Synthesis and Photochemistry of 5,7-Bis(diazo)-1,2,3,4-dibenzocyclohepta-1,3-dien-6-one. Generation and Reactions of Phenanthrenodiazacyclopentadiene, Phenanthrenocyclopropenone, and 9,10-Phenanthryne

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The title compound **15** was prepared as the first 1,3-bis(diazo) ketone incorporated into a seven-membered ring, and its photochemical pathways were investigated not only by product analysis study but also by using matrix isolation spectroscopy. Irradiation of **15** in alcoholic solvents gave 9-(alkoxycarbonyl)phenanthrene **16** as a main product, while similar irradiation in non-nucleophilic solvents provided diphenanthreno-*syn*-1,5-diazabicyclo[3.3.0]octadienedione (**20**). The formation of these products is interpreted as indicating that **15** eliminates one of two diazo functions upon photoexcitation to form 9-diazo-10-carbonylphenanthrene (**21**) which either reacts with alcohol by eliminating the second dinitrogen, leading to **16**, or undergoes dimerization to form **20**. Photolysis of **15** in an ethanol matrix at 77 K gave 9-ethoxyphenanthrene (**31**) as a new product along with **16**. Irradiation of **15**, matrix-isolated in Ar at 10 K monitored by IR, indicated that phenanthrenocyclopropenone (**28**) was formed as an initial product which then underwent photodecarbonylation to leave 9,10-phenanthryne (**32**), and that **32** reacted with CO to reproduce **28** upon photoexcitation. The cyclopropenone (**28**) was shown to be generated also by photolysis of 9,10-dicarboxyphenanthrene anhydride (**33**) in Ar matrix at 10 K. A plausible mechanism to explain the observed sequential decomposition of the two diazo functions in the room temperature photolytic run and the formal simultaneous elimination of two dinitrogens in the low temperature matrix run is proposed.

The photochemistry of 1,3-bis(diazo) carbonyl compounds is of special interest since it is expected to give new species as a result of intramolecular interaction of the carbenic center with carbene and/or diazo functions in the same molecule. To date, a limited number of bis(diazo) compounds have been synthesized, and their chemistry has been explored not only in fluid solution but also in rigid matrices. The results clearly show that they can indeed serve as useful precursors of various attractive molecules. The irradiation of 1,3-bis(diazo)-1,3-diphenylpropan-2-one (**1**) in methanol, for instance, produces methyl 2,3-diphenyl-3-methoxypropionate, presumably as a result of a Wolff rearrangement, together with methyl 2-phenylcinnamate and diphenylacetylene.[1] Photolysis of **1** with longer-wavelength light, on the other hand, produces diphenylcyclopropenone which is presumed to lead to the cinnamate and the acetylene. The cyclopropenone formation can be interpreted to result from the interaction of a diazo function and a neighboring carbene center. A similar reaction is also found in the catalytic decomposition of 2,4-bis(diazo)-1,5-diphenylpentane-1,3,5-trione (**2**), which ultimately produces dibenzoylacetylene by way of dibenzoylcyclopropenone.[2] The formation of cyclopropenone does not seem to occur, at least in fluid state photolysis at room temperature, when the bis(diazo) ketone functions are located in cyclic systems. Thus decomposition of 2,6-bis(diazo)cyclohexanone (**3**)[1] or 1,3-bis(diazo)-2-decalone (**4**)[3] in methanol produces isomeric methyl cyclopentene-3-carboxylates. However, when irradiation is carried out in an inert matrix at much lower temperature, the cyclopropenone is incorporated into a bicyclic system and is not only detected but also shown to be a precursor of a highly strained cyclic alkyne. Thus, the irradiation of **3**, matrix-isolated in argon at 8 K, gives the expected bicyclo[3.1.0]hexenone, which then undergoes photodecarbonylation to result in the formation of (cyclopropylidene)ethylene by way of cyclopentyne.[4] A similar reaction is observed with 1,3-bis(diazo)-1,2-dihydrophenalen-2-one (**5**), which eventually affords acenaphthyne by photodecarbonylation of initially formed acenaphthenocyclopropenone upon irradiation within an argon matrix.[4] More recently, cyclic poly(diazo)poly(keto) compounds, e.g., **6**[5], **7**−**9**[6] have been prepared and shown to be promising precursors for C_nO_m polycumulated compounds. Thus, irradiation of these highly diazotized molecules in inert gas matrices affords a new species of di- and monoxides of carbon with even and odd numbers of carbon atoms.

Motivated by these precedent observations, we have prepared 1,3-bis(diazo)indan-2-one (**10**), the first 1,3-bis(diazo) ketone incorporated into a five-membered ring. We have studied its photochemistry not only by product analysis but also by using matrix isolation spectroscopy, which indicates that the two diazo groups are decomposed consecutively in solution at room temperature as well as in matrices at cryogenic temperatures, and that the diazo ketocarbene **11**, produced by elimination of the first diazo group of **10**, is rather reluctant to undergo a Wolff rearrangement. It was also shown that **11** produced such highly strained compounds as the cyclopropenone **12** and propadienone **13** upon further irradiation

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(1) Trost, B. M.; Whitman, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7421.

(2) Regitz, M.; Geelhaar, H. J. *Chem. Ber.* **1969**, *102*, 1743.

(3) Borch, R. F.; Fields, D. L. *J. Org. Chem.* **1969**, *34*, 1480.

(4) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Mass, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.

(5) Maier, G.; Reisenauer, H. P.; Schäfer, U.; Balli, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 566.

(6) Maier, G.; Reisenauer, H. P.; Balli, H.; Brandt, W.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 905.

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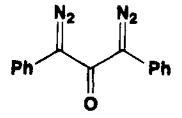

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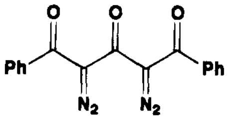

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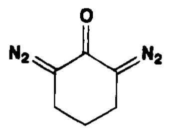

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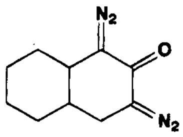

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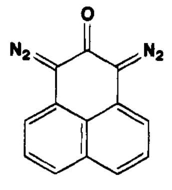

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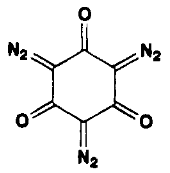

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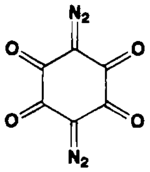

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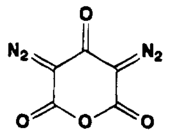

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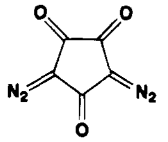

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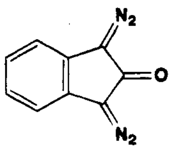
within matrices.[7] As a continuation of our efforts to utilize and expoit cyclic 1,3-bis(diazo) ketones as precursors for fascinating molecules, we synthesized the title bis(diazo) ketone **15**, the first 1,3-bis(diazo) ketone incorporated into a seven-membered ring, and investigated its photochemistry. We wish to report here that the photochemistry of **15** is in marked contrast to that of **10** in that it eliminates two diazo groups, apparently simultaneously, to produce the corresponding cyclopropenone which leads to phenanthryne upon further irradiation in a low temperature matrix. In solution, the first diazo group was cleaved to generate the diazo ketene intermediate which either underwent self-condensation to produce "bimane" or was trapped by nucleophiles to afford 9-carboxyphenanthrenes.



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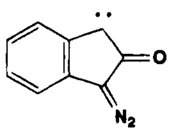

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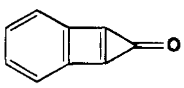

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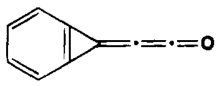

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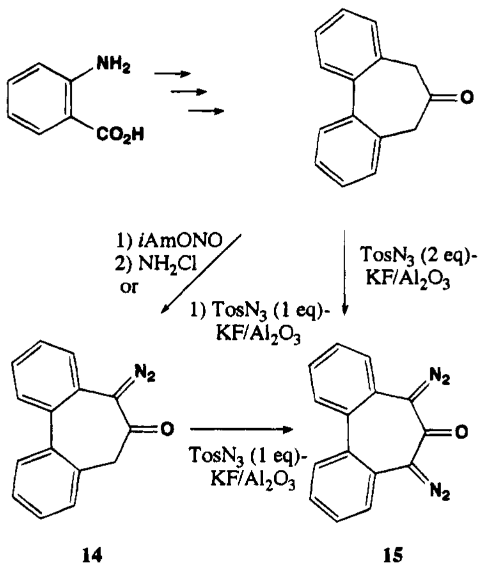
Results and Discussion

Preparation of 5,7-Bis(diazo)-1,2,3,4-dibenzocyclohepta-1,3-dien-6-one (15). The precursory ketone was conveniently prepared by six steps starting from anthronic acid following the procedure reported by Eistert[8] in 30% overall yield. Treatment of the ketone with isoamyl nitrite followed by Forster reaction, which has been shown to be a very convenient route to some 1,3-bis(diazo) ketones,[1,3,7] e.g., 1,3-bis(diazo)-2-indanone (**10**), always resulted in the isolation of only monodiazo ketone 5-diazo-1,2,3,4-dibenzocycloheptadienone (**14**). Direct diazo transfer with *p*-tosyl azide (2 equiv) using KF-Al_2O_3[9] gave superior results, giving the desired bis(diazo)ketone **15** in fair yield. The stepwise nature of the reaction was shown by the observation that use of 1 equiv of $TosN_3$ always resulted in the isolation of the mono(diazo) ketone **14**, which was then further diazotized to form **15** upon similar treatment with $TosN_3$ (Scheme 1). The bis(diazo) ketone **15** was obtained as a fairly stable orange crystal with a mp of 164−166 °C dec and was kept in the dark at ambient temperature (~10 °C) for at least a month without any appreciable decomposition.

Scheme 1



Photolysis of 15 in Nucleophilic Solvents. Irradiation (λ > 300 nm) of a solution of **15** in methanol caused rapid fading of the orange diazo color with copious evolution of nitrogen gas to give a pale yellow solution. Preparative TLC resulted in the isolation of 9-(methoxycarbonyl)phenanthrene (**16a**, 41%) as the nearly exclusive isolable product. Monitoring the photomixture by GC revealed two other minor peaks, which were attributed to 9,10-dihydro-9-(methoxycarbonyl)phenanthrene (**17a**) and phenanthrene (**18**) by GC-MS comparison with authentic samples. Plots of the product yields as a function of the irradiation time indicated that neither **17** nor **18** is derived by secondary photolysis of the major product **16**. The plot also showed the absence of an induction period in the formation of the ester **16**, suggesting that **16** must not be produced by way of an intermediate e.g., **19**, which should have a finite lifetime but may be masked during the analysis process. This was further confirmed by ^1H NMR analysis in which the premature photomixtures showed no significant signals ascribable to the intermediates. Thus the photochemical pathways of **15** and **10** are strikingly different not only in terms of product structure but also in reaction sequence.

Similar irradiation of **15** in other alcohols, i.e., ethanol and 2-propanol, also produced the corresponding esters

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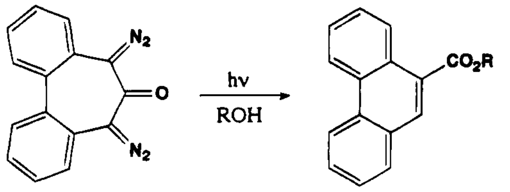
(7) Murata, S.; Yamamoto, T.; Tomioka, H. *J. Am. Chem. Soc.* **1993**, *115*, 4013.

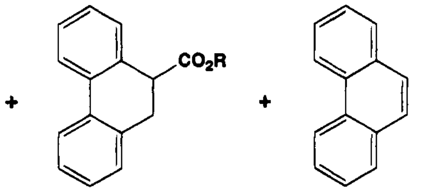
(8) Eistert, B.; Minas, H. *Chem. Ber.* **1964**, *97*, 2479.

(9) Yamasaki, J.; Ando, T. *Chem. Lett.* **1979**, 755.

Scheme 2

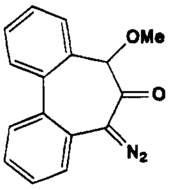


15 16



17 18

ROH	16	17	18
MeOH	41%	< 1%	< 1 %
EtOH	38	< 1	< 1
^{i}PrOH	32	< 1	< 1



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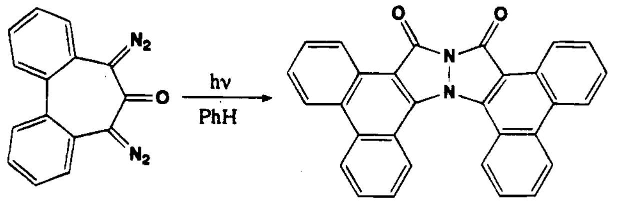
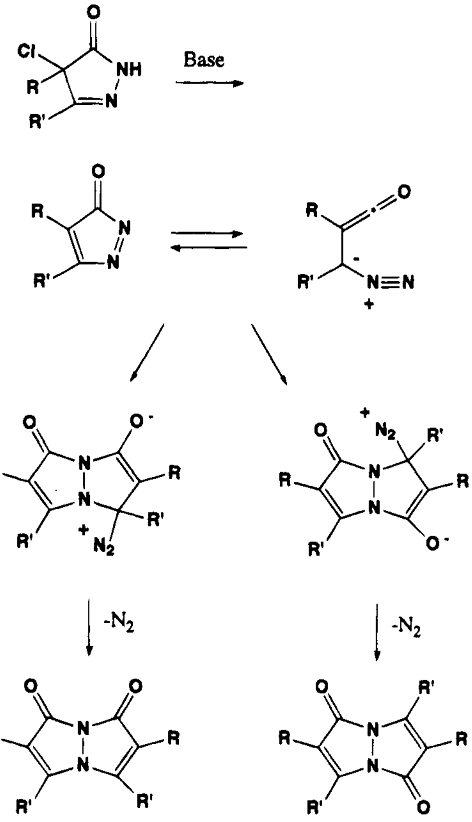
Scheme 3



15 20

Scheme 4



syn *anti*

16 and 17 and phenanthrene (18) in essentially similar yields. Photolysis in the presence of diethylamine produced the corresponding amides (32%) along with 18 (Scheme 2).

Photolysis of 15 in Non-Nucleophilic Solvents. Irradiation ($\lambda > 300$ nm) of 15 in dry benzene caused a rapid change of the original orange color to a deep yellow with generation of dinitrogen. Preparative TLC of the photomixture resulted in the isolation of a yellowish powder (mp > 300 °C), which was strongly fluorescent (λ_{max} = 514 nm in CH_2Cl_2) in dilute solution. The product was identified as 3,4,7,8-diphenanthreno-*syn*-1,5-diazabicyclo[3.3.0]octa-2,7-diene-4,6-dione (**20**) based upon the following spectroscopic data (Scheme 3). The mass spectrum (in beam EI) showed the parent peak at *m/e* 436 as the base peak. Additional peaks at *m/e* 408 (17.4%), 379 (18.6%), and 350 (14.0%) were thought to correspond to the fragments formed as a result of the loss of carbonyl groups and dinitrogen. Peaks at *m/e* 204 (11.6%) and 176 (31.8%) must correspond to phenanthrenocyclopropenone and phenanthrene, respectively, presumably accompanied by fragmentation. ^{1}H NMR (400 MHz) showed the presence of eight aromatic protons ranging from 7.43 to 9.14 ppm, and the infrared spectrum showed C=O stretching absorptions at 1740, 1690, and 1610 cm^{-1}. A series of diazabicyclooctadienediones were prepared and characterized by Kosower and co-workers by treatment of a chloropyrazolinones with bases and were given the brief name "bimane".[10,11] They noted that syn bimanes exhibit a striking, strong fluorescence in solution while the fluorescence of anti isomers is weak, and that three band are usually observed for the syn bimanes in the carbonyl region whereas antibimanes show one strong band often accompanied by a shoulder. These features were also observed for the product obtained by photolysis of 15 in benzene. Essentially the same results were obtained when the photolysis was carried out in acetonitrile or dichloromethane.

The determination of a mechanism for the formation of **20** from the photolysis of **15** presents interesting questions. A mechanism of formation of dioxabimanes in the reaction of halopyrazolinones with base, proposed by Kosower, is summarized in Scheme 4. The initial

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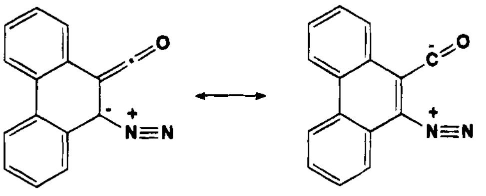
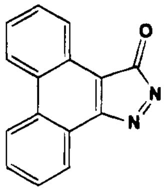
(10) (a) Kosower, E. M.; Pazhenchevsky, B.; Hershkowitz, E. *J. Am. Chem. Soc.* **1978**, *100*, 6516. (b) Kosower, E. M., Pazhenchevsky, B. *J. Am. Chem. Soc.* **1980**, *102*, 4983.

reaction of base with a halopyrazoline must lead to a 2,3-diazacyclopentadienone which then is in part converted into a diazo alkylketene, and 1,4-addition produces the syn bimane while 1,6-addition gives rise to the anti isomer.[10] It is quite probable that α-diazo ketene **21** is produced upon photoirradiation of **15** by initial elimination of one dinitrogen associated with and/or followed by Wolff rearrangement and that the α-diazo ketene in part can isomerize to the corresponding diazacyclopentadienone **22**. Thus, reaction of **21** with **22** with loss of dinitrogen results in the formation of **20**.[12] It has been shown that 3-indazolone (benzodiazacyclopentadiene, **23**) is generated by oxidation of 3-indazolinone at ~10 °C and can either be trapped by 1,3-diene to form Diels−Alder adducts or observed directly by spectroscopic means at low temperature.[13] In order to obtain evidence for the intervention of the intermediates, trapping experiments using dienes were carried out. Attempts to trap putative azacyclopentadiene **22** using such dienes as 1,3-butadiene, cyclopentadiene, *N*-methylpyrrole, and thiophene all resulted in the exclusive formation of **20**, no expected diene−**22** adducts being isolated. However, when the irradiation was carried out in a 1:1 furan−benzene solvent mixture, at least three products (**24**−**26**) other than bimane (**20**, 24%) were isolated as minor components after repeated elution of the photomixtures during preparative TLC. Careful analysis of these "trapped" products indicated that none of them contained the simple Diels−Alder type adduct of furan and diazacyclopentadienone. The predominant adduct was easily assigned as triphenylene (**24**, 17%) by direct comparison with an authentic sample, whereas the structures of two other products were tentatively assigned as **25** (3.3%) and **26** (1.8%) based on spectroscopic data. The structures of these "adducts" suggest that they must be produced by the reaction of furan with the diazoketene **21**, not with the diazacyclopentadienone **22**. The diverse nature of the reaction, even with the best trapping reagent, i.e., furan, limited further investigation of the mechanism of the formation of these adducts. However, it is very tempting to propose that the adducts **24** and **26** may be produced by a [4 + 3] addition while **25** is resulting from [2 + 3] addition, although other explanations are feasible (Scheme 5).



21 **21'**



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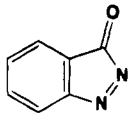

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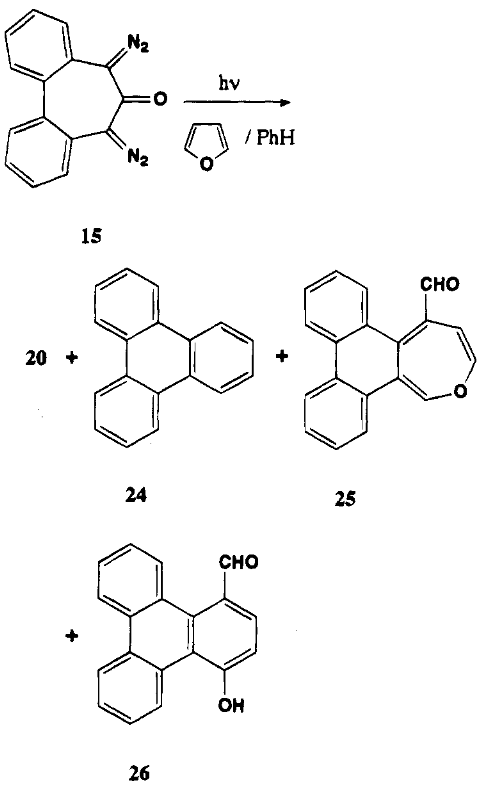
Scheme 5



Photolysis of 15 at Low Temperature. In order to obtain more insight into the intermediates involved in the photodecomposition of the bis(diazo) ketone **15**, and hence into the mechanism, irradiation was carried out at much lower temperature in organic matrices and the reaction was monitored by spectroscopic means coupled with product analysis.

A thin film of **15** as a suspension in Nujol in a liquid nitrogen-cooled NaCl plate gave an IR spectrum with absorptions at 2092 and 2066 cm^{-1} arising from the diazo group and 1598 cm^{-1} due to the carbonyl group (Figure 1a). Broad-band irradiation (λ > 300 nm) of the sample at 77 K resulted in the simultaneous disappearance of both absorption bands due to diazo and carbonyl groups and concurrent growth of new strong absorption bands at 1850 and 1840 cm^{-1}. Other prominant changes during the irradiation were almost complete disappearance of the bands at 1310, 1298, and 1246 cm^{-1} presumably due to the diazocarbonyl chains, while the absorption bands due to the C−H deformation of the aromatic group changed very little (Figure 1b).

What is the photoproduct? The band at 1850 cm^{-1} was obviously too low in frequency to be assigned as either ketene or diazo functional group. Thus, all the possible intermediates involving these functional groups, such as **21** or diazoketocarbene **27** are eliminated. On the other hand, it was a bit too high to be assigned as the carbonyl absorption of **22**, since 3-indazolone (**23**) was reported to show its carbonyl absorption at 1792 cm^{-1} in acetonitrile.[13] The most plausible functional group is then the cyclopropenone since cyclopropenone usually shows a

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[11] Marciano, D.; Baud'huin, M.; Zinger, B.; Goldberg, I.; Kosower, E. M. *J. Am. Chem. Soc.* **1990**, *112*, 7320 and references cited therein.

[12] Diphenylpyrazolone generated by oxidation of 3,4-diphenylpyrazolin-5-one has been shown to undergo similar dimerization with loss of dinitrogen to give 2,3,6,7-tetraphenylpyrazolo[1,2-*a*]pyrazole-1,5-dione in this case. Rees, C. W.; Yelland, M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 221.

[13] (a) Ullman, E. F.; Bartkus, E. A. *Chem. Ind.* **1962**, 93. (b) Adamson, J.; Forster, D. L.; Gilchrist, T. L.; Ress, C. W. *J. Chem. Soc.* **1971**, 981.

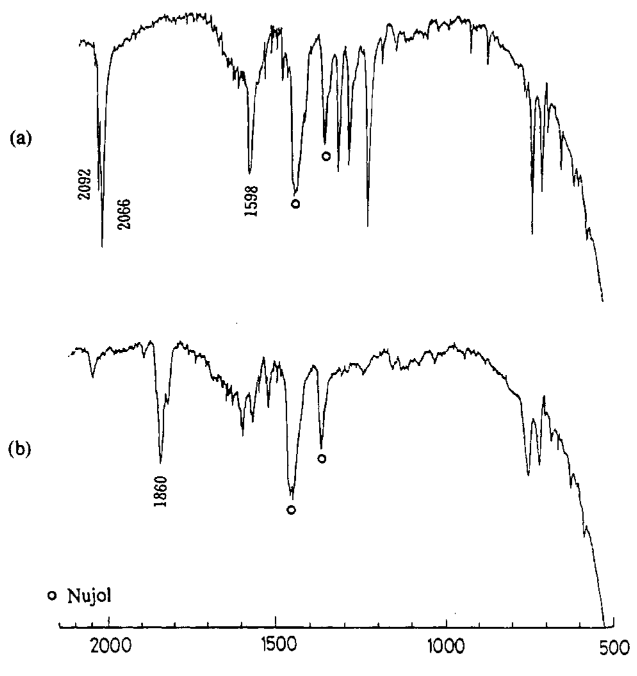
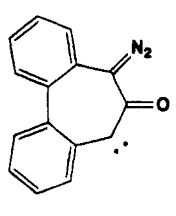


Figure 1. (a) IR spectrum of **15** in Nujol at 77 K. (b) IR spectrum obtained after irradiation of **15** at 77 K for 1 h at λ > 300 nm. Bands labeled N are for Nujol.

characteristic carbonyl stretching absorption at 1820–1870 cm^{-1} as rather strong, complex bands.[14-16] Benzocyclopropenone, for instance, is reported to exhibit its carbonyl absorption at 1838[17] or 1852[18] cm^{-1}. The other absorption bands usually observed with ordinary cyclopropenone are reported to appear at 1600–1660 cm^{-1}. Unfortunately, reliable assignment in this region was not possible due to the overlapping absorption of the carbonyl group of the remaining starting material as well as water deposited during the operation. Thus, the most plausible photoproduct consistent with the available data is phenanthrenocyclopropenone (**28**), which may be formed directly from **15** upon photoexcitation by the loss of two dinitrogens, since no bands ascribable to intermediates expected from discrete stepwise elimination of two diazo groups are observed. Irradiation of **15** with longer wavelength light (λ > 350 nm), in the hope of detecting any intermediate intervening in the reaction, again revealed no bands but the cyclopropenone bands, at least to the limit of our IR sensitivity.



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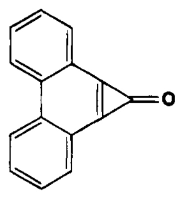

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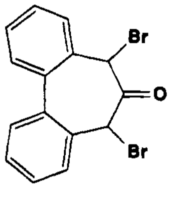
Prolonged irradiation of the matrix containing the cyclopropenone with shorter wavelength light (λ = 257 nm) resulted in a slight decrease in the original bands, but no appreciable formation of new absorption bands to the limit of our IR sensitivity, over a time range of 15 h. Warming the matrix containing **28** led to a gradual disappearance of the original absorption bands ascribable to **28** at above 250 K, suggesting a fairly thermally-stable but still very reactive intermediate. This is in accord with the observation that all attempts to generate and isolate **28** by base-induced dehydrobromination of 1,2,3,4-dibenzo-5,7-dibromocyclohepta-1,3-dien-6-one (**29**) were unsuccessful under the conditions from which dibenzocycloheptadienocyclopropenone (**30**, X = CH_2) and its ketone (**30**, X = CO) were isolated.[16b] TLC analysis of the spent solution indicated the presence of a complex mixture containing the bimane products **20** as a very minor component. On the other hand, irradiation of **15** in Nujol at room temperature did not show any sign of the cyclopropenone absorption bands, but produced the bands obviously ascribable to bimane **20**. TLC analysis indicated that the major product was **20**.



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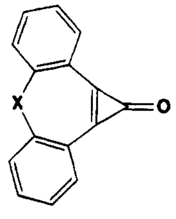

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The observations suggest that the intermediate detected at low temperature is different from that postulated in solution photolysis at ambient temperature, in the formation of the major product, i.e., **20**. In order to get clearer evidence for the intermediate at low temperature, trapping experiments were carried out using a reactive organic mixture, i.e., ethanol. The irradiation of **15** in ethanol glass at 77 K gave rise to 9-ethoxyphenanthrene (**31**, 36%) as a new product, along with (ethoxycarbonyl)phenanthrene (**16**, 36%) and phenanthrene (**18**, 10%), which were also produced in the ambient temperature photolytic run. The formation of **16** is explicable in terms of the nucleophilic attack of the alcohol on the cyclopropenone **28**. It is not easy, on the other hand, to draw a simple mechanism for the formation of **31** directly from **28**, but the formation is better explained in terms of phenanthryne (**32**) since generation of benzyme in ethanol by thermolysis of 1,2,3-benzothiazole 1,1-dioxides produced phenethol.[19] It is quite probable that the cyclopropenone **28** undergoes photodecarbonylation to produce **16** in a matrix, since benzocyclopropenone is known to generate benzyne by eliminating carbon monoxide upon photoexcitation in a matrix at low temperature.[17]

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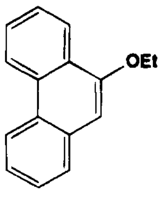

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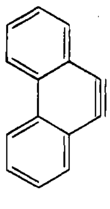

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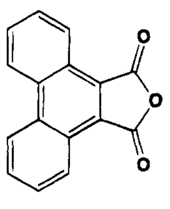

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Since it was very difficult to obtain clear-cut evidence of the production of phenanthryne by using Nujol matrix experiments, we then studied the photochemical fates of **15** by rare gas matrix isolation spectroscopy at much low temperature where resolution of the spectrum is usually very high owing to loss of rotational fine structure and perturbations by molecular association in the liquid phase. Deposition of **15** in an argon matrix at 20 K gave an IR spectrum with absorptions at 2094, 2076, and 1622 cm^{-1}, indicating that the sample was intact during the depositing process, although the bands were slightly shifted from those observed in Nujol, presumably due to a matrix effect (Figure 2a). Broad-band irradiation ($\lambda >$ 390 nm) of the sample at 10 K resulted in the simultaneous disappearance of both absorption bands due to the diazo and carbonyl groups and concurrent growth of product absorption bands at 1862 and 757 cm^{-1}. This is essentially the same as what is observed in Nujol matrix photolysis, indicating that the initial process is the same irrespective of sample conditions (suspension or matrix-isolated) and temperature (77 or 10 K). All attempts to detect an intermediate by changing the wavelength of the light and irradiation time were unsuccessful, suggesting again that the cyclopropenone might be produced either directly from the excited **15** or from thermally excited intermediates, without the intervention of a thermally relaxed, and hence detectable, intermediate. Continued irradiation of the matrix containing **28** with the same wavelength light did not result in any appreciable change in the absorption bands but irradiation with shorter wavelength light ($\lambda >$ 254 nm) gave rise to the absorption band due to carbon monoxide (2138 cm^{-1}) along with a slight shift of the C–H deformation absorption of the aromatic ring. The spectral changes are best explained in terms of photodecarbonylation of **28** to generate phenanthryne (**32**). The IR spectrum of phenanthryne is worthy of comment. Benzyne has been generated by photolysis of at least five precursors and detected using matrix isolation spectroscopy. The complete set of vibrational frequencies and absolute infrared intensities have been recently determined.[18] The major absorption bands (intensities and assignment) are 472 (81.0, ring def), 737 (47.4, CH wagging), 849 (24.8, ring def), 1039 (10.4, ring str), 1055 (7.4, CH def), 1451 (9.1, ring str), and 1394 (5.5, ring str and CH def) cm^{-1}, and a weak band at 1846 cm^{-1} (2.0) is unambiguously assigned as the CC triplet bond stretching vibration. In the observed spectrum, prominant bands that are related to those reported for *o*-benzyne are 752 (medium, CH wagging), 1036 (weak, CH def), and 1483 cm^{-1} (weak, ring str and CH def), although there are other absorption bands that are very weak and may not be unambiguously attributable to phenanthryne (**32**). The band at 1862 cm^{-1}, on the other hand, originally assigned as a cyclopropenone carbonyl absorption band, remained even when prolonged irradiation was carried out until no appreciable change in spectrum was observed. It is very tempting to assume that the 1862 cm^{-1} band is partially due to the $C{\equiv}C$ triple bond stretching vibration of phenanthryne, although it must also be due to cyclopropenone absorption, judging from the peak intensity.

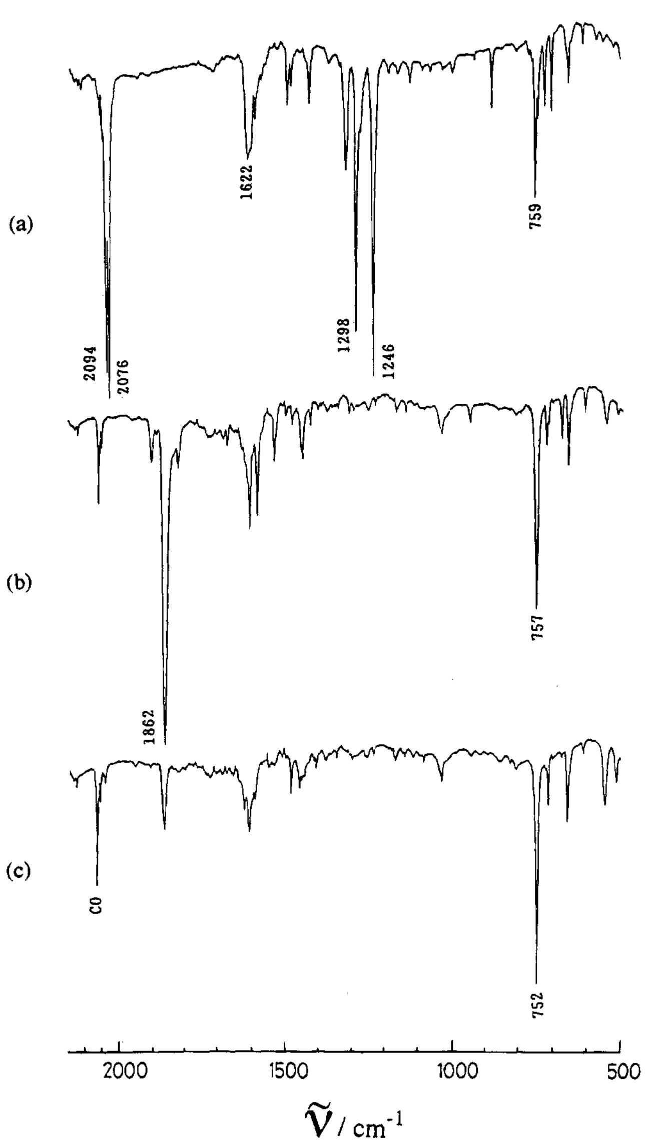
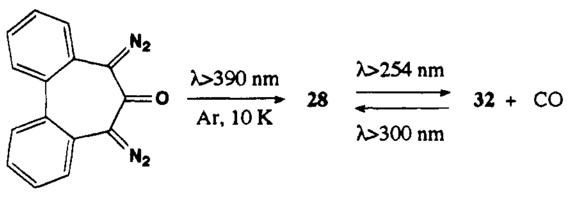


Figure 2. (a) IR spectrum of **15** matrix-isolated in Ar at 10 K. (b) IR spectrum obtained by irradiation of **15** in Ar at 10 K for at $\lambda >$ 390 nm. (c) IR spectrum obtained after irradiation of b at $\lambda >$ 300 nm and then at $\lambda >$ 254 nm.

Further support of this assignment was obtained from the observation that irradiation of the matrix containing CO and **32** with light of $\lambda >$ 300 nm resulted in regeneration of the absorption due to the cyclopropenone **28** at the expense of CO and **30**, and that shorter wavelength irradiation again produced CO and **32**. This observation is best explained to mean that phenanthryne reacts with CO upon photoexcitation to produce **28** and suggests why complete conversion of **28** to **32** was not attained (Scheme 6). Benzyne is shown to react with CO upon photoexcitation to give, in this case, cyclopentadienylidene-1,2-ethenone, which regenerates benzyne and CO upon shorter wavelength irradiation.[18] On the other hand, 3,3,6,6-tetramethylcyclohexyne generated by thermolysis of the corresponding cyclopropenone also reacts with CO upon photoexcitation to afford, in this case, the cyclopropenone.[20] The exact mechanism of this interesting photoreaction is not known. However, if one assumes that these reactions take place in a stepwise fashion by way of a common 1,3-biradical intermediate, the forma-

Scheme 6



15

tion of cyclopropenone can be easily understood in terms of coupling of the biradical while that of the ethenone could result from the Wolff type rearrangement of the ketene carbene form. In other words, the initial step of the reaction is the same in the two cases, while the following pathway is dependent on the structure. In this way, benzyne and phenanthryne might lead to formally different products in the photoreaction with CO.

In order to obtain more definitive evidence for the formation of phenanthryne, an attempt was made to generate phenanthryne from 9,10-dicarboxyphenanthrene anhydride (**33**) since phthalic anhydride is a well known precursor of *o*-benzyne in matrix photolysis.[18]

Irradiation of the anhydride (**33**) in an Ar matrix at 10 K with a conventional light source (500 W Xe and Hg arc lamps) did not result in appreciable decomposition of the starting material bands. However, irradiation with 355 nm light from a Nd:YAG laser for 1 h resulted in a significant decrease of the absorption of **33**. New absorption bands formed, with growth of the CO$_2$ bands, were in agreement with those attributed to the cyclopropenone **28** in the photolysis of **15**, thus indicating that **33** undergoes photodecarboxylation to leave **28**. Irradiation of the matrix containing **28** and **33** with 266 nm laser light resulted in formation of a band due to CO at the expense of **28**, suggesting that photodecarbonylation took place. Clear assignment of the bands due to **32** was, however, not possible due to the significant absorption bands of the anhydride remaining owing to its sluggish photodecarboxylation. These experiments clearly support the assignment that the initial photoproduct in the photolysis of **15** is the cyclopropenone although the anhydride **33** is found to be not a very efficient precursor for phenanthryne. This is in sharp contrast with the reported photolysis of phthalic anhydride, where benzyne is produced directly with simultaneous extrusion of CO and CO$_2$ as main products while the cyclopropenone is formed only in very small quantities.

Finally, trapping experiments using O$_2$ were carried out in order to obtain more insight into the intermediates involved in the photochemical transformation of **15**. Irradiation of **15** in Ar doped with 23% O$_2$ formed complex bands in the carbonyl regions presumably owing to the oxidation of carbenes, with no bands due to **28** being detected. Irradiation of **15** in Ar doped with 2% O$_2$ gave **28** as the main product along with small amounts of the oxidation products. Warming the matrix containing **28** and O$_2$ to 35 K in the dark, however, did not result in any appreciable change in the spectrum. All attempts to trap **28** and **32** with doped O$_2$, using Xe as a host matrix, by warming up to 70 K were also unsuccessful. These results may suggest that cyclopropenone and phenanthryene are not very reactive toward O$_2$.

Mechanism of Photochemical Processes of 15. The product analysis as well as spectroscopic studies indicate that intermediates involved in the photolysis of **15**, and therefore the decomposition pathways, are dependent on the reaction conditions. The formation of bimane **20** as a major product in the photolysis of **15** in benzene suggests that either the diazo ketene **21** or the diazacyclopentadienone **22** must be a major intermediate, which should be produced by elimination of one dinitrogen followed by or concerted with rearrangement. Although the formation of the ester **16** in alcoholic solvent can be explained in terms of the other intermediate, e.g., the cyclopropenone **28**,[12,13] it is better explained by nucleophilic attack of the alcohol on the ketene group of **21** and/or protonation on the diazo carbene followed by the elimination of dinitrogen, since the photolysis of **15** in benzene containing a small amount of methanol resulted in the formation of **16** at the expense of **20**. The sluggishness of the putative diazapentadienone **22** toward typical enophiles such as diene is initially rather surprising in light of the fact that the benzo analogue **23** is efficiently trapped even by a simple acyclic diene in Diels–Alder fashion.[13] This can be understood, at least qualitatively, in terms of the electron density difference between the two azadienones **22** and **23**. Thus, MNDO calculations suggested that, although the HOMO–LUMO energy difference between 1,3-butadiene and diazapentadienone was decreased in going from the **23**–butadiene to **22**–butadiene combination, electron densities at the aza double bond were significantly less in **22** than in **23** owing to the extended conjugation by two aromatic rings.

Intermediates generated in low temperature photolysis are not these postulated in the solution phase photolytic runs and are assigned as the cyclopropenone **28** and phenanthryne (**32**), based on the spectroscopic as well as product analysis studies. Formation of 9-(ethoxycarbonyl)phenanthrene (**16**) in the ethanol matrix photolytic run was better explained in terms of nucleophilic attack of the solvent on the cyclopropenone **28**, rather than on the diazo ketene intermediate **21**, presumably upon thawing. Support is lent to this assignment by the observation that attempts to generate **28** by triethylamine-induced dehydrobromination of the corresponding 1,3-dibromoketone **29** in benzene resulted in the formation of 9-carboxyphenanthrene, presumably by trapping of the cyclopropenone by a trace of water in the solvent. Ethoxyphenanthrene (**31**) must originate from phenanthryne (**32**). Although spectroscopic evidence for the intervention of **32** in 77 K Nujol matrix photolysis was not obtained, presumably because of the sample conditions, e.g., dispersed in Nujol in relatively high concentration, which should cause poor resolution of the spectrum, it is possible to generate **32** in ethanol matrix experiments where photodecomposition should be more efficient owing to better sample conditions, i.e., lower sample concentration in a transparent glass matrix. Moreover, matrix isolation spectroscopy provided clear evidence that the cyclopropenone undergoes photodecarbonylation relatively efficiently to produce **32**.

It is worth commenting on the difference in mechanism for the photochemical processes of five- (**10**) and seven-membered 1,3-bis(diazo) ketone **15**. Thus, in the photochemistry of **10**, ketodiazocarbene **11** retaining the precursor structure is formed as a result of elimination of one of the two diazo functions and **11** undergoes the Wolff rearrangement only upon photoexcitation. This is

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attributed to the strain in the transition state for ring contraction accompanied by the Wolff rearrangement and the partial double-bonding character of the CO−CN_2 bond of **11**.[7] In the case of **15**, on the other hand, diazo ketone **21** or azacyclopentadienone **22** seems to be generated in fluid phase photolysis while the cyclopropenone **28** is detected as an initial product in a matrix photolytic run, apparently as a result of elimination of two dinitrogens.

The apparent difference in the intermediates' structures under the two photolytic conditions is very interesting but not unprecedented. This must be partly related to the stability of the nascent intermediate under the reaction conditions. For instance, diazo ketene **21** and/or azapentadienone **22** may be easily trapped by nucleophiles in solution before undergoing subsequent unimolecular reaction. Under matrix conditions, on the other hand, intermediates are susceptible to unimolecular transformation since they are generated under chemically inert conditions and they have less opportunity to lose excess photoexcitation energy owing to the lack of intermolecular channels. It has been forewarned[21] that photochemical processes in noble gas matrices sometimes result in the generation of reactive intermediates in vibrationally excited states which undergo subsequent reactions faster than they dissipate to thermally relaxed states, and therefore an intermediate thought to be involved is often elusive, even under these conditions. The diazo ketone **15** is expected to undergo the Wolff rearrangement to give **21** and/or **22** quite easily owing to the aromatization energy gained through phenanthreno ring formation, by this process. In the matrix, either **21** or **22** will be produced with excess energy and will lose the second N_2 to form **28** before undergoing thermal relaxation. Since elimination of a dinitrogen from diazomethanes is estimated to entail less than 30 kcal mol^{-1},[22] these intermediates, produced from the electronically excited state of **15**, should still have enough excess energy for transfer to the vibrational mode of the second diazo group to eliminate the remaining N_2. The process is also favored by the generation of the phenanthreno structure of the final product.

The mechanistic scenario advanced above is the most plausible one in that it best explains the available data, given the rather dramatic dependence of the intermediate structure upon the photolysis conditions, if one assumes a consistent pathway under both conditions. However other explanations, e.g., multiphoton processes in the matrix, are also plausible at the present stage of investigation.

The present work has revealed that, like other related compounds, cyclic 1,3-bis(diazo) ketone **15** is an attractive precursor for several important molecules, i.e., bimanes, phenanthynocyclopropenone, and 9,10-phenanthryne, which can be selectively generated simply by controlling the reaction temperature. Generation and spectroscopic observation of phenanthryne in the photolysis of **15** is particularly noteworthy since phenanthryne has previously been only postulated based on trapping experiments.[23] A more elaborate study using labeled precursor molecules coupled with theoretical calculations to elucidate the structure is in progress.

Experimental Section

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and the GC mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ^{1}H and ^{13}C NMR spectra were determined with a JEOL JNM-EX 270 spectrometer and a JEOL JNM-GX-400 spectrometer. UV/vis and fluorescence spectra were determined with a Hitachi 220-S spectrometer and MPF-2A fluorescence spectrometer, respectively. Thin layer chromatography was done on a Merck Kiesselgel 60 PF_{254}. Column chromatography was carried out on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral). HPL and GPL were undertaken with a JASCO 800 chromatograph equipped with a UVIDEC-100-II UV/vis detector using a Fine pack C18-T5 column (4.6 × 25 cm) and Shodex GPC H-2001 (20 mm × 50 cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using an OV-17 on Diasolid L (5.0 mm × 50 cm).

Materials. Preparation of 5,7-Bis(diazo)-1,2,3,4-dibenzocyclohepta-1,3-dien-6-one (15). To a stirred solution of 1,2,3,4-dibenzocyclohepta-1,3-dien-6-one[8] (300 mg, 1.44 mmol) in anhydrous MeCN (15 mL) was added a mixture of KF-Al_2O_3[9] (1.26 g, 7 mmol) and *p*-toluenesulfonyl azide (567 mg, 2.88 mmol) at 0−5 °C, and the mixture was stirred at this temperature for 4 days. After all of the starting ketone was consumed as judged by TLC monitoring, the mixture was filtered to remove KF−Al_2O_3 and dissolved in CH_2Cl_2 (20 mL). The solution was extracted with 5% KOH aq and water and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by drying at 10^{-1} Torr left the desired bis(diazo) ketone as an orange solid in 75% yield: mp 164−165 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.02−7.64 (m, 8H); IR (KBr) 2060, 1595 cm^{-1}.

When the reaction was carried out using the azide in 1 equiv to the ketone, monodiazo ketone (**14**) was obtained in 43% yield as an orange solid: mp 116−118 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.72−7.20 (m, 8H), 3.60 (s, 2H); IR (Ar, 10K) 2094 (s), 2016 (s), 1611 (w), 1331 (m), 1298 (s), 1246 (s), 759 (m), 732 (w), 712 (w).

9,10-Dicarbonylphenanthrene anhydride (33),[24] **9-carboxylphenanthrene (16, R = H),**[25] **and 9-carboxy-9,10-dihydrophenanthrene (17, R = H)**[26] were prepared according to the reported procedures.

Irradiation for Product Identification. In a typical run, a solution of the diazo compound (20 mg) in solvent (10−20 mL) was placed in a Pyrex tube and degassed by subjecting the sample to a minimum of three freeze-degas-thaw cycles at pressure near 10^{-5} Torr before irradiation. Irradiation was carried out with a high pressure 300 W mercury arc lamp at room temperature until all the diazo compound was destroyed. The mixture was then concentrated on a rotary evaporator below 10 °C. Individual components were isolated by preparative TLC and identified by NMR and MS.

Following products were isolated in the irradiation of **15** in nucleophilic solvents and identified by ^{1}H NMR and GC-MS comparison with that of authentic specimens prepared from phenanthrene carboxylic acid. **9-(Alkoxycarbonyl)phenanthrenes. 16a:** ^{1}H NMR ($CDCl_3$) δ 8.95−8.89 (m, 1H), 8.79−8.69 (m, 2H), 8.49 (S, 1H), 7.99−7.96 (m, 1H), 7.80−7.61 (m, 4H), 4.06 (s, 3H); *m/e* (rel intensities) 273 (17), 236 (M^+, 100), 206 (15), 205 (97), 178 (13), 177 (75). **16b:** ^{1}H NMR ($CDCl_3$) δ 8.93−8.89 (m, 1H), 8.76−8.68 (m, 2H), 8.46 (s, 1H), 7.99−7.96 (m, 1H), 7.78−7.61 (m, 4H), 4.52 (q, *J* = 7.2 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H); MS *m/e* (rel intensities) 251 (17), 250 (M^+, 100), 222 (15), 206 (19), 205 (100), 178 (19), 177 (73), 176 (49). **16c:** ^{1}H NMR ($CDCl_3$) δ 8.96−8.86 (m, 1H), 8.76−8.66 (m, 2H), 8.41 (S, 1H), 8.03−7.93 (m, 1H), 7.82−7.61 (m, 4H), 5.42 (sept,

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J = 7.3 Hz, 1H), 1.49 (d, J = 7.3 Hz, 6H); MS m/e (rel intensities) 226 (1); 265 (19), 264 (M$^+$, 100), 223 (13), 222 (87), 206 (10), 205 (35), 178 (7), 177 (5). **9-(*N,N*-Diethylcarbamoyl)phenanthrene:** ^{1}H NMR (CDCl$_3$) δ 8.85–8.60 (m, 2H), 8.00–7.82 (m, 2H), 7.80–7.60 (m, 5H), 3.80–3.40 (m, 2H), 3.20 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H), MS m/e (rel. intensities) 278 (9), 277 (M$^+$, 100), 276 (43), 222 (87), 206 (21), 205 (35), 178 (14), 177 (61), 176 (36).

Irradiation of 15 in PhH gave **20** in 46% yield as a yellowish powder: mp > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.14 (d, J = 12.0 Hz, 2H), 2H), 8.75 (d, J = 12.0 Hz, 2H), 8.65 (d, J = 12.0 Hz, 2H), 8.20 (d, J = 12.0 Hz, 2H), 7.84 (dd, J = 12.0, 12.0 Hz, 2H), 7.77 (dd, J = 12.0, 12.0 Hz, 2H), 7.71 (dd, J = 12.0, 12.0 Hz, 2H), 7.43 (dd, J = 12.0, 12.0 Hz, 2H); MS (in beam EI, 300 °C) m/e (rel intensities) 436 (M$^+$, 100), 408 (18), 379 (19), 350 (14), 318 (7), 281 (4), 234 (8), 204 (12), 176 (32), 138 (10), 110 (8), 60 (9); IR (KBr) 3400 (m), 1740 (s), 1690 (m), 1610 (m), 1450 (w), 1420 (w), 1260 (w), 1140 (w), 760 (m), 720 (m) cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ϵ) 481 (3.8), 461 (3.8), 329 (4.3), 318 (4.3), 255 (4.7) nm; fluorescence (CH$_2$Cl$_2$) $\lambda_{\max}$ 514 nm.

Irradiation of 15 (150 mg) in furan (15 mL)–benzene (15 mL) mixture afforded the following products after TLC separation: **20** (36.3 mg, 24%); triphenylene (**24**, 7.5 mg, 17%); **25** (5.2 mg, 3.3%): yellow solid; mp > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.12 (s, 1H), 9.19–9.15 (m, 1H), 8.77–8.74 (m, 2H), 7.93–7.89 (m, 1H), 7.82–7.59 (m, 5H), 6.73 (dd, J = 0.66, 3.30 Hz, 1H), 6.69 (dd, J = 16.5, 3.30 Hz, 1H), MS m/e (rel intensities) 273 (8), 272 (M$^+$, 50), 271 (4), 244 (85), 24 (13), 217 (6), 216 (51), 215 (100), 214 (11), 231 (31), 189 (15), 188 (4), 187 (7); IR (KBr) 2920 (w), 2850 (w), 1680 (s), 1640 (s), 1450 (w), 1360 (s), 1330 (s), 1260 (w), 1220 (w), 1060 (w), 1020 (w), 950 (w), 940 (w), 740 (s) cm^{-1}; **26** (2.9 mg, 1.8%): yellow solid; mp 161–163 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.37 (S, 1H), 10.03 (m, 1H), 9.85–9.79 (m, 1H), 8.69–8.60 (m, 3H), 8.29 (d, J = 8.57 Hz, 1H), 7.77–7.50 (m, 5H); MS m/e (rel intensities) 273 (20), 272 (M$^+$, 100), 271 (20), 226 (15), 215 (26), 213 (12); IR (KBr) 2850 (w), 2360 (w), 1690 (s), 1645 (s), 1350 (m), 1330 (m), 1260 (m), 1210 (m), 1170 (m), 1040 (m), 1750 (s) cm^{-1}.

Irradiation of 15 in EtOH at 77 K was carried out by irradiating EtOH (1 mL) matrix containing **15** (2 mg) in a Pyrex tube suspended in a transparent Pyrex Dewar filled with liquid nitrogen. Analysis of the mixture by GCMS and ^{1}H NMR indicated the presence of **16** (R = Et, 36%), **18** (10%), and **31** (36%).

Attempts to Generate Cyclopropenone 28. A solution of **29**[27] (10 mg) in anhydrous PhH (5 mL) was treated with NEt$_3$ (10 mg), and the solution was refluxed for 20 min. Usual workup, followed by GC-MS and ^{1}H NMR analysis, indicated the presence of **16** (R = H) as major product.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard technique using an Iwatani Cryo Mini closed cycle helium cryostat.[28] For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing parts of a vacuum shroud were fitted with KBr windows for spectroscopic viewing, and the remaining parts were fitted with quartz for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 temperature controller.

Argon (Seitetsu Chemicals, 99.999%), dioxygen (Seitetsu Chemicals, 99.9995%), and xenone (Seitestu Chemicals, 99.99%), were mixed in a gas handling system by standard manometric techniques. Precursors molecules (i.e., **15** and **33**) were directly sublimed on the cold window while a large excess of the host gas was deposited simultaneously.

Irradiations were carried out using a Wacom 500 W xenon high pressure arc lamp or an Ushio 500 W mercury high pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelength specified). The third and fourth harmonics of a Quanta-Ray GCR-11 Nd: YAG laser were also used.

Irradiations of **15** in Ar at 10K gave the following products. **30**: IR (Ar, 10 K) 1862 (s), 1610 (w), 1587 (w), 1536 (vw), 1299 (w), 1246 (w), 952 (vw), 750 (m), 726 (w), 681 (w), and 663 (w) cm^{-1}. **32**: IR (Ar, 10 K) 1623 (vw), 1609 (vw), 1488 (vw), 1036 (vw), 752 (m), 720 (w), 662 (w), and 551 (w) cm^{-1}.

Low-Temperature Spectra at 77 K. Low temperature IR spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN1704) equipped with quartz outer windows and sapphire inner windows for irradiation and KRS5 outer windows and zinc selenide inner windows for IR measurement. The sample was mixed with Nujol and placed between two NaCl discs. The disc was placed in the cryostat, cooled to 77 K, and irradiated. The spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC4).

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Supplementary Material Available: Copies of ^{1}H NMR spectra of **20**, **25**, and **26** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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