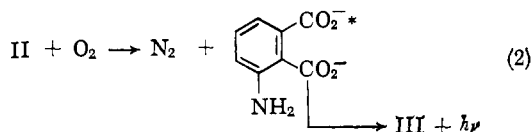
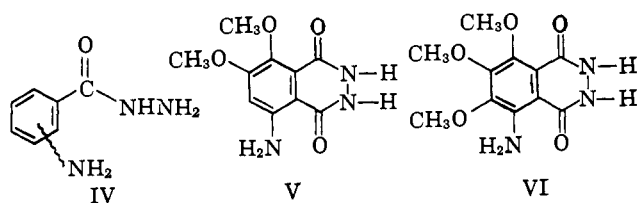


or protonated fully⁵—(emitting at 424 m μ), and an excited aminophthalate ion not bonded in this way (emitting at 485 m μ). As water is added to a dimethyl sulfoxide system, the chemiluminescence peak at 424 m μ develops at a slower rate than the fluorescence peak at 424 m μ (Fig. 1). This effect is not understood at present; it may be the result of emission of the aminophthalate ion from slightly different solvent cages in the two excitation pathways (*vide infra*), possibly as the result of the involvement of nitrogen in only the chemiluminescence pathway.¹ Similar fluorescence data have been obtained for three other phthalic hydrazides. Related experiments eliminate from consideration as possible light emitters in the reaction compounds such as aminophthalic anhydride, luminol, and sodium aminobenzoate.

The main steps in the chemiluminescence of luminol are then the reaction of the dinegative ion of luminol with oxygen to yield, ultimately, an excited singlet state of the aminophthalate ion, and the emission of a photon by this species. This view of the chemiluminescence is supported by the fact that a parallelism



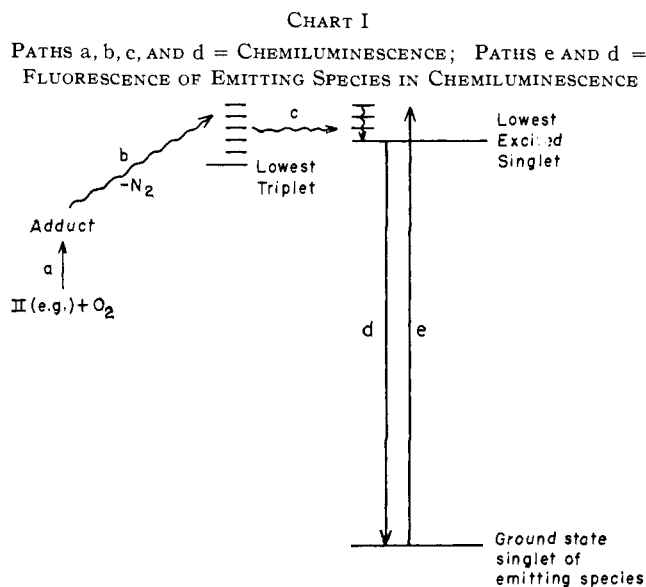
exists between the efficiencies of fluorescence of a number of aromatic acid anions and the chemiluminescent efficiencies of the corresponding hydrazides. Thus, the *o*- and *m*-aminobenzhydrazides (IV) are chemiluminescent (in dry dimethyl sulfoxide with potassium *t*-butoxide and oxygen) and the *o*- and *m*-aminobenzoates are fluorescent; the corresponding *para* derivatives, however, are neither chemiluminescent nor fluorescent in the visible region. Similar trends are noted in the hydroxybenzhydrazide series. In general, electron-supplying substituents increase the efficiency of emission in both chemiluminescence and fluorescence.⁶ Both compounds V and VI, to illustrate the point, are more efficient in chemiluminescence than luminol (by 13 and 30%, respectively, in dimethyl sulfoxide). Only these two compounds and a third reported by Gundermann and Drawert⁷ have been found to date to be more efficient than luminol in light production.



The quantum yield for the chemiluminescence of luminol in dimethyl sulfoxide is about 5%; this is the highest quantum yield yet measured for a chemiluminescent reaction.⁸ Since the fluorescence yield of the aminophthalate ion is about 5–10%,⁸ it is apparent that 50% or more of the luminol molecules yield aminophthalate ions in the excited state.

The precise mechanism of formation of excited state species from ground state molecules in solution at room temperature (eq. 2) is unknown. The only clue is that molecular oxygen is a reactant or product in

most, if not in all, chemiluminescent reactions.^{8b,9} Since oxygen is in a triplet ground state, adducts of oxygen may exist as triplet state complexes or diradicals.¹⁰ Loss of nitrogen from the adduct (or the gain of energy by some other process in the general case) could lead to a vibrationally excited triplet state of the potential emitter. Intersystem crossing to an isoenergetic level of the excited singlet state and emission of a photon would then complete the process (Chart I).^{11,12}



The light emitted in the chemiluminescence of luminol (*ca.* 350 to 600 m μ) has an energy equivalence of *ca.* 50 to 80 kcal. per mole. Generalizing from our results and examples in the literature, it seems probable that most exergonic reactions¹³ yielding fluorescent products and involving oxygen will be chemiluminescent.

Acknowledgment.—We thank the National Institutes of Health for its support of this work (Grant No. 10849), and Dr. Charles P. Kulier for valued assistance.

(9) See review articles listed previously.¹ For exceptions in bioluminescence, see J. W. Hastings and Q. H. Gibson, *J. Biol. Chem.*, **238**, 2537 (1963).

(10) D. Kearns and S. Ehrenson [*J. Am. Chem. Soc.*, **84**, 739 (1962)] have proposed that Yang's diradical [N. C. Yang and A. J. Castro, *ibid.*, **82**, 6208 (1960)] has a triplet ground state.

(11) The reverse process is well established [D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949)] often proceeding with high efficiency [H. L. J. Bäckström and K. Sandros, *ibid.*, **23**, 2197 (1955); W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961)]. Triplet states are efficiently quenched by oxygen [H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958)]; a delayed fluorescence type of luminescence from the ground vibrational level of the triplet state [C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1961)] seems unlikely, then, in chemiluminescence. See also ref. 2b and E. Chandross, *Tetrahedron Letters*, 761 (1963). The direct formation of an excited singlet state is, of course, possible; the virtual necessity of oxygen is not then apparent, however.

(12) Sodium aminophthalate is strongly phosphorescent at low temperatures.

(13) H. Eyring, "The Luminescence of Biological Systems," F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D. C., 1955, p. 244.

(14) National Science Foundation Cooperative Graduate Fellow, 1960–1963.

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Synthesis of a Methylene-cyclopropane

Sir:

The number of aromatic cyclopropenium compounds isolated in stable form over the past 6 years has steadily increased since Breslow's initial preparation of the

(5) Th. Förster, "Photochemistry in the Liquid and Solid States," L. J. Heidt, et al., Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 10.

(6) H. D. K. Drew and F. H. Pearman, *J. Chem. Soc.*, 586 (1937); A. Spruit-van der Berg, *Rec. trav. chim.*, **69**, 1536 (1950).

(7) K. D. Gundermann and M. Drawert, *Chem. Ber.*, **95**, 2018 (1962).

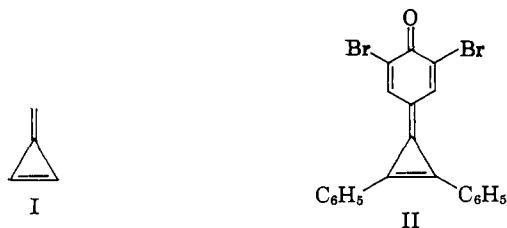
(8) Unpublished work by Professor H. H. Seliger and Dr. J. Lee, Department of Biology, The Johns Hopkins University.

TABLE I
 ELECTRONIC SPECTRA

Compound	Solvent	λ_{\max} , $m\mu$	$\log \epsilon$	λ_{\max} , $m\mu$	$\log \epsilon$	λ_{\max} , $m\mu$	$\log \epsilon$
V	Isooctane	244	4.42	299	4.26	423 (sh)	3.71
		252	4.43	312	4.12	452 (sh)	3.23
		268	4.33	382	3.89		
		286	4.24	400	3.87		
V	CH ₃ CN	242	4.39	286 (sh)	4.30	371	3.95
		250	4.39	295	4.35		
		267	4.34	308	4.24		
V	CH ₃ CN, HBF ₄	247	4.22	293	4.51	307	4.53
VIIa	CH ₃ CN-10% C ₂ H ₅ OH, 0.1 N HClO ₄ ^a	246	4.03	292	4.50	305	4.52
VIIa	4% CH ₃ CO ₂ H, 10% H ₂ SO ₄ ^b			293	4.48	306	4.49
VIIb	23% C ₂ H ₅ OH, 1 N HCl ^c			292	4.50	305	4.52

^a Ref. 9a. ^b Ref. 9b. ^c Ref. 10.

triphenylcyclopropenyl cation in 1957.¹ The highly strained resonance-stabilized methylenecyclopropene system (I) has, however, eluded previous synthetic efforts,² although Kende has recently reported³ the preparation of a stable crystalline quinocyclopropene (II). We now wish to report the successful synthesis of a stable substituted methylenecyclopropene by the convenient Wittig olefin route using a cyclopropenone derivative as the carbonyl moiety.⁴



Reaction of diphenylcyclopropenone (III)⁵ and carbethoxymethylenetriphenylphosphorane (IV)⁶ in benzene or methylene chloride solvent proceeds readily at room temperature as evidenced by a deepening yellow coloration of the initially colorless solution and the appearance of new absorption bands in the ultraviolet and visible spectrum of the solution. A slowly developing maximum, centered at about 380 $m\mu$ with considerable tailing into the visible, accounts for the color intensification in the reaction. Alumina chromatography of the solution after *ca.* 4-days reaction yielded a viscous yellow oil from which 1,2-diphenyl-4-carbethoxymethylenecyclopropene (V) was obtained as a bright yellow crystalline solid in 10–20% yield⁷ after some solvent manipulations, m.p. 72–75° (from hexane). *Anal.* Calcd. for C₁₉H₁₆O₂: C, 82.58; H, 5.85. Found: C, 82.89; H, 5.70. Triphenylphosphine oxide was also isolated from the same reaction in somewhat higher yields.

In the infrared V showed strong to moderate absorption at 5.45, 5.95, 6.50, 8.70, 12.90, 13.15, and 14.60 μ in good agreement with the major structural features of

(1) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957).
 (2) Cf. R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

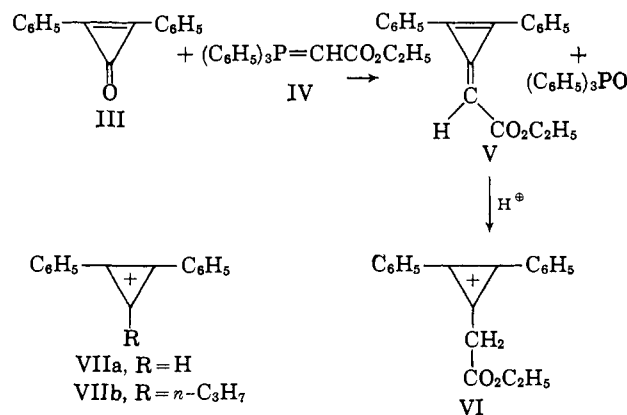
(3) A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963).

(4) W. M. Jones and J. M. Denham [*ibid.*, **86**, 944 (1964)] have isolated a stable methylenecyclopropene derivative from a reaction in which the attempt was made to generate diphenylcyclopropenylidene in the presence of dimethyl fumarate. The yield of methylenecyclopropene in this remarkable reaction was 48% with none of the desired spiroentene product being obtained.

(5) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959); M. Volpin, Y. Koreskov, and D. Kursanov, *Izv. Akad. Nauk SSSR*, 560 (1959).

(6) O. Isler, *et al.*, *Helv. Chim. Acta*, **40**, 1242 (1957). This stable methylenephosphorane is commercially available from the Aldrich Chemical Company, Milwaukee, Wisconsin.

(7) The range in yield is that obtained from several reactions run prior to information on conditions required for optimum yields. All reactions were conducted on approximately a 0.5 mmole scale. Studies are currently underway to improve the synthetic aspects of this reaction.



the proposed structure.⁸ The electronic spectra of V in isooctane and acetonitrile solvents are recorded in Table I. Three main absorption groups are noted in these spectra, two of which consist of a trio of bands centered around 250 and 300 $m\mu$ and are characteristic of the covalent diphenylcyclopropene chromophore. The remaining long wave length absorption band centered about 380–390 $m\mu$ in isooctane displays striking solvent sensitivity, a blue shift of approximately 15 $m\mu$ being observed for this band on change of solvent from isooctane to acetonitrile. The addition of a fraction of a drop of 48% fluoroboric acid to an acetonitrile solution of V destroyed the original spectrum and immediately produced the characteristic spectrum of the diphenylcyclopropenyl cation (VIIa).⁹ This is consistent with protonation at the *exo* carbon of V to give the resonance-stabilized cation VI under the acidic conditions. The reported spectrum of VIIa is included in Table I along with that for the propyldiphenylcyclopropenyl cation (VIIb).¹⁰

The n.m.r. spectrum of V offered the final structure proof and, in addition, provided evidence on the question of aromaticity and charge separation in methylenecyclopropenes. In carbon tetrachloride V exhibited proton absorption at τ 8.70 (triplet), 5.85 (quartet), 4.98 (singlet), and 2.70, 2.20, and 1.48 (unresolved multiplets); aromatic:aliphatic proton area ratio 1.5:1. Comparison of the *exo*-methylene proton signal for V at τ 4.98 with that for Feist's ester (VIII), τ 4.1,¹¹ and the more relevant methylenecyclopropane ester IX, τ 3.2,¹² revealed a significantly large upfield shift for the methylenecyclopropene proton. The increased shielding of this proton seems most readily accounted for by a sizable contribution of di-

(8) Moderate to strong absorption around 5.5 μ is characteristic of a disubstituted cyclopropene double bond, *cf. ref. 9b.*

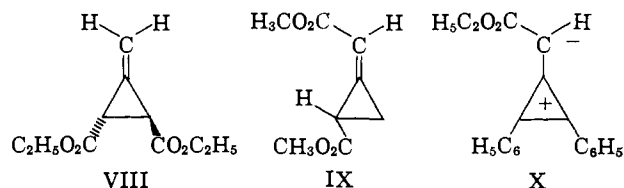
(9) (a) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960); (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

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

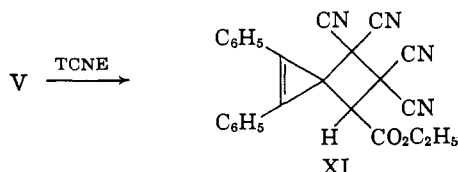
(11) M. G. Ettliger and F. Kennedy, *Chem. Ind. (London)*, 166 (1956).

(12) E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5386 (1959).

polar form X to the resonance hybrid. The effect of solvent on the long wave length absorption band of V in the ultraviolet likewise supports the view of a highly polar ground state. Further studies to check this point are currently in progress including dipole moment measurements of V and similar systems.



Preliminary observations on the stability and chemical reactivity of V suggest that the chemistry of methylenecyclopropenes may not be too unlike that of their reactive seven-membered ring counterparts, the heptafulvenes. Unless V is isolated and carefully stored in a highly pure solid form, it will resinify within a few weeks at normal room temperature conditions. Although no apparent reaction of V with dimethyl acetylenedicarboxylate is observed at room temperature,¹³ an immediate reaction with tetracyanoethylene (TCNE) in acetonitrile solvent is noted by disappearance of the long wave length band at 371 m μ and appearance of a new peak at 322 m μ . The retention of the typical absorption pattern of the covalent diphenylcyclopropenes in the 300 m μ region of this spectrum suggests the possible formation of the interesting spirohexene derivative XI. Our investigations of this and other reactions of V are continuing.



The application of the Wittig olefin synthesis to the preparation of other methylenecyclopropenes, and, similarly, to the preparation of heptafulvenes from tropone and tropolone derivatives is apparent. It is further apparent that the stability of and the nature of substituents on the methylenephosphorane and the method of its generation should have an important bearing on the success of the synthesis. The establishment of the relevant significance of these factors requires further investigation.

(13) For the pertinent reaction of dimethyl acetylenedicarboxylate with heptafulvene, see W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1980).

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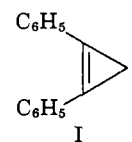
Attempts to Generate a Cyclopropenylidene. I. An Unexpected Synthesis of a Methylene-cyclopropene

Sir:

As a continuation of our investigations on small ring carbenes,¹ we have attempted to generate 2,3-diphenylcyclopropenylidene (I). We felt that this would be a particularly interesting species since its chemical properties would probably be more nucleophilic² in character than a typical alkylidene because of conjugation

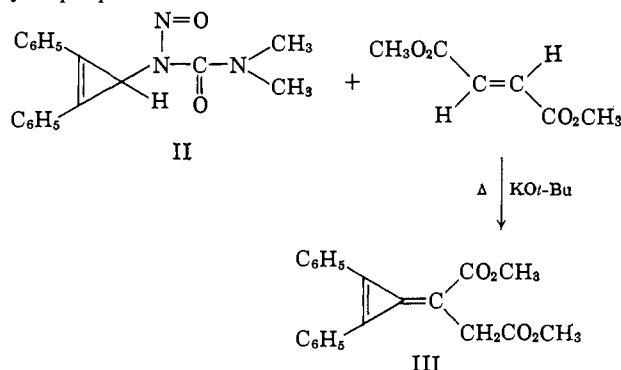
(1) Cf. W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

(2) For a review dealing with nucleophilic carbenes, see H. W. Wanzlick, *Angew. Chem. Intern. Ed. Engl.*, **1**, 75 (1962).



of the double-bond electrons with the vacant orbital of the carbene.

In this communication we wish to report the synthesis of one potential cyclopropenylidene progenitor, N,N-dimethyl-N'-nitroso-N'-(2,3-diphenyl-2-cyclopropenyl)urea (II). Furthermore, we wish to report that the reaction of this material with dimethyl fumarate and potassium *t*-butoxide at 98° gives rise to a good yield (48%) of an adduct that corresponds to the addition of 2,3-diphenylcyclopropenylidene to dimethyl fumarate and has the structure of the methylenecyclopropene III.



This result constitutes an unexpected synthesis of a rather elusive³ and inherently very interesting type of compound.

N,N-Dimethyl-N'-(2,3-diphenyl-2-cyclopropenyl)urea was synthesized from 1,2-diphenylcyclopropene-3-carboxylic acid⁴ via the acid chloride, the acid azide, the isocyanate, and the dimethylurea in the same manner as we have reported for the synthesis of N-(2,2-diphenylcyclopropyl)urea.¹ Under typical nitrosating conditions, the nitrosourea (II) is quite unstable. For this reason, a variation of White's method⁵ was used to effect the nitrosation of the urea. In a typical run, 0.9 g. of the urea was treated with an equimolar amount of dinitrogen tetroxide in 25 ml. of ether in the presence of an equimolar amount of sodium acetate at -55°. The mixture was stirred for 2 hr. at this temperature, an equal volume of cold pentane was added, and the mixture filtered. The residue of yellow solid was washed rapidly with very dilute sodium bicarbonate solution and water and dried. Recrystallization from benzene-pentane gave 73% of beautiful yellow crystals of the nitrosourea,⁶ m.p. 96-97° dec., analytical sample, m.p. 102° dec. The nitrosourea is stable for months in the refrigerator but is remarkably unstable to protonic acids (even as weak as methanol).

Thermal decomposition of this material in the presence of dimethyl fumarate has been carried out under a variety of conditions. The conditions that we have found to be most effective for producing the adduct III are as follows. To 200 ml. of degassed (with argon) heptane was added 0.5 g. of the nitrosourea and 3.0 g. of dimethyl fumarate. The mixture was refluxed for 30 min., cooled to room temperature, 0.250 g. of potassium *t*-butoxide added, and the mixture re-

(3) Cf. A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963), and references cited therein. For a very straightforward synthesis of this type of compound, see M. A. Battiste, *ibid.*, **86**, 942 (1964).

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

(5) See E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

(6) All new compounds gave correct elemental analyses.