

Figure 1. Interaction of fluorenone triplet with para-substituted dimethylanilines.

$3.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.¹² Results are summarized in Table I.

Table I. Photoreduction and Quenching of 0.003 *M* Fluorenone by Para-Substituted Dimethylanilines, $\text{X}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$, in Benzene

<i>p</i> -X	Quantum yield ^a	$k_{\text{H}}/k_{\text{ir}}^b$	k_{ir} , $\text{M}^{-1} \text{ sec}^{-1}$	σ^+
-CN	0.09	0.11	5.4×10^6	+1.00 ^c
-CO ₂ C ₂ H ₅	0.12	0.17	4.7×10^7	+0.48
-Br	0.23	0.28	3.3×10^8	+0.15
-Cl	0.31	0.34	2.8×10^8	+0.11
-H	0.44	0.52	6.0×10^8	0.00
-CH ₃	0.60	0.64	1.6×10^9	-0.31
-SCH ₃	0.29	0.31	6.7×10^9	-0.60
-OC ₂ H ₅	0.35	0.37	9.6×10^9	-0.78 ^d
-NHCOCH ₃	~0.02		4.1×10^{10e}	-0.60
-N(CH ₃) ₂	~0.02		1.6×10^{10e}	-1.70

^a Observed quantum yields for photoreduction of fluorenone by 0.01 *M* dimethylanilines. ^b The fraction $f = k_{\text{H}}/(k_{\text{H}} + k_{\text{e}})$, intercept of plot of $1/f$ vs. $1/c$ divided by φ_{iso} . ^c σ^- value for *p*-CN. ^d Value is for *p*-OCH₃. ^e Value of k_{q} , determined by use as quencher for photoreduction of fluorenone by dimethylaniline.

Values of k_{ir} are high, slopes of the inverse plots are small, and quantum yields at 0.01 *M* amine are little less than the extrapolated values. Values of k_{ir} range from $5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ for *p*-CN to $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for *p*-N(CH₃)₂. A linear plot of $\log k_{\text{ir}}$ vs. σ^+ may be constructed, $\rho = -1.83$. This supports development of positive charge at N and the charge-transfer mechanism. Most of the values of σ^+ are based on development of positive charge at carbon α to phenyl.¹³ The first and last members of the series are exceptional. For *p*-CN, σ^- fits the plot, indicating important stabilization of the ground state. *p*-N(CH₃)₂ lies off the plot since the rate has become essentially diffusion controlled and can no longer respond to increasingly negative σ^+ .

Quantum yields for reduction pass through a maximum. They rise from 0.09 at *p*-CN to 0.60 at *p*-CH₃, as electron-attracting substituents decrease not only k_{ir} but also f , and favor quenching. Substituents with more negative values of σ^+ than methyl raise k_{ir} but

(12) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(13) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

enhance k_{e} . *p*-Ethoxy and *p*-methylthio show lower quantum yields while *p*-dimethylamino and *p*-acetamido hardly photoreduce and are very effective quenchers. Their high values of k_{ir} are determined by study of them as quenchers of the photoreduction of fluorenone by dimethylaniline. This quenching may result from stabilization of the cationic part of the CT complex by interaction with electrons of the second substituent.



Alternatively, conjugation of n electrons of two such substituents with the aromatic ring may allow the triplet to interact directly with and be quenched by the aromatic system. The quenching depends on or is enhanced by the presence of the two substituents, since the related monosubstituted compounds, acetanilide, phenyl methyl thioether, and phenetole, do not quench this reaction. However *p*-ethoxyacetanilide is an effective quencher, $k_{\text{q}}(k_{\text{ir}}) \sim 7 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$.

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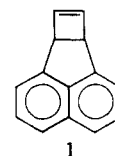
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Naphtho[1,8]bicyclo[3.2.0]hepta-2,6-diene. Synthesis and Rearrangement to Pleiadiene¹

Sir:

In conjunction with our interest in the chemistry of cyclobutane systems bonded to the peri positions of a naphthalene moiety,² we have synthesized naphtho-[1,8]bicyclo[3.2.0]hepta-2,6-diene (1). This compound,



in addition to being useful for the synthesis of a number of derivatives of this ring system, has also interesting thermal and photochemical behavior.

Initially, the synthesis of 1 was effected in 2.4% overall yield from acenaphthylene as outlined in Chart I.³

The structures of adducts 2a and 2b were confirmed by conversion to the corresponding methyl esters and comparison of their nmr spectra with those reported by Rautenstruch and Wingler.⁴ Identification of 1, mp 118–119°, was made chiefly on the basis of its spectral data: nmr (CCl₄) τ 2.3–3.0 (multiplet, 6 H, aromatic), 3.72 (singlet, 2 H, -CH=CH-), and 5.39 (singlet, 2 H, benzylic CH); ir (CHCl₃) 2934, 1617,

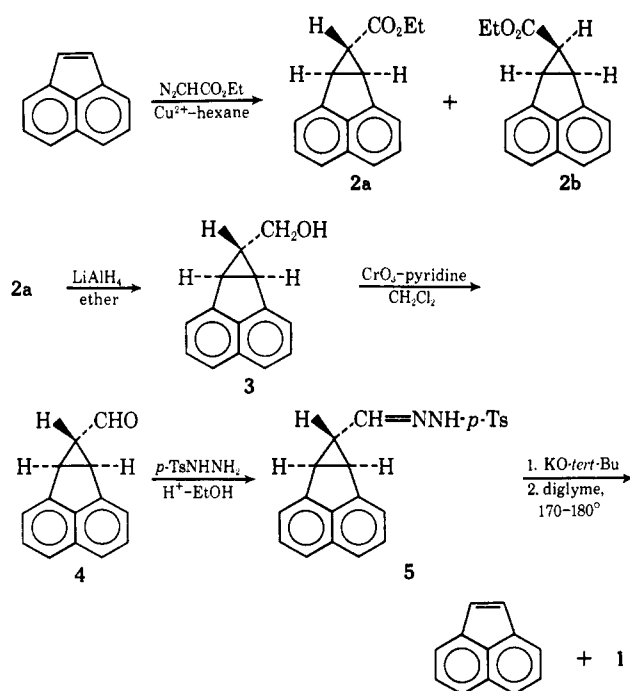
(1) The partial support of this research by the National Science Foundation (GP 13085) is acknowledged with pleasure.

(2) (a) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, in press; (b) see abstracts of 21st National Organic Chemistry Symposium, Salt Lake City, Utah, 1969, pp 62–70; (c) presented in part at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, Switzerland, 1970.

(3) Satisfactory analyses and spectral data were obtained for all key compounds.

(4) V. Rautenstruch and F. Wingler, *Tetrahedron Lett.*, 4703 (1965).

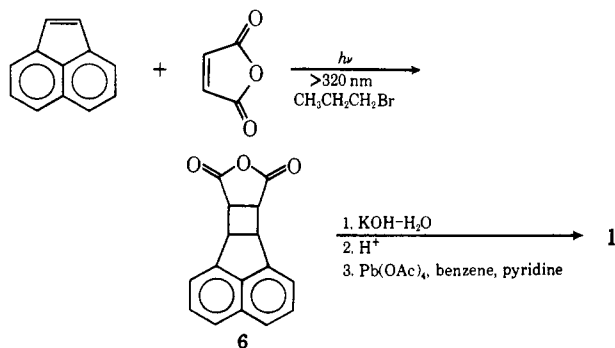
Chart I



1605, 1491, 1130, 900, and 850 cm^{-1} ; uv (cyclohexane) λ_{max} 229 (ϵ 64,000), 282 (7300), 290 sh (7800), 294 (9100), 302 (6000), 307 (5600), 317 (1400), and 321 nm (1000). In the mass spectrum the most significant peaks were the parent ion (m/e 178, 100%) and that arising from loss of acetylene (m/e 152, 52%). Chemical confirmation for the structure of **1** was obtained by catalytic hydrogenation (1 equiv of H_2 consumed), followed by ozonolysis and esterification to yield dimethyl *cis*-1,2-cyclobutanedicarboxylate.⁵

The intriguing chemical possibilities for **1** led us to seek a more convenient synthesis. The method of choice was suggested by a recent report concerning heavy-atom solvent effects on the photochemical cycloaddition of acenaphthylene to acrylonitrile.⁶ Thus, we were able to obtain adduct **6** from acenaphthylene and maleic anhydride using *n*-propyl bromide as a solvent, and to synthesize **1** by the route shown in Chart II.

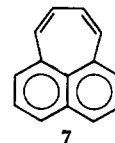
Chart II



In a typical experiment, a solution of 5.00 g of acenaphthylene and 10.00 g of maleic anhydride in

450 ml of *n*-propyl bromide was irradiated for 4.0 hr with a Hanovia 450-W lamp, using a uranium glass filter sleeve ($\lambda > 320$ nm). The anhydride adduct **6** was accompanied by acenaphthylene dimers, which could be removed easily by filtration of the basic hydrolysis solution. Yields of the diacid were 25–30%. The oxidative bisdecarboxylation⁷ of the diacid proceeded smoothly to give **1** in 28% yield by refluxing the reaction mixture for 2 hr.

We were particularly interested in the possibility of rearranging **1** to its valence isomer, pleiadene (**7**).⁷ The thermal behavior of **1** was first examined by heating



a 10-mg sample for 30 sec at 250° in a capillary tube. The resultant red mixture was separated by preparative glpc and was shown to be a 2:3 mixture of **1** and **7**. The pleiadene was identified by comparison of its melting point, ultraviolet spectrum, and the melting point of its maleic anhydride adduct with those reported.⁸ In addition, the nmr spectrum (CCl_4) was consistent with this structure: τ 2.85–3.65 (slightly asymmetric multiplet, 6 H, aromatic) and 3.90–5.00, centered at 4.45 (two multiplets, 4 H, diene bridge).

A more efficient conversion of **1** to **7** was effected by passing a benzene solution of **1** through a 14-in., glass helix packed tube heated to 390–410°. After two passes, complete conversion was effected as determined by nmr analysis. Alumina chromatography of the red residue gave pure **7** in 82% yield. Thus, this method constitutes a very convenient synthesis of **7**.⁸

When we investigated the photochemistry of **1**, we found that although the disrotatory photochemical opening of **1** to **7** is allowed by simple orbital symmetry considerations,⁹ no reaction could be observed at room temperature. Thus, irradiation of a 5.3×10^{-3} M hexane solution of **1** for 4 hr with a 450-W Hanovia lamp gave only unchanged **1**. It was only when **1** was irradiated in a rigid glass at 77°K that the expected ring opening was observed. Thus, irradiation of a 3.6×10^{-3} M solution of **1** in 1:5 methylcyclohexane-isopentane immersed in liquid nitrogen for 100 min with a Pyrex-filtered 450-W Hanovia lamp gave a 3.5% conversion to **7**, as determined by uv-visible spectroscopy.

The photochemical behavior of **1** is formally analogous to that of the benzo-substituted compound **8**, which was recently reported by Kolc and Michl¹⁰ to undergo ring opening only when irradiated at low temperatures in a rigid glass. Since the conversion of **1** to **7** was enhanced by simultaneous irradiation of the glass with a second lamp filtered to remove light absorbed by **1** ($\lambda > 340$ nm), it seems reasonable to

(7) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

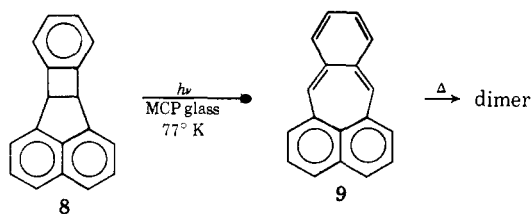
(8) V. Boekelheide and G. K. Vick, *J. Amer. Chem. Soc.*, **78**, 653 (1956).

(9) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(10) J. Kolc and J. Michl, *J. Amer. Chem. Soc.*, **92**, 4147, 4148 (1970).

(5) N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959).

(6) B. F. Plummer and R. A. Hall, *Chem. Commun.*, **44** (1970).



assume that this transformation is mechanistically similar to that of **8** to **9**. Thus, initial excitation of **1** appears to produce an unreactive excited state which possesses a sufficient lifetime at 77°K to absorb a second photon, giving rise to a higher excited state having the proper symmetry for rearrangement to **7**.

Further studies of the chemistry of this ring system are in progress.

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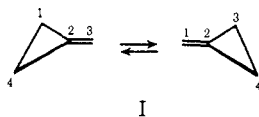
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The Photochemical Methylenecyclopropane Rearrangement

Sir:

The relationship between thermal and photochemical energy surfaces for concerted isomerizations has become recognized as a subject of paramount theoretical importance.¹ In this context and reflecting current interest in the scope and mechanism of degenerate thermal rearrangements (e.g., **I**) in the methylenecyclopropane series,² we now report the first example of a *reversible photochemical methylenecyclopropane rearrangement*. Our results to date on four members of this class (II–V) indicate that (1) reversible photoisomerization occurs between benzylidenecyclopropane (II) and 1-phenyl-2-methylenecyclopropane (III), (2) cheletropic³ photofragmentations to olefins and vinylidenecarbenes compete to varying degrees with the photoisomerizations, (3) certain of the cheletropic fragmentations may occur from vibrationally excited primary photoproducts, (4) singlet excited states are involved in the photoisomerizations and photofragmentations, and (5) the observed photoisomerizations differ markedly from thermal pathways reported for these compounds in the literature.



Photolysis at 30° of a 1% acetonitrile solution of benzylidenecyclopropane (II)⁴ under N₂ in a quartz

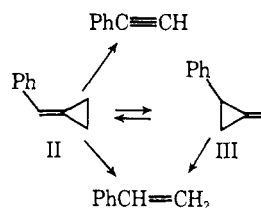
(1) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(2) For recent contributions defining the mechanism of the methylenecyclopropane rearrangement, see J. J. Gajewski, *ibid.*, **90**, 7178 (1968), and W. von E. Doering and H. Roth, *Tetrahedron*, **26**, 2825 (1970). The latter paper contains a thorough review of this field.

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 152–163.

(4) K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966). Com-

nmr tube using a 450-W high-pressure mercury source gave three new products as monitored by glpc.⁵ After 30 min there was 54% loss of starting II accompanied by the formation of 18% 1-phenyl-2-methylenecyclopropane (III), 3% styrene, and 2% phenylacetylene. The identity of III was established by glpc collection from the photolysis mixture and comparison, by nmr and co-injection, with authentic III prepared from phenylallene and diazomethane using Ph₃PCuCl catalysis.⁶ When II was irradiated in a Pyrex tube using xanthone (0.07 M in C₆H₆) as triplet sensitizer (*E*_T = 74 kcal) there was negligible loss of starting material and only traces of photoisomer III were detected.



Reversibility was demonstrated by photolysis of authentic III under the conditions employed for II. After 40 min there was 30% loss of III accompanied by the formation of 6% photoisomer II and 11% styrene. Longer irradiations of either II or III led to extensive material loss (by glpc) apparently from side reactions of the starting methylenecyclopropanes to high molecular weight by-products. Attempted xanthone photosensitization of III led to disappearance of starting material but neither II nor styrene could be detected.

Irradiation under N₂ of a 10% acetonitrile solution of diphenylmethylenecyclopropane (IV)⁷ by a low-pressure mercury source led in 5.5 hr to 22% disappearance of starting material and formation of 6% 1,1-diphenyl-2-methylenecyclopropane (V) plus 0.11% of 1,1-diphenylethylene; these products were also observed using a 450-W source. Isomer V was identified by glpc collection and comparison by nmr and mass spectra and co-injection with an authentic sample prepared by photolysis of diphenyldiazomethane in liquid allene.⁸ Attempted photoreversal from V by similar irradiation of a 1.5% solution for 45 min caused 8% loss of starting V and formation of 7% 1,1-diphenylethylene as the only new glpc peak. Irradiation of an acetone solution of IV above 290 nm failed to effect photosensitized conversion to V. Likewise, xanthone (0.1 M in C₆H₆ under N₂) did not produce the

pound II, purified by silica gel chromatography and short-path distillation below 30° at 0.3 mm, was homogeneous by glpc and exhibited the reported nmr spectrum. Cf. E. E. Schweizer and J. G. Thompson, *Chem. Commun.*, 666 (1966).

(5) Glpc analyses were conducted using 6 ft × 1/8 in. columns of 10% UCON on Chromosorb W98 and columns of 10% SE-30 on ABS at oven temperatures of 100° for II and III, 140–160° for III and IV.

(6) R. Noyori, H. Takaya, Y. Nakanishi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969). Pure III was homogeneous by glpc and showed the expected nmr signals in CDCl₃ at δ 1.21 (1 H, m), 1.73 (1 H, t), 2.60 (1 H, t), 5.54 (2 H, q), and 7.16 (5 H, s).

(7) K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966). Compound IV was recrystallized from petroleum ether to constant mp 65.0–65.5°, and showed ir, uv, and nmr spectra identical with those in the literature. Pure IV was homogeneous to glpc and contained no trace of isomer V.

(8) M. Jones, M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970). Nearly pure V was separated from nitrogen-containing by-products by preparative tlc over silica gel and characterized by the nmr signals in CDCl₃ at δ 1.91 (2 H, t), 5.59 (1 H, t), 5.78 (1 H, t), and 7.25 (10 H, s). Glpc analysis showed no contamination by IV.