosen for these measurements had very similar dimensions.

The low-resolution epr spectra obtained were utilized to derive total epr absorptions (by measurement of the areas) from which the relative intensities of the epr spectra were calculated. By assuming that the monoradical **1** is completely in the paramagnetic form under the conditions used (room temperature, low concentration[16]), concentrations of the paramagnetic species in PMP of diradicals **3**, **4**, and **5** were calculated by comparison with the result for monoradical.

Acknowledgment. We are grateful to Dr. P.-k. C. Huang for preparation of the bis(pyridinium iodides).

Attempts to Generate Diphenylcyclopropenylidene. IV[1,2]

W. M. Jones,[3] Mary E. Stowe, E. E. Wells, Jr., and Eldridge W. Lester

Contribution from the Department of Chemistry, University of Florida,
Gainesville, Florida 32601. Received October 20, 1967

Abstract: Attempts have been made to generate the potentially nucleophilic carbene, 2,3-diphenylcyclopropenylidene, and the corresponding diphenyldiazocyclopropene. The methods explored include oxidation of the hydrazone, decomposition of salts of the tosylhydrazone, reaction of the appropriate N-nitrosocarbamate with base, and α eliminations of carboxylic acids from the diphenylcyclopropenyl acetate, benzoate, *p*-nitrobenzoate, and N,N-dimethylcarbamate. Oxidation of the hydrazone failed at the hydrazone synthesis stage. Only the azine could be isolated under acidic conditions, and basic conditions opened the ring. Although the lithium, sodium, and potassium salts of the tosylhydrazone were successfully prepared, under no conditions attempted (from photolysis at Dry Ice temperature to pyrolyses at temperatures as high as 200°) was there observed any evidence for diazocyclopropene or carbene formation. Reaction of the N-nitrosocarbamate with base tended to give products resulting from formation of the diphenylcyclopropenyl cation but, in the presence of dimethyl fumarate, there was formed a small amount (less than 10%) of the spiropentene **13** suggesting that under these conditions there was formed at least a little of the carbene and/or possibly the diazocyclopropene. α Elimination of acetic acid, benzoic acid, and *p*-nitrobenzoic acid from the esters **22a–c** occurred with base in the presence of dimethyl fumarate to the extent of up to 14% as was indicated by amount of methylenecyclopropene **14** formed. Finally, base-induced decomposition of the N,N-dimethyl-O-carbamate **12** was by far the best method for generating what is believed to be the diphenylcyclopropenylidene. In the presence of dimethyl fumarate it gave the 1:1 adduct in yields up to almost 70% (determined spectrophotometrically). The mechanism of the carbamate reaction is discussed.

Sufficient suppression of the normal electrophilicity[4] of a singlet carbene by delocalization of electrons into its vacant p orbital should give rise to a species with nucleophilic properties due to the ever-present pair of nonbonded electrons on the carbene carbon atom. This has, in fact, been found to be the case in a number of instances where the nonbonded electrons of heteroatoms[5] (oxygen and nitrogen are apparently the only

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[1] This research was supported by the U. S. Army Research Office (Durham) and by the National Science Foundation.

[2] Taken in part from the Ph.D. Thesis of M. E. Stowe and from the M.S. Thesis of E. W. Lester.

[3] Alfred P. Sloan Fellow, 1963–1967.

[4] *Cf.* J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p 43; W. Kirmase, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 164.

[5] The question of the actual intermediacy of nucleophilic carbenes in many cases has been clouded by the fact that the correspondng carbene dimer (*e.g.*, tetraminoethylenes) give many of the same products with electrophiles[6] as would be expected from the carbene itself. However, there are still a number of cases that probably do indeed involve intermediate carbene formation (including, in fact, reactions of the dimer with electrophiles[6]). For examples of these as well as leading references to earlier work, see: D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966); R. W. Hoffmann and H. Hauser, *Tetrahedron*, 21, 1891 (1965); H. Quast and S. Hunig, *Chem. Ber.*, **99**, 2017 (1966); *Angew. Chem. Intern. Ed. Engl.*, **3**, 800

two thus far observed that succeed in accomplishing this purpose) have served as the source of electron donation. The resulting species have been found to be inert to typical alkenes and reactive with a rather wide variety of electrophiles.

Another source of π electrons that could be delocalized into the vacant orbital of a singlet carbene and in this way decrease its electrophilicity is the carbon–carbon double bond. This delocalization would be most effective if the resulting π system formed an aromatic ring. Two obvious examples are cyclopropenylidene[7] (**1**) and cycloheptatrienylidene[8] (**2**). The purpose of this paper is to report the results of our attempts to generate 2,3-diphenylcyclopropenylidene.[9]

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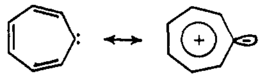

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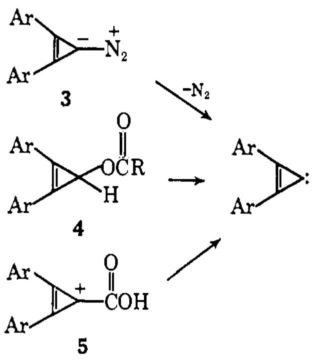
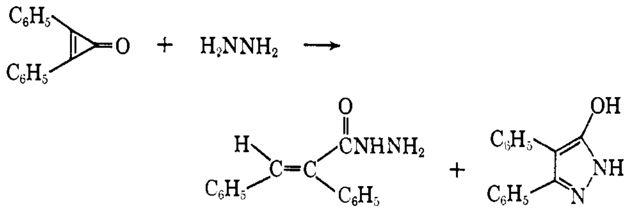
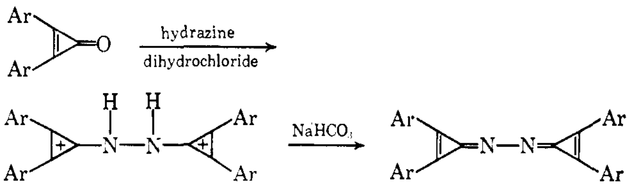
In our attempts to generate this intermediate, we have taken essentially three differnet approaches. In the first, we have attempted to synthesize diazodiphenylcyclopropene (**3**) by conventional methods. This intermediate would probably give the carbene spontaneously at ordinary temperatures.[10] In our second approach, we have studied the α elimination of carboxylic acids from O-cyclopropenyl esters and carbamates **4**. A third method that has been explored and is reported elsewhere[9] involves decarboxylation of 1-carboxy-2,3-diphenylcyclopropenium perchlorate (**5**).



Attempts to Synthesize Diazodiphenylcyclopropene. Of the variety of methods that have been developed to synthesize diazoalkanes,[11] relatively few appeared potentially useful for generating diazodiphenylcyclopropene (**3**). The methods that were tried but ultimately failed (insofar as we could determine) include hydrazone oxidation[12] and the Bamford–Stevens[13] reaction (pyrolysis or photolysis of the tosylhydrazone anion). The former failed at the synthesis stage. Thus, whereas most carbonyl compounds can be converted to their hydrazones by simply allowing them to react with anhydrous hydrazine in a suitable solvent, the reaction of diphenylcyclopropenone with hydrazine under nonacidic conditions gives only ring-opened products.[14]



Under acidic conditions, hydrazine (as the dihydrochloride) does not open the ring but, instead, gives only the brilliant reddish orange diphenylcyclopropenone azine **6** as its colorless dihydrochloride. Under no circumstances could the reaction either be stopped at the hydrazone stage nor could an equilibrium be established in which the hydrazone was present in appreciable quantities either as the free base or its salt. The azine structure was confirmed not only by routine methods



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but also by hydrolysis (an extremely facile reaction) back to the ketone. One notable property of the azine is the effect of solvent on its visible spectrum. It was found that as the solvent polarity is increased, the position of the wavelength absorption shifts to shorter wavelengths. For example, changing the solvent from cyclohexane to chloroform causes a shift from 420 to 385 mμ. This effect, which has been observed in methylenecyclopropenes,[15] indicates a ground state

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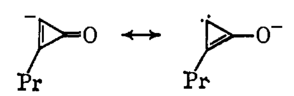
(1964); H. Balli, *Angew. Chem. Intern. Ed., Engl.*, **3**, 809 (1964); H. Quast and E. Frankenfeld, *ibid.*, **4**, 691 (1965); H. W. Wanzlick and A. Hanns, *Chem. Ber.*, **99**, 1580 (1966); H. W. Wanzlick and H. J. Kleiner, *Angew. Chem. Intern. Ed. Engl.*, **3**, 65 (1964). For an excellent review of earlier work in this area, see H. W. Wanzlick, *ibid.*, **1**, 75 (1962). For the first example of an intermediate of this type, see R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

(6) D. M. Lemal, R. A. Lavall, and K. I. Kawano, *ibid.*, **86**, 2518 (1964); H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *ibid.*, **87**, 2055 (1965); N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963).

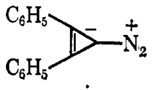
(7) R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966), have pointed out that perhaps one factor contributing to the acidity of the ring hydrogen of *n*-propylcyclopropenone is contribution of a cyclopropenylidene resonance form.



(8) For a report on a possible generation of cycloheptatrienylidene, see W. M. Jones and C. L. Ennis, *ibid.*, **89**, 3069 (1967). For reports of annelated cycloheptatrienylidenes (which do not show nucleophilic properties) see S. Murahashi, I. Moritani, and M. Nishino, *ibid.*, **89**, 1257 (1967), and references cited therein.

(9) For preliminary reports of our work in this area, see W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); W. M. Jones and M. E. Stowe, *Tetrahedron Letters*, 3459 (1964); see also W. M. Jones and S. D. McGregor, *J. Am. Chem. Soc.*, **90**, 123 (1968).

(10) This would be expected for at least two reasons. First, the carbene being formed should be abnormally stable due to its incorporation into an aromatic system. Second, the diazocyclopropene should be destabilized relative to other diazoalkanes because in this case the normally important resonance form of type i would be antiaromatic[28] and should therefore contribute only little to stabilizing the hybrid.



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(11) *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp 21–23.

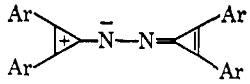
(12) For recent references, see A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.*, 467 (1966).

(13) W. R. Bamford and T. S. Stevens, *ibid.*, 4735 (1952); for more recent references, *cf.* W. Kirmse, B. G. von Bulow, and H. Schepp, *Ann.*, **691**, 41 (1966).

(14) L. Wolgemuth, Ph.D. Dissertation, University of Michigan, 1964.

(15) *Cf.* M. A. Gattiste, *J. Am. Chem. Soc.*, **86**, 942 (1964); W. M. Jones and R. S. Pyron, *ibid.*, **87**, 1608 (1965).

that is more polar (or, possibly of reversed polarity) than its excited state.[16] In the azine, the polarity probably results from significant contributions of resonance forms **7** and possibly **8** to the ground state of the molecule. The second method that we tried that failed to give the diazocyclopropane was the Bamford–Stevens reaction.[13] The diphenylcyclopropenone tosylhydrazone (as its hydrochloride) was successfully prepared from the ketone and tosylhydrazine.[17] The only precaution that is required is that reasonably anhydrous solvents must be used since the hydrazone is very readily hydrolyzed to the ketone. We typically used 1% hydrogen chloride dissolved in anhydrous absolute ethanol as the reaction medium from which the salt of the tosylhydrazone crystallized in 85% yield. The salt could be readily converted to the free tosylhydrazone by simply stirring with aqueous sodium bicarbonate. Manipulation of the free tosylhydrazone required some care. For example, attempts to recrystallize it from methylene chloride–pentane with gentle warming led to essentially no recovery of the tosylhydrazone but, instead, to a mixture of the toluenesulfinic acid salt of the tosylhydrazone and a product that analyzed for dimerization of the tosylhydrazone with the loss of one molecule of toluenesulfinic acid. We have not yet been successful in identifying this dimer although it has been found that at least one (and probably only one) of the cyclopropene rings is still intact. Although the tosylhydrazone is highly unstable in some solvents, it could be conveniently purified by rapid recrystallization from tetrahydrofuran–pentane mixtures or pyridine–pentane mixtures. In general, it appeared to be reasonably stable in basic solvents. The free tosylhydrazone was converted, under varying conditions, to what are believed to be its lithium salt (dark red), its sodium salt (dark red), and its potassium salt (deep purple). These salts were exposed to conditions ranging from photolyses at Dry Ice–acetone temperatures to pyrolyses at 200°. In quite a variety of cases the salt of *p*-toluenesulfinic acid (frequently without concomitant nitrogen evolution) was observed as a product (in some cases in rather high yield) but under no circumstance did we observe any products suggestive of the diazocyclopropene or the cyclopropenylidene. Typically, the cyclopropene ring was completely destroyed and tlc showed essentially a continuum of products from the original spot to the solvent front. In many cases, dimethyl fumarate was used *vide infra* as a possible carbene trap. In no case was there observed even a trace of the readily detectable methylenecyclopropene product. Thus, the Bamford–Stevens reaction, which has been found to be so generally useful for generating other diazoalkanes, was finally, and reluctantly, abandoned.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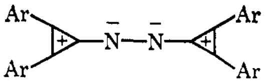
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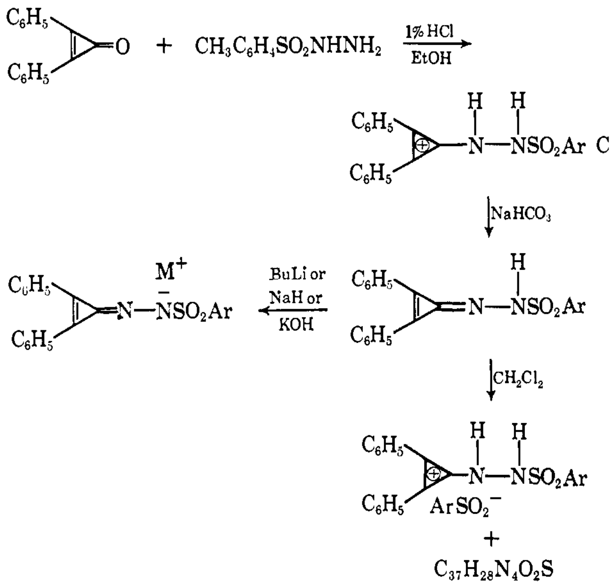
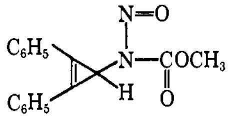


Finally, an attempt was made to effect the generation of diazodiphenylcyclopropene by reaction of the N-nitrosocarbamate **9** with base. The mechanism of this type of reaction has been rather carefully examined[18] and although there is still some doubt as to the details of the last step, there is little doubt but that the reaction proceeds through a diazotate and probably the corresponding hydroxide. Application of this mechanism to the cyclopropenyl system immediately points up the problem that is inherent in application of this method to potentially nucleophilic carbenes, that is, loss of nitrogen from an intermediate before base can abstract the necessary proton. This, in fact, appears to be the case—for example, reaction of the nitrosocarbamate **9** with sodium methoxide gave the diazo ether **10** that would result from coupling of the intermediate diazotate with the cyclopropenyl cation. However, what was really quite surprising was the fact that the reaction when run in the presence of dimethyl fumarate apparently does give some of the diazocyclopropene since there was observed in up to 10% yield the spiropentene **13** that would result from addition of the diphenylcyclopropenylidene to dimethyl fumarate. Since this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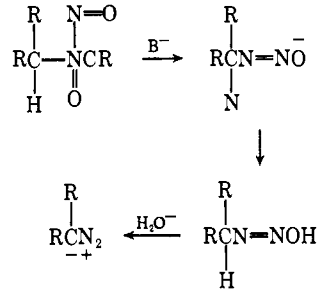

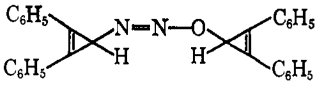
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[16] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954); E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3253 (1958).

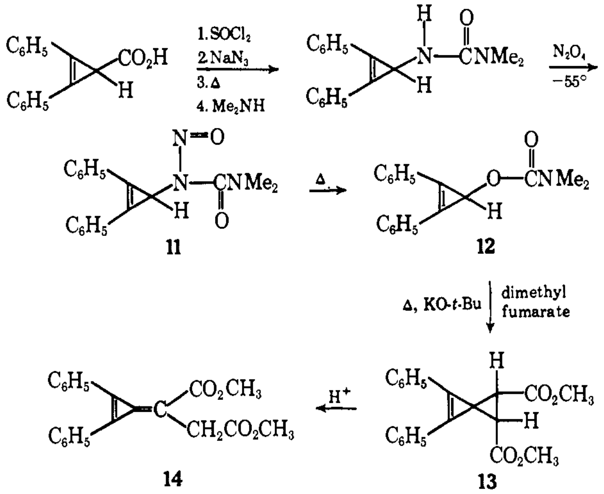
[17] For other reports of the synthesis of this compound as well as other ketone derivatives of diphenylcyclopropenone, see: Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Japan*, **37**, 1897 (1964); T. Eicher and G. Frenzel, *Z. Naturforsch.*, **20b**, 274 (1965). Most of these results have been independently confirmed in these laboratories.

[18] *Cf.* W. M. Jones and D. J. Muck, *J. Am. Chem. Soc.*, **88**, 3798 (1966), and references cited therein.

was obtained in much higher yield by a method to be discussed below, discussion of its properties and mode of formation will be deferred until later.

α Elimination from an O-Cyclopropenyl Carbamate

In the early stages of this work, the nitrosourea **11** was synthesized as a possible precursor to diazodiphenylcyclopropene. What was not realized at that time was the fact that nitrosoureas that are potentially useful as diazoalkane precursors are limited to those with at least one N–H since the course of this reaction apparently involves transfer of this proton to the nitroso oxygen.[19] For this reason, it is certainly not surprising that N,N-dimethylnitrosourea **11** was found to be essentially inert to base under typical diazoalkane forming conditions. However, it was found that the material is heat sensitive and, in fact, when it is heated in the presence of a base and dimethyl fumarate, it gives a rather high yield (up to 48% isolated, 70% spectrophotometrically) of a product that corresponds to a 1:1 adduct of diphenycyclopropenylidene to dimethyl fumarate—the methylenecyclopropene **14**. When the course of the reaction was monitored using the ultraviolet spectrum as the probe, it was noted that a series of interesting transformations occurred. During the first 20–30 min of reflux, the initial typical diphenylcyclopropene spectrum (maximum at 304 mμ with shoulders at 291 and 319) about doubled in intensity and the maximum shifted to 298 mμ. Work-up at this point yielded very little methylenecyclopropene. As the reaction continued (over 9–10 hr) the typical diphenylcyclopropene spectrum gradually changed to give a single broad absorption that centered at 328 mμ. However, work-up of the reaction under conditions that exposed the product to even traces of acid caused a dramatic change in the spectrum with complete disappearance of the broad absorption at 328 mμ and appearance of the methylenecyclopropene spectrum with its long wavelength absorption at 375 mμ. In other words, the ultraviolet spectra indicated that there were at least two distinct species between the nitrosourea and the final isolated methylenecyclopropene. The first of these was isolated by simply heating the nitrosourea for about 30 min in base-free heptane followed by removal of the solvent. Characterization showed this material to be the O-carbamate **12**. Not only did the spectrum of the isolated carbamate match that of the first intermediate in the reaction but subjecting this material to the conditions outlined above gave essentially the same yield of the methylenecyclopropene as did the nitrosourea.



Isolation of the second intermediate was originally accomplished by manual separation of its crystals from those of dimethyl fumarate since all other techniques (including chromatography under the mildest conditions) caused very rapid isomerization to the methylenecyclopropene. However, it was later found that this could be accomplished more easily by subliming excess dimethyl fumarate from the crude reaction mixture followed by simple recrystallization of the residue. The product that was isolated showed both analytical and spectral properties consistent with the spiropentene structure **13**.[20–22] The spiropentene is a remarkably unstable material. As was alluded to above, it undergoes isomerization to the methylenecyclopropene on exposure to moisture, any protic solvent or simply heating. When placed on either alumina or silica gel it undergoes instantaneous ring opening.

The ultraviolet spectrum of the spiropentene is interesting in that it differs appreciably from other diphenylcyclopropenes. Thus whereas 1,2-diphenylcyclopropenes in polar solvents typically show a maximum absorption at about 300–310 mμ[23] with lower intensity absorptions on either side, the spiropentene shows a single broad maximum at 328 mμ. The cause of this bathochromic shift and loss of fine structure is not clear. The two most obvious abnormalities in this structure are the presence of the cyclopropane ring substituted with carbonyl groups with its σ bonds perfectly oriented for interaction with the *cis*-stilbene chromophore and the additional strain introduced into the cyclopropene ring as a result of the contraction of its 3,3-exocyclic bonds. Although the importance of neither of these effects can be assessed, it is probably worth noting that White and Anhalt[24] have found that a decrease in the bond angle of the sp^2-hybridized carbon atoms of ring structures containing the *cis*-stilbene chromophore leads to a significant bathochromic shift in the long wavelength maximum. (For example, from the five- to the three-membered ring, the position of the maximum shifts from 272 to 317 mμ.) Such a decrease is consistent with (although not strongly supported by) the electron-diffraction study of spiropentane reported by Donohue, *et al.*[25]

The rather dramatic instability of the spiropentene is probably the result of a combination of factors. In the first place, simple extrapolation from other strained molecules[26] predicts this ring system to have on the order of 90 kcal/mol of ring strain. According to

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(19) W. M. Jones and D. L. Muck, *J. Am. Chem. Soc.*, **88**, 68 (1966).

(20) For a discussion of this structural assignment, see W. M. Jones and M. E. Stowe, *Tetrahedron Letters*, 944 (1964).

(21) Although, to the best of our knowledge, this is the only known example of a spiropentene, the literature does record at least one case where a spiropentene has been suggested as a possible reaction intermediate.

(22) See E. V. Dehmlow, *ibid.*, 4003 (1965).

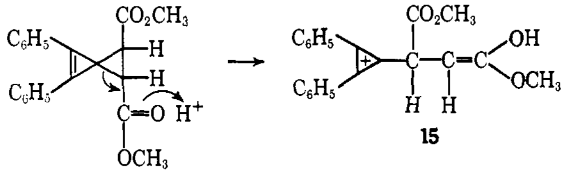
(23) To the best of our knowledge, the highest reported maximum absorption appears at 318 mμ (lower intensity absorption at 300 mμ). See R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1967), and references cited therein for this example as well as the spectra of quite a wide variety of substituted 1,2-diphenylcyclopropenes.

(24) E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965).

(25) J. Donohue, G. L. Humphrey, and V. Schomaker, *J. Am. Chem. Soc.*, **67**, 332 (1954).

(26) *Cf.* N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

Baird and Dewar's calculations, this would place this molecule at the top of the list of isolated molecules containing three-membered rings. This is true whether one takes as his criterion of strain energy the total in the ring system (of systems containing three, four, or five members) or strain per carbon in the ring system involved. A second factor that also certainly enhances ring opening to the methylenecyclopropene is the stability of the ring opened intermediate that probably precedes the methylenecyclopropene. Thus, for example, acid induced enolization of an ester function would lead to the stable cyclopropenyl cation **15**. An analogous zwitterionic intermediate can be envisaged for thermal opening.



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Mechanism of Spiropentene Formation

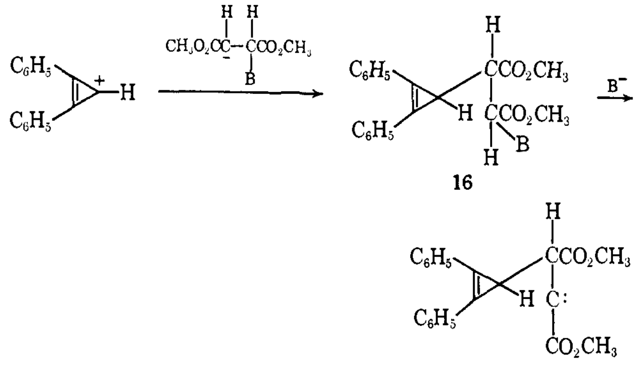
Formation of the spiropentene is what would be expected from reaction of a nucleophilic diphenylcyclopropenylidene with the electrophilic alkene, dimethyl fumarate. However, if this carbene is a real intermediate, it must be generated through a base induced α elimination of the elements of N,N-dimethylcarbamic acid from the intermediate carbamate **12**. This fact causes some concern. In most α eliminations, formation of the carbene (or carbenoid)[27] is either preceded by formation of the carbanion or involves a transition state with considerable carbanion character.[28] Such a mechanism is, of course, quite distasteful in the cyclopropene system in light of the theoretically predicted and experimentally verified instability of the cyclopropenyl carbanion.[29]

This carbanion instability prompted us to consider a variety of other possible methods for forming the spiropentene under our reaction conditions.

In view of the fact that the starting material is a cyclopropene substituted with an ionizable heteroatom, one intermediate which must obviously be considered as a possible spiropentene precursor is the diphenylcyclopropenyl cation. This cation could act in this capacity in at least three ways. It could add directly to the double bond followed by a (highly unlikely) γ elimination, it could react with a 1:1 complex of the double bond with base followed by reactions outlined below, and it could simply lose a proton to the base to give the carbene.

Direct attack on the double bond is essentially excluded by our finding that the reaction is not enhanced by increasing the nucleophilicity of the double bond. Thus, not only does a more nucleophilic double bond (*e.g.*, cyclohexene) not give any observable addition product when substituted for the dimethyl fumarate but, in a competition experiment involving equimolar amounts of cyclohexene and dimethyl fumarate, the yield of the fumarate adduct was completely unaffected.

Spiropentene formation from addition of the cyclopropenyl cation to an adduct of dimethyl fumarate and the base is also unlikely for the following reasons. Formation of the spiropentene from the adduct **16** of the cation with the base–fumarate anion would require either γ elimination to go directly to the product or α elimination to give a carbene which could insert into the cyclopropene carbon–hydrogen bond. The former possibility is extremely unlikely on simple mechanistic grounds. The latter possibility, which would incorporate the cyclopropene hydrogen into the final spiropentene, was excluded by carrying out the reaction with deuterated cyclopropene; the spiropentene product showed essentially no deuterium.

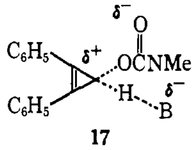


16

The final possibility that the cation could simply lose a proton to give the carbene could not be excluded. Attempts were made to determine if the cation would give rise to the spiropentene product by refluxing diphenyl cyclopropenylhexafluorophosphate with dimethyl fumarate and base. However, the finding that no reaction occurred cannot be taken as strong evidence against a cation intermediate because of the extreme insolubility of the salt in the solvent heptane.

A cyclopropenyl radical was also considered as a possible intermediate. However, the fact that the reaction is apparently base catalyzed—albeit remarkably insensitive to the amount of base used[30] (see Experimental Section)—very strongly suggests an ionic mechanism of some type. Furthermore, the neutral free-radical inhibitor, diphenylpicrylhydrazyl, had no effect on the yield of the reaction.

A combination of all of the above considerations has led us to the conclusion that this reaction probably does involve a carbene that is formed by an α-elimination mechanism. However, in contrast to most α eliminations this probably proceeds either through a lop-sided transition state of the type **17** in which considerably more carbon–oxygen bond breaking has occurred than carbon–hydrogen breaking or, possibly, even by a two-step mechanism involving initial ionization followed by proton abstraction from the cation.[5]



17

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[27] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

[28] Reference 4, Chapters 3, 6.

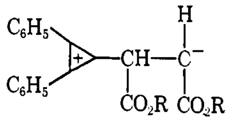
[29] *Cf.* R. Breslow, J. Brown, and J. J. Gajewski, *J. Am. Chem. Soc.*, **89**, 4383 (1967).

[30] The need for only a trace of base can be made consistent with a base-induced α elimination if the base is actually acting as a catalyst. A strong odor of dimethylamine accompanying the reactions suggests that this is indeed the case.

$$BH + Me_2NCO_2^- \longrightarrow Me_2NH + CO_2 + B^-$$

Stereochemistry of the Reaction

Conjugation of the cyclopropenyl double bond with the vacant orbital in the cyclopropenylidene would probably stabilize the singlet spin state relative to the triplet enough to cause the former to be the ground state of this intermediate.[31] According to Skell's chemical criterion for carbene multiplicity,[32] such a species should react stereospecifically with a double bond. However, in contrast to other singlet carbenes, cyclopropenylidene in its reaction with an α,β-unsaturated carbonyl compound could quite conceivably lead to a dipolar intermediate of type **18** that would be so stabilized by the cyclopropenyl moiety and the ester carbonyl that the reaction would actually occur in two steps and nonstereospecifically. In view of this interesting possibility, we undertook to examine the stereochemistry of this reaction using as our trapping agents dimethyl fumarate and its geometrical isomer, dimethyl maleate. It was found that even in the presence of only traces of base reaction with dimethyl fumarate and dimethyl maleate gave one and the same spiropentene in about 50 and 30% yields, respectively. There was no detectable trace of a second spiropentene. This conclusion is based on the following facts. The nmr spectrum of the crude reaction mixture resulting from reaction in the presence of either ester showed exactly the same changes upon isomerization to the methylene cyclopropene; the only resonances that changed during this isomerization were the two at τ 6.34 (singlet) and 6.92 (singlet). In both cases, the area ratio of these two peaks was 6:2 and represent the ester methyls and the cyclopropane hydrogens, respectively. Since the cyclopropane hydrogens for the *cis*- and *trans*-spiropentenes **19** and **20** should be well separated (cyclopropane models show differences of about 0.3 ppm),[33] we must conclude that both starting materials lead to one and the same spiropentene.[34] Unfortunately, the significance of this conclusion is clouded by several factors. In the first place, the reaction conditions cause partial isomerization of dimethyl maleate to dimethyl fumarate. Although the degree of isomerization was not extensive (over a 13-hr period 11% had isomerized) it is still possible that the observed spiropentene arose from exclusive reaction with the dimethyl fumarate. Assuming that the nmr would detect 5% of a second isomer, this would require that the reaction of the carbene with the fumarate be more than 150 times faster than reaction with the maleate (probably on the order of 300 times faster). This is considerably larger than the difference between the reaction of 1,3 dipoles with dimethyl fumarate and dimethyl maleate[35] (maximum of 58) but is not enough difference, in our opinion, to exclude this as a possible explanation of these results. Another fact that clouds interpretation of these observations is the fact that we have not been able to isolate a second spiropentene and as a result we can say nothing about the geometrical stability of the spiropentenes to the reaction conditions. Thus, at this time, the question of the stereochemistry of the addition of diphenylcyclopropenylidene to a double bond must remain open.



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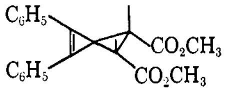

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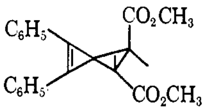
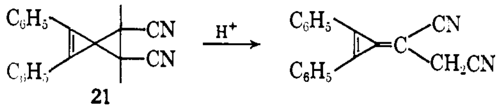


20

Extension to Other Acceptors and Cyclopropenyl Esters

Attempts to vary the acceptor olefin have met with only limited success.

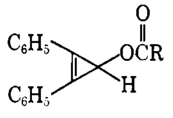
Fumaronitrile affords the spiropentene **21** which undergoes isomerization, albeit more sluggishly than the diester, to the corresponding methylenecyclopropene.



21

Evidence was also found for similar reactions with diethyl fumarate and N,N,N′,N′-tetramethylfumaramide. No evidence was found to indicate formation of an adduct with cyclohexene, *trans*-stilbene, tetrachloroethylene, diphenylacetylene, or dimethyl acetylenedicarboxylate.

Finally the success experienced with the carbamate suggested the possibility of similar α eliminations from other cyclopropenyl esters. The esters **22** were therefore prepared and treated with excess potassium *t*-butoxide in refluxing heptane in the presence of dimethyl fumarate. Inspection of the reaction mixture by tlc showed a bright yellow spot with R_f identical with that of an authentic sample of the methylenecyclopropene **14**. Isolation of this material by column chromatography confirmed that it was the methylenecyclopropene. Yields of **14** were determined by method B (Experimental Section). The three esters gave yields of 6 (20), 14 (24), and 2.5% (54 hr), respectively. It is interesting that these esters apparently do undergo α eliminations as does the carbamate but from a synthetic standpoint, they do not approach the carbamate as an effective source of the adduct.



22a, $R = CH_3$
b, $R = C_6H_5$
c, $R = p\text{-}NO_2C_6H_4$

Experimental Section

General. Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared spectra were recorded with a Beckmann Model IR10 unless otherwise specified. Ultraviolet spectra were recorded with either a Cary 14 or Cary 15 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were determined with a Varian A-60A high-resolution spectrometer. Chemical shifts are reported in

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(31) Reference 4, p 45.

(32) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(33) K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963); D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(34) When isomerization was complete, the uv spectrum of the crude reaction product showed that all spiropentene had been consumed.

(35) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

parts per million (ppm) from tetramethylsilane. The potassium *t*-butoxide used was obtained from K & K Laboratories. The heptane was Phillips Pure Grade *n*-heptane, bp 98–99°. Analytical thin layer chromatography (tlc) was on *ca.* 0.25-mm silica gel layers. Spots were visualized by quenching of the fluorescence of an indicator (256 mμ) in the silica gel.

Diphenylcyclopropenone Azine. To a solution of hydrazine dihydrochloride (0.14 g, 1.35 mmol) in 50 ml of reagent grade methanol was added 0.56 g (2.72 mmol) of diphenylcyclopropenone.[36] The resulting mixture was stirred at room temperature for 2 hr. The resulting solid was filtered, and the solution was concentrated to give a second crop of crystals. The combined yield of diphenylcyclopropenone azine dihydrochloride, mp 208° dec, was 0.7 g (50%). This material showed significant infrared absorption (KBr, cm^{-1}) at 3500, 2200 (broad shoulder), 1900, 1675, 1595, and 1535. Its ultraviolet spectrum showed maxima (acetonitrile, mμ (ε)) at 316 (34,100), 304 (39,200), 302 (39,400), 266 (9600), 242 (14,700), and 230 (40,800).

Diphenylcyclopropenone azine dihydrochloride was converted to the free azine by vigorously stirring a mixture of the dihydrochloride with 10% sodium bicarbonate in the presence of methylene chloride at room temperature. The free azine formed a bright reddish orange solid which was immediately extracted into the methylene chloride layer. The methylene chloride layer was separated and dried over sodium sulfate and the solution decanted. The methylene chloride solution was heated to boiling, and pentane was added until cloudiness appeared and lingered for a short time and then disappeared. Cooling the solution afforded bright reddish orange crystals of azine, mp 241.5–242° dec. The azine showed significant infrared absorptions (cm^{-1}) at 1840 and 1590. The ultraviolet spectrum of the azine varied with the nature of the solvent. In cyclohexane, containing 1% chloroform, it showed absorption (mμ (ε)) at 420 (4300), 344 (5000), 328 (12,300), 314 (14,500) 300 (13,800), 291 (36,900), 274 (41,300), and 244 (30,400). In acetonitrile, it showed absorptions at 390 (3200), 331 (3780), 318 (8720), 305 (10,000), 280 (27,300), 273 (28,00), and 248 (20,400). In methanol, it showed absorptions at 375 (2750), 315 (4200), 302 (9630), 271 (24,500), and 244 (20,100). An increase in the polarity of the solvent is reminiscent of the effect that has been observed in methylenecyclopropenes and cyclopropenylidienecyclopentadienes.[37] Support for the azine structure was obtained by hydrolyzing a sample of the azine with alcoholic HCl. In less than 30 min, the azine was essentially quantitatively hydrolyzed to diphenylcyclopropenone.

Anal. Calcd for $C_{30}H_{20}N_2$: C, 88.2; H, 4.9; N, 6.87; mol wt, 408. Found: C, 88.02; H, 4.96; N, 6.70; mol wt, 416.

Diphenylcyclopropenone Tosylhydrazone. Diphenylcyclopropenone tosylhydrazone was synthesized in essentially the same manner that has been previously recorded.[17] In a typical experiment *p*-toluenesulfonylhydrazine (0.538 g, 2.72 mmol) was dissolved in 10 ml of 1% solution of anhydrous HCl in absolute ethanol, and 0.56 g (2.72 mmol) of solid diphenylcyclopropenone was added and the solution stirred at room temperature. At the end of 2.5 hr, the resulting precipitate was filtered and the solution concentrated to give a second crop of crystals. The combined yield of diphenylcyclopropenone *p*-toluenesulfonylhydrazone hydrochloride, mp 208–209° dec, was 1.04 g (93.5%). Eicher and Frenzel report[17] mp 206–208°. The hydrochloride showed significant absorptions in the infrared (KBr, cm^{-1}) at 2700 (broad shoulder), 1900, 1595, and 1540. The hydrochloride was conveniently converted to the free tosylhydrazone by vigorously stirring with 10% aqueous sodium bicarbonate solution for about 1 hr at room temperature. The resulting faint yellow solid was filtered and recrystallized from either a mixture of pyridine–pentane or tetrahydrofuran–pentane to give nearly white crystals, mp 157.5° dec. Eicher and Frenzel report[17] mp 145–148°. The free tosylhydrazone shows infrared absorptions (KBr, cm^{-1}) at 3290, 1960, 1925 (weak), 1597, and 1565. The ultraviolet spectrum of the free tosylhydrazone was found to be only slightly sensitive to the nature of the solvent. For example, in a 1% solution of chloroform in cyclohexane the ultraviolet spectrum showed absorptions (mμ (ε)) at 333 (3390), 330 (2900), 290 (2760), 254 (10,500), and 236 (21,500). In methanol the absorptions appeared at 324 (8380), 300 (6630), 290 (5770) 254 (12,200), and 233 (25,200).

Anal. Calcd for $C_{22}H_{18}N_2O_2S$: C, 70.5; H, 4.82; N, 7.49; S, 8.56. Found: C, 70.39; H, 4.77; N, 7.23; S, 8.69.

Attempt to Purify Diphenylcyclopropenone *p*-Toluenesulfonylhydrazone by Recrystallization from Methylene Chloride–Pentane. When a sample of tosylhydrazone was warmed for about 10 min in methylene chloride followed by dilution with pentane, a nearly white solid, mp 220° dec, separated. This solid was shown to be the toluenesulfinic acid salt of the parent tosylhydrazone by treating it with aqueous sodium bicarbonate solution to yield the free tosylhydrazone and *p*-toluenesulfinic acid which was characterized as the corresponding 2,4-nitrophenyl sulfone. When the filtrate from above was treated with more pentane a second solid separated, mp 125° dec. Analysis and molecular weight of this material are consistent with dimerization of the tosylhydrazone with loss of 1 mol of toluenesulfinic acid.

Anal. Calcd for $C_{37}H_{28}N_4O_2S$: C, 74.99; H, 4.6; N, 9.45; S, 5.4; mol wt, 593. Found: C, 74.86, 75.04; H, 4.85, 4.98; N, 9.12, 9.37; S, 4.93; mol wt, 565, 574.

Hydrolysis of this material with 95% ethanol containing a few drops of concentrated HCl led to the formation of diphenylcyclopropenone in an amount corresponding to 74% for 1 mol of diphenylcyclopropenone moiety per molecule of unknown. This material also showed the interesting characteristic of turning to a brilliant red material upon standing in nonpolar solvents. The red material has not yet been characterized.

Preparation of Lithium and Sodium Salts of Diphenylcyclopropenone *p*-Toluenesulfonylhydrazone and Attempts to Decompose to Diphenylcyclopropenylidene. In a typical preparation the sodium salt was formed in the following manner. Tetrahydrofuran (25 ml) was distilled directly from lithium aluminum hydride into a baked, argon-swept flask. A closed, solid addition tube containing the diphenylcyclopropenone tosylhydrazone (500 mg, 1.34 mmol) was attached to the flask. After cooling the flask and contents to 0°, 80 mg (1.76 mmol) of sodium hydride (52.6% dispersion in mineral oil) was added, and gas evolution was noted. Usually sufficient NaH was consumed in this step to leave about 1.4 mmol for reaction with the tosylhydrazone. The tosylhydrazone was then added all at once from the solid addition tube. About 1.5 hr was required for gas evolution (1 mol) to cease. That the gas was hydrogen was demonstrated by ignition. The resulting dark red solid was shown to be the tosylhydrazone salt by converting it back to the tosylhydrazone hydrochloride with concentrated hydrochloric acid. The sodium salt is unstable to the atmosphere. Attempts to convert this material to the diazocyclopropene included low-temperature photolysis both in solution and as a suspension. Pyrolyses were attempted on the dry salt, in concentrated solutions, and in very dilute solutions. Under some of these conditions the sodium salt of *p*-toluenesulfinic acid was formed in yields as high as 90% but under no circumstance was any evidence for either the diazocyclopropene or the carbene obtained. In fact, in many cases where the sodium salt of the toluenesulfinic acid was isolated no nitrogen evolution was observed. Analysis of the crude reaction mixtures invariably showed complex mixtures of products.

The lithium salt was prepared in essentially the same manner as described above with the exception that butyllithium was employed as the base. In a typical experiment diphenylcyclopropenone tosylhydrazone (300 mg, 0.804 mmol) was placed in a baked, nitrogen-swept flask. Tetrahydrofuran (10 ml) (distilled from lithium aluminum hydride) was added by syringe. After cooling to −78°, *n*-butyllithium (0.804 mmol in hexane) was added dropwise by syringe. Concurrent with the addition, the solution turned a deep red brown. After stirring for 1 hr, the solution was warmed to −30° and the solvent removed by vacuum distillation to give a deep red glass. On warming in a melting point apparatus, the glass lost its color at 100° and charred at 280°, but did not melt. The infrared spectrum of the red glass showed no absorption at the 3.06 position of N–H absorption in the tosylhydrazone. The cyclopropene doublet at 1850 and 1890 cm^{-1} was present. The glass gave a strongly positive flame test for lithium. Dissolution of the glass in acetonitrile containing a drop of fluoroboric acid gave a solution which had the uv spectrum of cyclopropenone tosylhydrazone fluoroboric acid salt.

Attempts to convert the lithium salt to diazocyclopropene met with as little success as was observed with the sodium salt.

The potassium salt or possibly a hydrate was conveniently prepared in the following manner. To a vigorously stirred suspension of 1.0 g of the tosylhydrazone in 20 ml of 30% aqueous potassium carbonate was added an excess of 40% aqueous potassium hydroxide. A deep reddish purple solid formed which was filtered and washed with 30% potassium carbonate solution followed by very rapid vacuum drying. This material was characterized as the potassium salt of the tosylhydrazone by conversion to the known

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[36] R. Breslow, L. Altman, A. Krebs, E. Mohaos, I. Murata, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).

[37] *Cf.* W. M. Jones and R. S. Pyron, *ibid.*, **87**, 1608 (1965).

trichloroacetic acid salt of this material. Attempts to convert the salt to the diazocyclopropene or the carbene met with essentially the same types of failure as described above.

1,2-Diphenylcyclopropene-3-carboxylic Acid. The acid was prepared by the method of Breslow, *et al.*[38] To a mixture of 80.0 g (0.45 mol) of diphenylacetylene and 10 g of electrolytic copper dust heated to 135° was added over a period of 8 hr 25 ml (0.246 mol) of freshly distilled ethyl diazoacetate. After addition of the ethyl diazoacetate was complete, the mixture was cooled to near room temperature and poured into a solution of 30 g of potassium hydroxide in 150 ml of methanol. This mixture was refluxed for 3 to 4 hr, cooled to room temperature, and most of the methanol was removed on a rotary evaporator using a warm water bath. About 300 ml of water was added to the residue, and the insoluble portion was filtered and washed well with water. The filtrate and water washings were acidified slowly with hydrochloric acid, giving the cyclopropene acid as a brown precipitate. This was taken up in chloroform and passed through Florex. Removal of the chloroform solvent from the eluent gave a light yellow solid which could be purified further by recrystallization from acetone. The crude solid after washing with ether to remove traces of color could be used for later steps of the synthesis without further purification. The yield of acid was 16 g (28%), mp 208–209° (lit.[33] mp 209–211°).

2,3-Diphenyl-2-cyclopropenecarbonyl Chloride. To 20 ml of thionyl chloride in a 250-ml, round-bottomed flask was added 13.0 g (0.55 mol) of 1,2-diphenylcyclopropene-3-carboxylic acid. The mixture was stirred for 30 min at room temperature, and the excess thionyl chloride was removed on a rotary evaporator using a water bath at *ca.* 40°. The last traces of thionyl chloride were removed with a vacuum pump, leaving a light tan solid which was used in the preparation of the acid azide without further purification.

2,3-Diphenyl-2-cyclopropenecarbonyl Azide. The acid chloride prepared as described above was dissolved in 150 ml of dry acetone and cooled to 0°. To the cooled solution was added a solution of 10 g (0.155 mol) of sodium azide in 25 ml of water. The mixture was stirred at 0° for 1 hr and then poured into 500 ml of ice water. The mixture was stirred for about 15 min, and the azide was filtered and washed with water, dilute sodium bicarbonate solution, and again with water. The yield of the crude azide after drying was 14 g (98%). This material was used without further purification.

2,3-Diphenyl-2-cyclopropenyl Isocyanate. A 500-ml, round-bottomed flask was filled about half full with dry benzene. To this flask was attached a condensor and addition funnel. Benzene was distilled out of the condensor through the addition funnel until no more droplets of water could be detected in any of the apparatus. To the refluxing benzene was added dropwise an ether solution of 14 g (0.053 mol) of the acid azide in *ca.* 200 ml of dry ether. The ether solution was added at such a rate as to allow most of the ether to distill off as it was added. After the addition was complete (about 1 hr), the solution was refluxed for 2–3 hr longer. The solution was cooled to room temperature, and the benzene was removed on a rotary evaporator using a water bath heated to 50–60°. The residual isocyanate, which was a red oil, was used in the next step of the synthesis without further purification.

Methyl N-(2,3-Diphenyl-2-cyclopropenyl)carbamate. To 100 ml of methanol containing 1 equiv of sodium methoxide was added a benzene solution of 2,3-diphenyl-2-cyclopropenyl isocyanate which had been prepared from 5.0 g (0.019 mol) of the corresponding acid azide as described previously. After addition of the benzene solution of the isocyanate, the solution was stirred at room temperature for 45 min. The solution was filtered, and the solvent was removed on a rotary evaporator. The residue was taken up in hot benzene–hexane (1:1) and the carbamate crystallized by cooling. Recrystallization in the same manner afforded 3.2 g, 63%, of the carbamate, mp 49–49.5°.

The ultraviolet spectrum of the carbamate (CH_3CN, mμ (log ε)) showed maxima at 223 (4.33), 231 sh (4.25), 290 sh (4.39), 304 (4.50), and 319 (4.42). The infrared spectrum (KBr) showed absorptions at 3300, 3020, 2950, 1805 (cyclopropene), 1680 (carbonyl), 1500, 1445, 1315, 1250, 1095, 1040, 1010, 920, 775, and 685 cm^{-1}. The nmr spectrum (in τ values) in $CDCl_3$ showed phenyl multiplets at 2.22 and 2.57, a broad resonance centered at 4.97 assigned to the N–H, a doublet centered at 5.95 (J = 5 cps) assigned to the ring proton, and a singlet at 6.30 assigned to the methyl protons. Relative area of the absorptions were in the ratio 10.6:0.9:1:3.

Anal. Calcd for $C_{71}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.73; H, 5.57; N, 5.08.

Methyl N-Nitroso-N-(2,3-diphenyl-2-cyclopropenyl)carbamate. To 50 ml of anhydrous ether were added 2.2 g (8 mmol) of methyl N-(2,3-diphenyl-2-cyclopropenyl)carbamate and 0.66 g (8 mmol) of sodium acetate. The mixture was cooled to −35° with stirring, and 7 ml of anhydrous ether containing 1.2 g (13 mmol) of N_2O_4 was added. The mixture was stirred at −30 to −40° for 2 hr. After this time the mixture was cooled to −50° and poured into an ice-cold 10% sodium bicarbonate solution. The ether layer was washed twice with 10% sodium bicarbonate and then with water. During this process it was necessary to add 100 ml of ether. After drying with sodium sulfate, the ether layer was concentrated to a yellow oil on a rotary evaporator. About 10 ml of anhydrous ether was added, and the solution was filtered through magnesium sulfate. Cooling gave the yellow nitrosocarbamate in 78% yield, mp 61–62°.

The ultraviolet spectrum of the nitrosocarbamate (CH_3CN, mμ (log ε)) had maxima at 220 (4.38), 228 (4.37), 285 sh (4.32), 300 (4.44), and 315 (4.30). The infrared spectrum showed absorptions at 3060, 3030, 2960, 1800 (cyclopropene), 1750 (carbonyl), 1600, 1495, 1445, 1395, 1325, 1300, 1200, 1170, 1140, 1120, 1050, 1020, 960, 920, 790, 765, and 695 cm^{-1}. The nmr spectrum (in τ values) in $CDCl_3$ showed multiplets at 2.17 and 2.53 and two unresolved singlets at 6.03 and 6.08. The relative area ratio of the combined phenyl multiplets to the two unresolved singlets was 10:3.99.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.26; H, 4.76; N, 9.31.

Decomposition of Methyl N-Nitroso-N-(2,3-diphenyl-2-cyclopropenyl)carbamate in the Absence of an Acceptor. In a typical reaction 0.634 g (2.16 mmol) of the nitrosocarbamate was placed in 50 ml of ether and cooled to 0°. To this was added 0.652 g (12 mmol) of sodium methoxide. The mixture was stirred at 0° until gas evolution ceased. (This amounted to 40–45% of theory.) The solution was filtered and concentrated to about one-half of the original volume. Cooling gave a colorless crystalline material (presumably an etherate of **10**), mp 90–100° dec, in 80–90% yield. The nmr spectrum (in τ values) in $CDCl_3$ showed resonances at 2.60 (multiplet), 5.32 (singlet), 5.47 (singlet), 6.53 (quartet, J = 7.5 cps), and 8.83 (triplet, J = 7.5 cps), having relative area ratios of 21:1:1:2:3. The ultraviolet spectrum showed absorptions at 233, 230 sh, 304, and 319 mμ. On addition of HBF_4 the spectrum changed to give absorptions at 245, 290, and 304 mμ. The infrared spectrum (Nujol) run on a Perkin-Elmer Infracord showed a cyclopropene absorption at 1800 cm^{-1} as well as absorptions at 1600 (w), 1370, 1330, 1180, 1150, 1110, 1020, 1010, 760 (s), and 685 (s) cm^{-1}.

When recrystallized from methylene chloride–hexane, the ether was eliminated to give a new solid, mp 145–146° dec. The ultraviolet spectrum (CH_3CN, mμ (log ε)) had maxima at 222 (4.60), 228 (4.61), 304 (4.61), and 319 (4.58). The nmr spectrum (in τ values) in $CDCl_3$ showed resonances at 2.60 (multiplet), 5.32 (singlet), and 5.47 (singlet), having relative area ratios 20:1:1. From spectra data and analysis this compound was concluded to be **10**.

Anal. Calcd for $C_{30}H_{22}N_2O$: C, 84.48; H, 5.20; N, 6.57. Found: C, 84.28; H, 5.39; N, 6.54.

Decomposition of Methyl N-Nitroso-N-(2,3-diphenyl-2-cyclopropenyl)carbamate in the Presence of Dimethyl Fumarate. In a typical reaction 0.265 g (0.88 mmol) of the nitrosocarbamate and 0.764 g (5.3 mmol) of dimethyl fumarate were dissolved in 80 ml of ether and cooled to 0°. The base (either sodium methoxide or potassium *t*-butoxide) was added from a solid addition tube (5 mmol of base added), and gas evolution was followed using a gas buret. Gas evolution was not rapid proceeding to the extent of 40–50% in 2 hr. Gas evolution was more rapid if a few drops of methanol were added after addition of the base, evolution being complete in 30–40 min but remaining in the 40–50% of theoretical range. Complete gas evolution could be obtained at room temperature, but gas measurements could not be as accurately determined due to vaporization of the solvent. Using hexane as solvent a run at room temperature with added methanol gave 100% gas evolution. Yields of spiropentene (detectable in the nmr) were determined by conversion to methylenecyclopropene by method B (see below) and were always less than 10%, based on starting nitrosocarbamate.

N,N-Dimethyl-N′-(2,3-diphenyl-2-cyclopropenyl)urea. The isocyanate prepared as described above was taken up in dry ether and cooled in an ice bath in a flask equipped with a stirrer and gas inlet tube, and dimethylamine was passed into the cold solution for 30–45 min. Filtration gave the urea and evaporation of some of

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[38] R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

the ether solution gave an additional gram of the product. The yield of the urea was 11 g (70%, mp 156–158°). The infrared spectrum of the dimethylurea showed significant absorptions (KBr, cm^{-1}) at 3600, 1800, 1630, and 1600. The nmr spectrum showed resonances at J = 7.17 cps (singlet, NMe_2) 5.87 (doublet, J = 5 cps, cyclopropenyl hydrogen) and at 2.18–2.90 (phenyl, multiplets).

Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.70; H, 6.48; N, 10.07. Found: C, 77.68; H, 6.59; N, 10.06.

N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea. In a 200-ml flask fitted with magnetic stirrer were placed 50 ml of anhydrous ether and 5.0 g (0.018 mol) of N,N-dimethyl-N′-(2,3-diphenyl-2-cyclopropenyl)urea. The mixture was cooled with stirring to −55° and 1.47 g (0.018 mol) of sodium acetate and 25 ml of anhydrous ether containing 1.90 g (0.021 mol) of N_2O_4 were added. Stirring was continued at −55 to −60° for 1.5 hr, after which time 75 ml of precooled pentane was added. The temperature was lowered to −60°, and the mixture was stirred at this temperature for 1 hr. Filtration followed by rapid washing with dilute bicarbonate solution and water gave the crude nitrosourea. This was taken up in benzene and dried over sodium sulfate. The dried benzene solution was concentrated to about 20 ml using a rotary evaporator, and pentane was added. Cooling gave 3.6 g (65%) of the nitrosourea, mp 101–102°.

The ultraviolet spectrum of the nitrosourea in methylene chloride showed absorptions (mμ (log ϵ)) at 291 (4.30), 304 (4.41), and 3.39 (4.30). The nmr spectrum (in τ values) in CCl_4 showed phenyl multiplets at 2.22 and 2.58, a singlet at 5.93, and a singlet at 7.08 with relative areas of 4.0:5.8:0.8:5.2. The infrared spectrum (KBr, cm^{-1}) had absorptions at 3100, 2950, 1805, 1700, 1495, 1460, 1445, 1330, 1250, 1220, 1120, 1090, 1070, 1010, 920, 815, 770, 760, and 690.

Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.41; H, 5.58; N, 13.59.

Preparation of Base-Treated Flask. The reaction flask was filled about half full of heptane, and about 300 mg of potassium *t*-butoxide was added. The mixture was brought to reflux with stirring and allowed to reflux for 1–2 hr. After this time, the mixture was cooled to room temperature; the mixture was poured out, and the flask was washed with heptane several times. Any solid remaining on the walls of the reaction flask was wiped away with tissue paper, and the flask was again rinsed with heptane. The flask was then placed in an oven to dry.

Base-Induced Decomposition on N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea in the Presence of Dimethyl Fumarate. The solvent for these decompositions was degassed by passing a stream of nitrogen through the solvent at reflux for about 5 min. The solvent was then cooled to room temperature under nitrogen before the reactants were added. All reactions were run under a nitrogen atmosphere.

In a typical reaction 0.56 g (1.6 mmol) of the nitrosourea was added to 200 ml of degassed heptane, and the solution was refluxed with stirring for 30 min. At the end of this reflux period, the solution was cooled to room temperature and 3.0 g (21 mmol) of dimethyl fumarate and 0.215 g (1.9 mmol) of potassium *t*-butoxide were added. The mixture was refluxed for 9 hr, or until inspection of the ultraviolet spectrum of aliquots taken at 1-hr intervals showed no decrease in the absorption at 300 mμ.

The spiropentene was isolated from these reactions by cooling to room temperature, filtering, and removing the heptane from the filtrate by vacuum. The residue was then placed in a sublimation apparatus, and the dimethyl fumarate was removed under vacuum. The residue was dissolved in warm dry hexane and cooled to give the spiropentene in 18% yield. No melting point could be obtained for the spiropentene as heating effected conversion to the isomeric methylenecyclopropene.

Variation of the concentration of base had little effect on the yield. Satisfactory results were obtained even in the absence of added base if the reaction flask was first treated with base as described above.

The ultraviolet spectrum (mμ (log ϵ)) in acetonitrile had maxima at 234 (4.55), 240 sh (4.50), and 328 (4.48). The nmr spectrum (in τ values) in $CDCl_3$ showed phenyl multiplets at 2.16 and 2.59, a singlet assigned to the ester methyls at 6.34, and a singlet assigned to the cyclopropyl ring protons at 6.92 with relative areas of 10:6.6:1.9. The infrared spectrum (KBr, PE21, cm^{-1}) showed absorptions at 3000, 2940, 2980, 1800, 1700, 1495, 1425, 1400, 1325, 1304, 1190, 870, 785, 755, and 685.

Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.35; H, 5.45.

The methylenecyclopropene was isolated from these reactions by cooling the reaction solution to room temperature and chromatographing over acid-washed alumina. The methylenecyclopropene was eluted as a bright yellow band with ether. Removal of the ether and recrystallization from ether–pentane gave the bright yellow methylenecyclopropene in 40–50% yield, mp 127–127.5°.

The ultraviolet spectrum (mμ (log ϵ)) of the methylenecyclopropene in acetonitrile had maxima at 244 (4.33), 252 (4.34), 268 (4.26), 298 (4.29), and 378 (3.83). The nmr spectrum in $CDCl_3$ showed phenyl multiplets at 1.67, 2.07, and 2.45, a singlet at 6.18, assigned to the protons of one methyl group, and two unresolved singlets at 6.30 and 6.34 assigned to the other methyl and the methylene protons, having relative area ratios of 10:3:5.4. The infrared spectrum showed significant absorptions (KBr, cm^{-1}) at 1850, 1740, 1670.

Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.39; H, 5.66.

2,3-Diphenyl-2-cyclopropenyl N,N-Dimethylcarbamate. To 150 ml of degassed heptane was added 1.5 g (4.8 mmol) of N,N-dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea. The mixture was refluxed for 30 min and cooled to room temperature and the heptane removed under vacuum at room temperature or below. To the orange residue was added 10 ml of anhydrous ether, and the solution was concentrated with a stream of nitrogen until a precipitate began to form. Ether was added dropwise with stirring until the precipitate dissolved. The solution was scratched vigorously and cooled to give 0.50 g of the carbamate, mp 97–99° dec, 37.4%.[27]

The ultraviolet spectrum of the carbamate had maxima (CH_2Cl_2, mμ (log ϵ)) at 227 (4.37), 232 sh (4.34), 289 sh (4.44), 304 (4.56), and 320 (4.44). The infrared spectrum (Nujol) recorded on a Perkin-Elmer Infracord showed significant absorptions at 1820 (cyclopropene) and 1690 cm^{-1} (carbonyl). The nmr spectrum (in τ values) $CDCl_3$ showed phenyl multiplets at 2.12 and 2.53, a singlet assigned to the ring proton at 4.82, and a singlet assigned to the methyl groups at 7.10 with relative areas of 11.6:1:6.

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.22; H, 6.04; N, 4.82.

Base-Induced Decomposition of 2,3-Diphenyl-2-cyclopropenyl N,N-Dimethylcarbamate in the Presence of Dimethyl Fumarate. To 200 ml of degassed heptane was added 0.240 g (0.83 mmol) of the carbamate, 1.18 g (8.2 mmol) of dimethyl fumarate, and 0.062 g (0.55 mmol) of potassium *t*-butoxide. The mixture was refluxed with stirring for 9 hr. The ultraviolet spectrum of an aliquot at this time showed a broad maximum at 325–330 mμ. A sample of the reaction mixture was removed, and the yield was determined by method A to be 47%, and a second sample was employed to determine the yield by method B to be 67%.

Determination of the Yields of Methylenecyclopropene. Method A. An aliquot of the reaction mixture was extracted with concentrated hydrochloric acid. The acid extracts were diluted with water and extracted with small portions of ether until the ether extract showed no yellow color. The combined ether extracts were washed with water or dilute sodium bicarbonate solution and dried over sodium sulfate. The combined ether extracts were then diluted to a standard volume with acetonitrile, and the yield was calculated using the difference in absorbance at 378 mμ in neutral and acidic solvent. Yields were reproducible for a given reaction, but they were 15–20% lower than yields calculated by method B.

Method B. A portion of the reaction mixture was placed under vacuum to remove the heptane solvent. The residue was taken up in ether and placed on a dry column of silica gel using a nylon tube 1 in. in diameter and of sufficient length to permit the use of a 300:1 ratio of absorbent to sample. The column was developed with pentane keeping the solvent head of the developing solvent at a height of 1 to 2 cm. When the column had been completely developed, a total of 100 ml of solvent was eluted from the bottom of the column, and the solvent was changed to ether. The yellow band was allowed to migrate until it was separated from the top of the column by a distance of 6 in. The nylon column was then cut open and the yellow band removed and extracted with acetonitrile. A standard solution was made of the extracts, and the yield was determined spectroscopically as described in method A. If the solvent were removed after elution of the band under vacuum, the methylenecyclopropene could be isolated and was shown to be relatively pure by melting point (125–126°).

N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl-1-*d*)-urea. To 25 ml of ethyl diazoacetate (K & K Laboratories) was added 7 ml of D_2O. This was stirred for several hours; the layers were separated, and 12 ml of fresh D_2O was added to the ether layer. The mixture was stirred at room temperature overnight. The partially deuterated diazo ester was dried over sodium sulfate and distilled under vacuum.

This sample of partially deuterated ethyl diazoacetate was used to prepare 1,2-diphenylcyclopropene-3-*d*-3-carboxylic acid. Insolubility of the acid made determination of the deuterium content by nmr impractical. The acid was converted to N,N-dimethyl N′-(2,3-diphenyl-2-cyclopropenyl-1-*d*)urea as described previously for the unlabeled compound. From the mass spectrum, run on a Hitachi RMU 6E mass spectrometer, the urea was calculated to be 56.7 ± 0.7% deuterated in the 1 position of the cyclopropenyl ring.

This urea was nitrosated following the usual procedure. Determination of the deuterium content of the nitrosourea by its mass spectrum proved impossible because it gave only peaks of low *m/e* values. It was therefore assumed that there was no loss of deuterium on nitrosation. The nmr spectrum of the nitrosourea in CCl_4, while not giving an accurate measure of the deuterium content, showed an appreciable decrease in the intensity of the ring proton peak relative to the methyl groups.

Decomposition of N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl-1-*d*)urea in the Presence of Dimethyl Fumarate with Added Base. A sample of the partially deuterated nitrosourea was treated with potassium *t*-butoxide and dimethyl fumarate in heptane in exactly the same manner as described above. Following the removal of the heptane solvent, the residue was taken up in anhydrous ether and the ether solution transferred to a sublimation apparatus. The ether was removed with an aspirator and the residue was placed under vacuum (0.005 mm) overnight. The resulting residue was taken up in warm dry hexane, and the spiropentene was allowed to crystallize by cooling overnight. The nmr spectrum (in τ values) of the spiropentene in $CDCl_3$ showed resonances at 6.18 (singlet), 6.34 (singlet), and 6.92 (singlet). The ratio of the area of the resonance at 6.34 to the area of the resonance at 6.92 was essentially 6 to 2. The mass spectrum of the spiropentene showed less than 1% monodeuterated product.

Base-Induced Decomposition of the Dimethylnitrosourea in the Presence of Dimethyl Fumarate and Diphenylpicrylhydrazyl. A base-induced decomposition was run as above using 0.5 g of the nitrosourea in the presence of 11.7 mg of diphenylpicrylhydrazyl. The yield of spiropentene was calculated to be 50% by method B after 9 hr at reflux.

Base-Induced Decomposition of N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea in the Presence of Dimethyl Maleate. These reactions were run in the same manner as those in which dimethyl fumarate was used as an acceptor. In a typical reaction 0.5 g (1.63 mmol) of the nitrosourea was placed in 200 ml of degassed heptane and refluxed for 30 min to effect conversion to the carbamate. The solution was cooled to room temperature and 2 ml (20 mmol) of dimethyl maleate and 0.009 g (0.08 mmol) of potassium *t*-butoxide were added. The mixture was refluxed for 13 hr. At the end of the reflux period the yield of methylenecyclopropene was calculated by method A to be 30%.

The ratio of dimethyl fumarate to dimethyl maleate determined by vpc was 1:15 after 2 hr at reflux. At the end of the reaction the ratio was 1:8.

The solution was placed under vacuum, and the heptane was removed at room temperature or below. Most of the dimethyl maleate was removed from the residue under vacuum. Inspection of the nmr spectrum of the residue in $CDCl_3$ showed only one resonance (at τ 6.92) which could definitely be attributed to the spiropentene. This resonance disappeared on standing overnight with concurrent formation of the spectrum of the methylenecyclopropene. The nmr spectrum of these reaction residues was rather complex (much more so than in the reactions with dimethyl fumarate) but the presence of a second resonance which disappeared on standing could have been detected if such an absorption had an area of as little as 5% of the resonance at τ 6.92.

Inspection of the ultraviolet spectrum of the nmr sample after standing overnight showed no remaining absorption at 330 mμ.

Base-Induced Decomposition of N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea in the Presence of Fumaronitrile. In a typical reaction 0.5 g (1.63 mmol) of the nitrosourea was added to 200 ml of degassed heptane in a base-treated flask prepared as described previously. The mixture was refluxed with stirring for 30 min, then cooled to room temperature. To the cooled solution was added 1.0 g (12.8 mmol) of fumaronitrile. The mixture was then refluxed for 21 hr.

On cooling to room temperature the crude spiropentene precipitated. Recrystallization from chloroform pentane afforded 0.091 g, 20.8%, of the spiropentene. No melting point could be determined as heating effected conversion to the isomeric methylenecyclopropene.

The ultraviolet spectrum showed maxima (dioxane, mμ (log ϵ)) at 232 (4.33), 238 sh (4.28), and 321 (4.35). The infrared spectrum (KBr, cm^{-1}) showed absorptions at 3035, 2230, 1830, 1450, 1375, 1280, 1075, 1030, 825, 760, 690 and 680. The infrared spectrum showed no carbon–carbon double-bond absorption. The nmr spectrum (in τ values) run in $CDCl_3$ had phenyl multiplets at 2.23 and 2.40 and a singlet assigned to the cyclopropyl ring protons at 7.30. The relative areas of the combined phenyl multiplets to the ring protons was 10:1.93.

Anal. Calcd for $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 84.80; H, 4.37; N, 10.22.

The corresponding methylenecyclopropene could be isolated from these reactions by cooling the reaction mixture to near room temperature and chromatographing over acid-washed alumina. Elution with pentane and pentane–ether mixture in which the proportion of ether was gradually increased to 100% gave the yellow methylenecyclopropene in 19% yield. An analytical sample of recrystallized benzene–pentane had mp 180°.

The ultraviolet spectrum showed maxima (dioxane, mμ (log ϵ)) at 243 sh (4.45), 251 (4.49), 261 (4.45), 271 (4.47), 284 (4.30), 292 sh (4.27), 307 sh (4.06), and 37.78 (3.95). The nmr spectrum (in τ values) in $CDCl_3$ had phenyl multiplets at 1.96, 2.09, and 2.36 and a singlet assigned to the methylene protons at 6.48 with relative area ratios of 10:2.05. The infrared spectrum (KBr, cm^{-1}) had absorptions at 3060, 2950, 2250, 2190, 1855, 1815, 1595, 1560, 1480, 1445, 1410, 1355, 1235, 1195, 1165, 1140, 1100, 1080, 1020, 920, 905, 840, 765, 720, and 685.

Anal. Calcd for $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44. Found: C, 84.84; H, 4.61; N, 10.58.

Decomposition of N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea in a Base-Treated Flask in the Presence of Diethyl Fumarate. The flask was prepared as has been described. To 200 ml of degassed heptane in a base-treated flask was added 0.5 g (1.63 mmol) of the nitrosourea, and the mixture was refluxed for 30 min. After cooling to room temperature, 2 ml (12.3 mmol) of dimethyl fumarate was added. The mixture was refluxed for 8 hr. The ultraviolet spectrum of the reaction mixture at this time showed a broad maximum in the region of 330 mμ. The heptane was removed on a rotary evaporator with a water bath at a temperature of less than 70°, and 10 ml of hexane was added to the residue. Cooling overnight gave a fluffy white solid which was recrystallized from hexane.

The ultraviolet spectrum of this material in cyclohexane had maxima (mμ (log ϵ)) at 236 (4.57), 243 sh (4.51), and 332 (4.50). The infrared spectrum showed absorptions (KBr, cm^{-1}) at 2975, 1810, 1710, 1490, 1440, 1360, 1290, 1175, 1165, 1150, 1030, 860, 780, 750, and 680.

On heating or treatment with dilute acid, this material turned yellow and gave an ultraviolet spectrum similar in shape and positions of maxima to the methylenecyclopropene. These data would seem to indicate that the spiropentene is formed from diethyl fumarate, although a satisfactory analysis could not be obtained for this material.

N,N,N,N′-Tetramethylfumaramide. To 14 ml of dimethylamine in 100 ml of anhydrous ether cooled in a Dry Ice bath was added in small portions with stirring 6 ml of fumaryl chloride to 30 ml cold ether. The mixture was stirred in the Dry Ice bath for 1 hr and then extracted with a saturated aqueous solution of potassium carbonate. The organic layer was separated and dried with sodium sulfate. Removal of the solvent gave 1 g of a white solid, mp 70–75°. From the infrared spectrum, this appeared to be a hydrated form of the desired amide. The solid was dissolved in benzene and the benzene was distilled off on a steam bath to a volume of 5 ml (100 ml of benzene removed). Cooling gave a white solid, mp 129–130° (lit.[39] mp 130°). The infrared spectrum of this solid also appeared to have an O–H absorption at 3500 cm^{-1}. The material was sublimed at 100° (0.05 mm) to give a white solid, mp 129–130°. The infrared spectrum (KBr) recorded on a Perkin-Elmer Infracord showed a weaker absorption at 3500 cm^{-1} as well as absorptions at 2950, 1630 (s) (C=O), 1495, 1420, 1390, 1260, 1140, 1060, 980, 775, and 760 cm^{-1}. The amide apparently hydrates readily on exposure to moist air.

Decomposition of N,N-Dimethyl-N′-nitroso-N′-(2,3-diphenyl-2-cyclopropenyl)urea in the Presence of N,N,N′,N′-Tetramethylfumaramide in a Base-Treated Flask. To 20 ml of degassed heptane

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[39] H. B. Kostenbauder and T. Higuchi, *J. Am. Pharm. Assoc.*, **45**, 810 (1956).

in a base-treated flask was added 0.2 g (0.65 mmol) of the nitrosourea. The mixture was refluxed for 45 min and cooled to room temperature, and 1 g (6.2 mmol) of the amide was added. The mixture was refluxed for 18 hr and then cooled to room temperature. On cooling, a precipitate separated which was a mixture of the starting amide and an orange solid. Recrystallization from dry benzene gave an orange crystalline material, mp 245–250°. The ultraviolet spectrum of this material in acetonitrile was similar in shape to the spectra of the methylenecyclopropenes obtained with dimethyl fumarate and fumaronitrile with maxima at 250, 260, 270, 300, and 400 mμ, however, on addition of a few drops of HBF$_4$ the spectrum changed to resemble that of covalently bonded diphenylcyclopropenyl compound. The infrared spectrum run on a Perkin-Elmer Infracord (KBr) showed absorptions at 3500 w, 2950, 1850 and 1800 (methylenecyclopropene), 1640 s and 1610 s (carbonyls), 1490, 1450, 1370, 1340, 1190, 1145, 1120, 1075, 825, 760, 745, 710, and 685 cm^{-1}.

Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.53; H, 6.61; N, 7.64.

When attempts were made to recrystallize some of the orange solid, the solutions on standing overnight lost the deep orange color, and from these solutions a colorless solid was isolated in small amounts which turned orange when an attempt was made to determine the melting point. This material turned orange at 80–100° and melted at 220–250°. An infrared spectrum of this material (KBr) recorded on a Perkin-Elmer Infracord showed absorptions at 3500, 2910, 1795 (cyclopropene), 1650 and 1610 (carbonyls), 1495, 1400, 1225, 1140, 1090, 1065, 995, 920, 900, 760, and 685 cm^{-1}. The ultraviolet spectrum in acetonitrile showed maxima at 311, 295, and 281 mμ. Attempts to purify this material failed.

The reaction with the amide was repeated a number of times; duplication of conditions used in the successful run was attempted in all. No more of the orange solid thought to be the methylenecyclopropene or the unknown colorless material was isolated.

Diphenylcyclopropenyl Hexafluorophosphate. The hexafluorophosphate was prepared by a method developed by Farnum.[40] Hexafluorophosphoric acid (65%) (4.8 ml) was added dropwise with stirring to 25 ml of acetic anhydride with ice-bath cooling. The solution was kept at 0° while 2.5 g (0.01 mmol) of finely powdered 1,2-diphenylcyclopropene-3-carboxylic acid was added in small portions over a period of 2 hr. The mixture was stirred for 30 min after the addition of the acid was complete. After cooling to −5° and inducing crystallization by scratching, 25 ml of benzene was added, and the mixture was chilled to freezing. Filtration, washing with cold acetic anhydride benzene (1:1), and then with benzene followed by air drying gave 2.5 g, 70%, of the salt, mp 170–180° dec (lit.[40] mp 170–180° dec). The ultraviolet and infrared spectra were in agreement with reported data.

Reaction of Diphenylcyclopropenyl Hexafluorophosphate with Dimethyl Fumarate and Potassium *t*-Butoxide. To 200 ml of degassed heptane was added 3.0 g of dimethyl fumarate and 30 mg of potassium *t*-butoxide. The mixture was brought to reflux, then cooled to room temperature. To the cooled mixture was added 0.397 g (1.18 mmol) of diphenylcyclopropenyl hexafluorophosphate. The mixture was refluxed for 20 hr, during which time the reaction was monitored by ultraviolet spectroscopy and tlc. There was no noticeable change in either during the reflux period. The cation proved only slightly soluble in heptane. Inspection of the reaction mixture by tlc showed no methylenecyclopropene formation.

2,3-Diphenyl-2-cyclopropenyl Acetate. To an acetic anhydride solution containing 3.0 g (8.9 mmol) of diphenylcyclopropenyl hexafluorophosphate was added with stirring a slurry of 0.720 g (8.8 mmol) of sodium acetate in 20 ml of acetic anhydride. The mixture was allowed to stir at room temperature for 10 min after which time 20 ml of benzene were added. The mixture was cooled to 0°, and the solid which separated was removed by filtration. The benzene was removed from the solution on a rotary evaporator, and the solution was concentrated under vacuum to a volume of 20 ml at which point a solid began to form. Cooling and filtration gave 2.0 g, 91%, of the acetate which could be recrystallized from acetic anhydride and dried under vacuum to give a white solid, mp 112–112.5°.

The ultraviolet spectrum of the acetate had maxima (CH$_3$CN, mμ (log ε)) at 221 (4.33), 229 sh (4.24), 285 sh (4.37), 298 (4.43), and 313 (4.34). The infrared spectrum (IR10; cm^{-1}) showed absorptions at 3080, 2930, 1800, 1730, 1495, 1445, 1370, 1325, 1305, 1250, 1240, 1175, 1125, 1075, 1055, 900, 760, and 690. The nmr spectrum (in τ values) of the acetate in CDCl$_3$ showed phenyl multiplets at 2.17 and 2.55, a singlet assigned to the ring proton at 4.82, and a singlet assigned to the methyl group at 7.97 having relative areas of 4:6:1:3.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.77; H, 5.78.

2,3-Diphenyl-2-cyclopropenyl Benzoate. To 300 ml of AR benzene was added 2 ml of acetic anhydride. The solution was stirred for a few minutes and 5.0 g (0.015 mol) of diphenylcyclopropenyl hexafluorophosphate and 2.3 g (0.016 mol) of sodium benzoate were added. The mixture was allowed to stir at room temperature for a period of 20 hr. The insoluble portion was filtered off and the solution was concentrated under vacuum to a volume of approximately 5 ml. To this was added dry hexane, and the solution was cooled giving the benzoate in 21% yield. The benzoate was recrystallized from hexane giving colorless needles, mp 112–115°.

The ultraviolet spectrum of the benzoate showed maxima (CH$_3$CN, mμ (log ε)) at 222 (4.47), 228 (4.57), 284 sh (4.45), 290 (4.42), 298 (4.59), and 319 (4.57). The infrared spectrum (IR10; cm^{-1}) showed absorptions at 3060, 3010, 2980, 1800 (cyclopropene), 1700 (carbonyl), 1600, 1485, 1445, 1335, 1250, 1165, 1120, 1100, 1065, 1025, 910, 885, 855, 750, 725, 710, and 680. The nmr spectrum (in τ values) in CDCl$_3$ showed phenyl multiplets at 2.09 and 2.54 and a singlet assigned to the ring proton at 4.54 with relative area ratios of 15:1.05 (combined phenyl multiplets to singlet).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.57; H, 5.19.

2,3-Diphenyl-2-cyclopropenyl *p*-Nitrobenzoate. To 300 ml of AR benzene was added 2 ml of acetic anhydride. This solution was stirred for a few minutes and 5.0 g (0.015 mol) of diphenylcyclopropenyl hexafluorophosphate and 3.0 g (0.016 mol) of sodium *p*-nitrobenzoate were added. The mixture was stirred at room temperature overnight. The insoluble portion was filtered off and the benzene removed under vacuum to a volume of 125 ml; a precipitate began to form almost immediately. The solution was cooled for 1 hr and filtered to give a 19% yield of the *p*-nitrobenzoate which was a fluffy white solid, mp 165–167°.

The ultraviolet spectrum of the ester had maxima (CH$_3$CN, mμ (log ε)) at 200 (4.48), 228 sh (4.40), 285 sh (4.54), 297 (4.60), and 313 (4.46). The infrared spectrum (IR10; cm^{-1}) had absorptions at 3050, 2915, 1800 (cyclopropene), 1710 (carbonyl), 1610, 1530, 1345, 1270, 1170, 1130, 1100, 1010, 895, 855, 750, 720, and 685. The nmr spectrum (in τ values) in CDCl$_3$ showed a singlet at 1.77, phenyl multiplets at 2.09 and 2.47, and a singlet assigned to the ring proton at 4.44 having relative area ratios of 4:4.5:6.5:1.

Anal. Calcd for $C_{22}H_{15}NO_4$: C, 73.94; H, 4.23; N, 3.92. Found: C, 74.19; H, 4.39; N, 3.93.

Reaction of 2,3-Diphenyl-2-cyclopropenyl Esters with Potassium *t*-Butoxide in the Presence of Dimethyl Fumarate. To 200 ml of degassed heptane were added 1.0 mmol of the ester, 10 mmol of dimethyl fumarate, and 3 mmol of potassium *t*-butoxide. The mixture was refluxed for periods varying from 20 to 54 hr. The yields of methylenecyclopropene were calculated by method B at the completion of the reflux periods and are given in the text, along with the reflux times.

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(40) D. G. Farnum, private communication.