After irradiation (2 h) with a long wavelength hand TLC lamp (366 nm transmission maximum), evaporation (room temperature, 100 mmHg) and preparative GC (5 m × 4 mm 10% SE 30 Chromosorb P, 60 mL He/min, injection port: 250 °C, column: 190 °C, detector: 220 °C) yielded three components: 2.4 mg (22%) of **7** (t_R 9-11 min); 2.7 mg (25%) of a mixture (t_R 11-13 min); 1.8 mg (17%) of **13** (79% pure, t_R = 13-15 min) as colorless oils with strong musty odors. For **13**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.23-7.16 (m, 2 H), 7.16-7.09 (m, 2 H), 6.54 (d, J = 11.9 Hz, 2 H), 6.00-5.90 (m, 2 H), 2.33 ('t', J = 2.8 Hz, 4 H). This spectrum compares well with that described in ref 21.

C. NMR Scale Irradiation of 1-d_2 in Methylene Chloride at 366 nm. A solution of **1**-d_2 (5 mg, 0.03 mmol; 87% deuteriated in positions 3 and 9) in methylene chloride (spectrophotometric grade) was prepared as in **A** and irradiated at 366 nm for 54 min. According to ^{2}H NMR, all of the starting material was replaced by **9** and **12**-d_2. For **9**: ^{2}H NMR (77 MHz, CH_2Cl_2, reference CD_2Cl_2) δ 6.11, 6.03, 5.98, 5.93. For **12**-d_2: ^{2}H NMR (77 MHz, CH_2Cl_2) δ 5.83 (1.7), 5.75 (1.6), 5.56 (3.3), 3.50 (1.0).

Thermal Rearrangement of 2. An NMR tube containing a cold (-78 °C) solution of **2** in chloroform-d was equilibrated in a 300-MHz NMR spectrometer at 293 K for 10 min. Spectra were subsequently collected at 10-min intervals (eight scans took 37 s) and always integrated by using the same amplitude. The following absorptions were chosen for integration. **2**: δ 6.27-6.16 (4 H); **14**: δ 5.33 (1 H); **15**: δ 6.67 (2 H). The sum of the integrals of each scan was normalized to 100. The rate constant k = 1.55 × 10^{-4} s^{-1} corresponds to a half-life of 74 min at 20 °C.

Thermal Rearrangement of 2-d_2. A solution of the dibromo chlorosulfone precursor[3] (93 mg, 0.24 mmol) and 99.8% deuterium oxide (2.9 μL, 2.9 mmol) in anhydrous tetrahydrofuran (1.5 mL) was cooled to -70 °C, treated with 1.6 M potassium *tert*-butoxide in tetrahydrofuran (3.6 mL, 5.8 mmol), and slowly warmed to 0 °C within 1 h. After another hour at 0 °C, the reaction mixture was worked up with water and pentane at 0 °C as described above.

According to 300-MHz ^{1}H NMR ($CDCl_3$, 263 K), the hydrocarbon mixture consisted of triene **2**, the tricyclo[5.3.0.0^{2,8}]deca-4,9-diene contaminant, and isobullvalene (**14**) in a ratio of 53:43:4 with a deuterium incorporation of about 30% in the 9- and 10-positions of the diene and triene. Careful evaporation of the $CDCl_3$ and condensation mg (19%) of material that was dissolved in carbon tetrachloride and heated until all was converted into lumibullvalene-d_2 (**15**-d_2). ^{2}H NMR analysis in CCl_4 with δ ($CDCl_3$) 7.26 ppm as standard revealed the presence of three deuterium signals at 3.13, 5.57 and 6.63 ppm in a ratio of 1:2:1.

Thermal Rearrangement of 3. An NMR tube containing 15 mg of **3** in 1 mL of C_6D_6 was warmed in an 80 °C oil bath for 3.5 h. In order to obtain kinetic data, the olefinic singlets were integrated at various times. Computational and graphical determinations yielded half-lives of 68 and 63 min, respectively.

For **22**: ^{1}H NMR (500 MHz, C_6D_6) δ 6.17 (dd, J = 8.9, 11.2 Hz, 1 H), 6.03 (dd, J = 3.8, 11.2 Hz, 1 H), 5.74-5.66 (m, 2 H), 5.37 (s, 1 H), 5.32 (d, J = 3.2 Hz, 1 H), 4.93 (s, 1 H), 4.79 (d, J = 2.6 Hz, 1 H), 3.42-3.39 (m, 1 H), 1.80 (dd, J = 6.3, 12.6 Hz, 1 H), 1.55 (dd, J = 5.9, 9.4 Hz, 1 H), 1.36-1.32 (m, 1 H); ^{13}C NMR (125 MHz, C_6D_6) ppm 152.13, 149.32, 137.90, 133.96, 120.10, 127.54, 105.25, 103.10, 44.45, 27.47, 25.19, 22.09; MS, m/z (M^+) calcd 156.0917, obsd 156.0939.

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Chemical and Physical Properties of Anthronylidene

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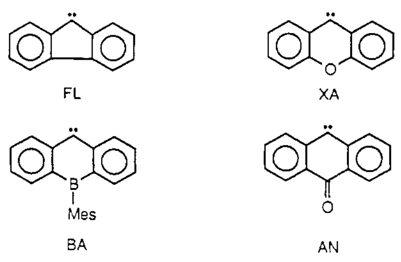
Irradiation of diazoanthrone (DAAN) leads to loss of nitrogen and to formation of the carbene anthronylidene (AN). The triplet ground state of this carbene was detected at low temperature by ESR and optical spectrometric methods and at room temperature in fluid solution by laser flash photolysis. The rate constants for the reaction of ^{3}AN with olefins, saturated hydrocarbons, and alcohols were determined spectrometrically. Combination of these kinetic measurements with the results of chemical competition studies permits estimation of the energy gap separating the ground triplet state from the lowest singlet state of AN (ΔG_{ST}) to be 5.8 ± 0.6 kcal/mol. This value is compared with that for other related carbenes and with the estimate obtained from MINDO/3 calculations for AN.

The chemical and physical properties of carbenes are remarkably sensitive to electronic perturbation. This is primarily a result of the relatively small energy difference between the highest occupied and lowest unoccupied molecular orbitals for these species.[3] Small changes in the energies of these orbitals can invert the state spin multiplicities from their usual order of triplet below singlet. It has been understood for some time on a theoretical level that there are two distinct ways to affect the energies of these orbitals.[4] The first is through a change in geometry, primarily the bond angle at the carbene carbon atom. Calculations predict that as this angle contracts, the energy of the singlet carbene decreases relative to that of the triplet. The second variable that controls the singlet-triplet gap is related to electronic perturbation.[5] This is clearly revealed experimentally in the comparison of

Chart I



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fluorenylidene (FL)[6] with xanthylidene (XA)[7] and mesitylboraanthrylidene (BA),[8] see Chart I, where the symmetry of the lowest unoccupied molecular orbital changes in this series. Chemical and spectroscopic analysis of these carbenes show that BA has a triplet ground state while the ground state of XA is a singlet. The properties of FL are more difficult to classify; its ground state is a triplet, but it reacts mainly from the singlet state only ca. 2 kcal/mol higher in energy.

We undertook the systematic study of anthronylidene (AN) as part of the effort to extend the range of the examined electronic perturbations of aryl carbenes. Anthronylidene has been the subject of previous investigations.[9] Devolder and co-workers recorded its ESR spectrum in frozen media and concluded that the ground state of this carbene is a triplet. In a related experiment, this group also reported the electronic absorption spectrum of triplet AN. They assigned a strong band at 353 nm and two weaker, broad bands at 520 and 565 nm to absorptions of the triplet carbene. Of most relevance to the present report is the work of Reverdy and co-workers who studied the chemical properties of AN formed from thermolysis or photolysis of diazoanthrone (DAAN). Their preliminary[10] conclusion is that the singlet and triplet states of this carbene are in rapid equilibrium and that both states participate in reactions that lead to the isolated products. This behavior implies a relatively small energy gap (ΔG_{ST}) separating the singlet from the triplet ground state for this carbene.

We report herein the results of product, kinetic, and spectroscopic experiments on the reactions of AN at room temperature with a range of substrates. These experiments define more accurately the properties of this carbene and permit estimation of ΔG_{ST}.

Results and Discussion

(1) Photolysis of DAAN in Frozen Media. DAAN is a stable, red-brown solid conveniently prepared by the method of Regitz[11] from the reaction of anthrone with tosyl azide. We observe two paramagnetic species when the irradiation of diazoanthrone in a 2-methyltetrahydrofuran (MTHF) glass at 77 K is followed by ESR spectral analysis. The first is characteristic of triplet anthronylidene (^{3}AN),[9] and the second corresponds to a doublet, presumably, at least in part, the anthronyl radical (ANH$^\bullet$). All of the ESR signals disappear when the sample is warmed to room temperature and then refrozen. The optical absorption spectrum of DAAN irradiated in deoxygenated (MTHF) at 4 K exhibits three notable features; a sharp, intense UV band with a maximum at 352 nm and two weak broad bands at 523 and 564 nm. These bands also disappear when the sample is warmed.

(2) Nanosecond Laser Flash Photolysis of DAAN. Irradiation of a rigorously deoxygenated benzene solution of DAAN at room temperature with the output of a pulsed nitrogen laser (10 ns, 337 nm, 7 mJ) yields a transient product whose absorption spectrum recorded 100 ns after the laser pulse shows three prominent maxima (354, intense; 521 and 561 nm, weak), Figure 1. The transient species is formed within the rise time of the laser. The decay rate of the transient absorptions are unaffected when tetramethyldiazetine dioxide (TMDD, [5 × 10^{-5} M], a diffusion-controlled quencher of electronically excited triplet states)[12] is added to the solution before the flash photolysis experiment. Irradiation of DAAN in acetonitrile solution gives a similar transient product spectrum. Comparison of the low-temperature and transient absorption spectra at early times suggests tentative assignment of the short-lived species observed at room temperature in benzene or acetonitrile solution to triplet anthronylidene (^{3}AN). This assignment is supported by a series of kinetic and product studies.

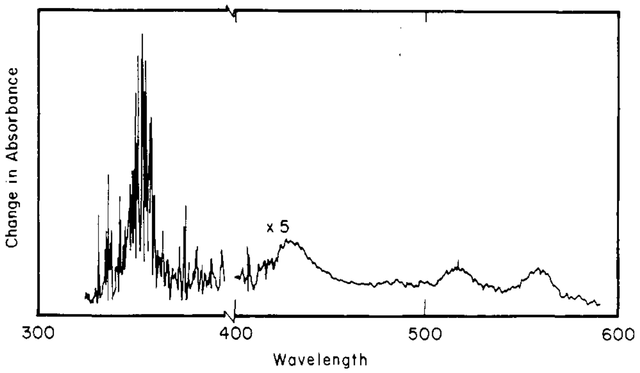

Figure 1. Absorption spectrum of transient product recorded 100 ns after pulsed irradiation of diazoanthrone in benzene solution at room temperature.

Laser flash photolysis of DAAN in cyclohexane yields a transient product whose absorption spectrum is qualitatively similar to that of the intermediate formed by the irradiation of DAAN in benzene or acetonitrile solution (λ_{max} 352, 422 intense; 525 and 571 nm, very weak). However, the chemical behavior of the species detected in cyclohexane is different from that of the intermediate observed by flash photolysis of the diazo compound in the other solvents. The reactions of the intermediate formed in cyclohexane solution are characteristic of the anthronyl radical (ANH$^\bullet$) and not of the carbene (see below). It has been known for a long time that the spectra of triplet carbenes and those of the structurally related radicals are often very similar.[13]

(3) Chemical and Kinetic Behavior of AN. The chemical properties of carbenes are customarily associated with reactions originating from a radical-like triplet state or from an electrophilic singlet state. Consequently, ether formation from alcohols[14] and stereospecific cyclopropanation of olefins[15] are commonly attributed to the singlet state, while the reaction with oxygen,[16] hydrogen atom abstraction,[17] and nonstereospecific cyclopropanation are believed to be characteristic reactions of carbenes in their triplet state.[15]

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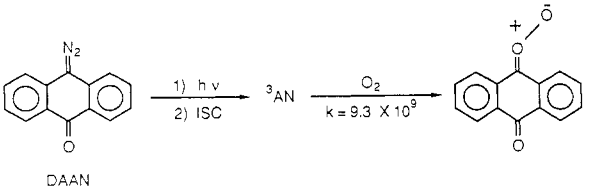
(A) Reaction of AN with Oxygen. When an oxygen-saturated benzene solution of DAAN is irradiated with the pulsed laser, the transient absorption features described above are not detected; however, a new broad band centered at 465 nm is observed in the spectrum. The oxygen-dependent transient species is formed on a nanosecond time scale and has a lifetime of several hundred microseconds. Irradiation of DAAN in a nitrogen-purged (low O_2 concentration) benzene or acetonitrile solution produces the same new transient product. However, under these conditions it takes about 2 μs for the new species to grow fully into the spectrum. The oxygen-related 465-nm absorption band is formed at the expense of the carbene bands at 354, 521, and 561 nm. Analysis of the time-dependent behavior of the transient signals at 354 and 561 nm reveals that oxygen increases their rate of decay without changing the intensity of their initial absorption. This behavior reveals that oxygen reacts with the detected transient and not with a precursor species to it.

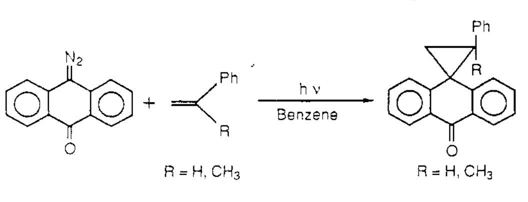
Irradiation of DAAN in cyclohexane solution containing a low concentration of dissolved O_2 (nitrogen-purged) gives results significantly different from those obtained from irradiation in benzene solution under these conditions. Oxygen reacts very slowly with the transient species detected in cyclohexane, and it inhibits formation of the transient by reacting rapidly with its precursor.

These findings are consistent with assignment of the transient species detected immediately after the laser pulse in benzene and acetonitrile to ^{3}AN. Other related triplet carbenes are known to react rapidly with oxygen to form carbonyl oxides whose absorption spectra are similar to that of the oxygen-dependent product detected in the photolysis of DAAN.[16,18] In the present case, anthraquinone *O*-oxide formed by rapid combination of ^{3}AN and O_2 is the species that absorbs strongly at 465 nm when O_2-saturated benzene solutions of DAAN are irradiated, eq 1. Apparently, photolysis of DAAN in cyclohexane solution also gives the triplet carbene, but its rapid reaction with the solvent to give ANH$^\bullet$ competes with the trapping by oxygen. The rate constant for the reaction of ^{3}AN with oxygen (k_{O_2}) can be determined by competition between its reaction with α-methylstyrene (see below) and with oxygen in benzene solvent. The change of the absorbance of the transient at 354 nm ultimately affords $k_{O_2} = 9.3 \pm 0.2 \times 10^9$ M^{-1} s^{-1}, a value close to the diffusion limit for reactions in this solvent.



(1)

(B) Reaction of AN and ANH$^\bullet$ with Styrene. Irradiation (Rayonet, 350 nm) of DAAN in deoxygenated benzene containing freshly distilled styrene (5 M) gives the expected cyclopropane[9] in essentially quantitative yield, eq 2. This reaction can be followed by laser transient absorption spectroscopy. The rate constant for decay (k_{obsd}) of the transient absorbance monitored at 354 nm increases linearly with styrene concentration. These rate constants can be fit to a pseudo-first-order rate law that gives the bimolecular rate constant for the reaction of AN with styrene ($k_{sty.}$) = 6.4 ± 0.2 × 10^7 M^{-1} s^{-1}). Similar values are obtained when the decay of the transient product is monitored at 521 (6.6 ± 0.1 × 10^7) or 561 nm (5.8 ± 0.7 × 10^7). These observations indicate that the same transient species is responsible for the three absorption features.



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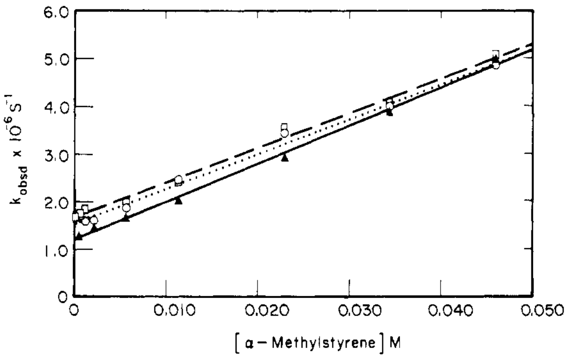

Figure 2. Pseudo-first-order rate constants for the decay of the transient as a function of α-methylstyrene concentration, monitored at 354 nm (solid line); 521 nm (dotted line), and 561 nm (dashed line).

Quite significantly, the rate of decay of the transient species formed by irradiation of DAAN in cyclohexane is unaffected by addition of styrene (0.1 M) to the reaction mixture. Moreover, again opposite to behavior in benzene solution, the initial absorbance intensity of the transient (extrapolated to time equals zero) at 354 nm decreases as the concentration of styrene in the cyclohexane solution is increased. Obviously the different chemical behavior of similarly absorbing species in benzene and cyclohexane solution show that they are not the same chemical entity. The transient product detected by the irradiation of DAAN in benzene reacts completely with styrene in ca. 2 μs to form cyclopropane. These observations support assignment of the transient species observed immediately after the laser pulse in benzene solution to the carbene and that observed in cyclohexane to the anthronyl radical. The difference in the reactions of these intermediates with styrene allows rates of reaction of AN in cyclohexane to be measured by competition with its conversion to ANH$^\bullet$. At long times (>1 μs) after the laser pulse in benzene solution the transient spectrum may be a composite of that of the carbene and the radical. Hydrogen atom abstraction from benzene by anthronylidene has been suggested previously from product studies that showed biphenyl formation.[9]

(C) Reaction of AN with α-Methylstyrene. Irradiation of DAAN in deoxygenated benzene containing freshly distilled α-methylstyrene (1.02 M) leads to the expected cyclopropane (97%), eq 2. The bimolecular rate constant for the reaction of AN with α-methylstyrene ($k_{\alpha MS}$) was obtained from analysis of the decay of the transient absorption spectrum as described above. This procedure affords $k_{\alpha MS} = 8.0 \pm 0.2 \times 10^7$ M^{-1} s^{-1} when measured at 354 nm, and 7.4 ± 0.2 × 10^7 and 7.2 ± 0.2 × 10^7 by monitoring the absorptions at 521 or 561 nm, respectively, Figure 2. When this experiment is carried out with (*E*)-α-methyl-β-deuteriostyrene[7] (0.99 M), NMR spectral analysis of the resulting cyclopropane reveals that it had been formed with complete randomization of olefin stereochemistry. Control experiments show that α-methyl-

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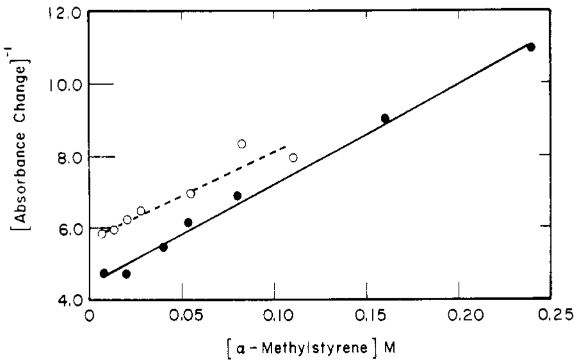
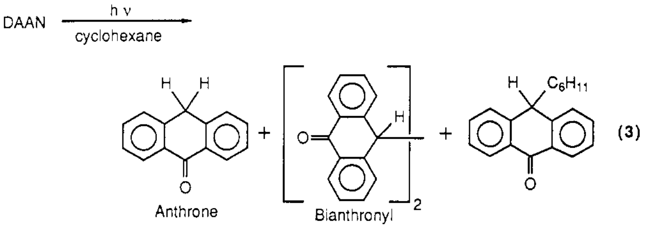


Figure 3. Solid line: plot of the reciprocal of the relative yield of ANH$^\bullet$ monitored at 352 nm 1 μs after pulse irradiation of diazoanthrone in benzene solution containing 1.85 M cyclohexane and various concentrations of α-methylstyrene. Dashed line: plot of the reciprocal of the relative yield of ANH$^\bullet$ monitored at 352 nm 13 μs after pulse irradiation of diazoanthrone in benzene solution containing 1.31 M isopropyl alcohol and various concentrations of α-methylstyrene.

styrene is not significantly isomerized under the irradiation conditions. These findings are consistent only with exclusive cyclopropanation by the triplet carbene under these conditions. These experiments support assignment of the transient absorption spectrum measured in benzene to ^{3}AN.

(D) Reaction of AN with Cyclohexane. Photolysis of a deoxygenated cyclohexane solution of DAAN (98% conversion) gives three major products, eq 3. This result



is characteristic of the formation of the cyclohexyl and anthronyl radicals. Anthraquinone (from residual oxygen) is also formed in this reaction, but in these experiments its yield was not quantified.

The spectral overlap of ^{3}AN with ANH$^\bullet$ prohibits direct measurement of the rate of reaction of ^{3}AN with cyclohexane by laser spectroscopy. However, the desired rate constant ($k_{C_6H_{12}}$) was obtained by analysis of the competition of ^{3}AN for cyclohexane and α-methylstyrene. Reaction of the carbene with cyclohexane gives the anthronyl radical which can be uniquely detected spectroscopically in the presence of the α-methylstyrene. A plot of the reciprocal of the relative yield of ANH$^\bullet$ against the α-methylstyrene concentration at fixed cyclohexane concentration is shown on Figure 3. Analysis of the kinetic network for this competition gives eq 4, which shows that

$$\frac{1}{[\mathrm{ANH}\bullet]} = C\left[1+\frac{k_{\alpha\mathrm{MS}}[\alpha\mathrm{MS}]}{k_{C_6H_{12}}[C_6H_{12}]}\right] \qquad (4)$$

Where C = a proportionality constant relating ΔOD to concentration of ANH•

the ratio of the intercept to slope from this plot gives the ratio of $k_{\alpha\mathrm{MS}}$ to $k_{C_6H_{12}}$. The rate constant for reaction with α-methylstyrene was determined independently (see above); its substitution into the slope to intercept ratio gives $k_{C_6H_{12}} = 7.2 \pm 0.5 \times 10^6$ M^{-1} s^{-1}. A related experiment with C_6D_{12} instead of cyclohexane gives the rate constant for the reaction of ^{3}AN with C_6D_{12} ($k_{C_6D_{12}}$) equal to 1.1 ± 0.15 × 10^6 M^{-1} s^{-1}. As expected, comparison of these rate constants reveals a primary kinetic isotope effect of ca. 6.5 for reaction of ^{3}AN with cyclohexane. This value is consistent with rate-determining hydrogen atom abstraction from cyclohexane by the triplet carbene.

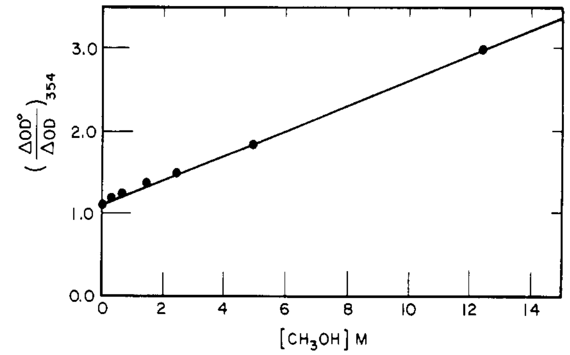
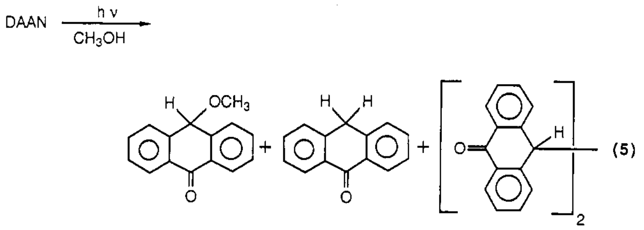


Figure 4. Stern–Volmer analysis of the relative yield of ^{3}AN, monitored at 354 nm, after pulse irradiation of diazoanthrone in benzene solution containing various concentrations of methanol.

Additional support for the hydrogen abstraction–radical recombination sequence in the reaction of ^{3}AN with cyclohexane comes from a cross-over experiment. Photolysis of DAAN in a 6.5:1 mixture of cyclohexane-d_{12} and cyclohexane gives the expected 10-cyclohexylanthrone. Analysis of this product by mass spectroscopy shows ca. 30% of the 10-deuterio-10-(perhydrocyclohexyl)anthrone. This compound can only be formed from combination of a 10-deuterioanthronyl radical with a perhydrocyclohexyl radical.

(E) Reaction of AN with Alcohols. Photolysis of DAAN in deoxygenated methanol affords anthrone, methyl 9-anthronyl ether, bianthronyl, and several minor unidentified products, eq 5. Analysis of this reaction by laser



spectroscopy reveals that the lifetime of the ^{3}AN in benzene decreases as the methanol concentration increases. Addition of methanol to benzene solutions of DAAN also reduces the amount of ^{3}AN formed from irradiation. Thus, the initial absorbance of the carbene at 354 nm decreases as the methanol concentration is raised, Figure 4.

The precursor to ^{3}AN trapped by methanol is presumed to be the singlet carbene (^{1}AN). Singlet states of carbenes react rapidly with alcohols to give ethers.[7] By assuming that the singlet carbene reacts with methanol at the diffusion-limited rate, an estimate of the rate constant of intersystem crossing from the singlet to the triplet carbene (k_{ST}) of 3 × 10^{10} s^{-1} is obtained from this experiment. This value is similar to those revealed directly by picosecond time-scale measurements on fluorenylidene,[6] boraanthrylidene,[8] and diphenylmethylene.[19]

Irradiation of DAAN in deoxygenated isopropyl alcohol gives four major products that account for 84% of the consumed DAAN, eq 6. The change in absorbance at 354 nm of the transient spectrum in benzene solutions containing isopropyl alcohol responds in the same way to alcohol concentration as for photolyses in the presence of methanol described above. The rate constant for reaction of ^{3}AN with isopropyl alcohol (k_{IPA}) can be obtained from

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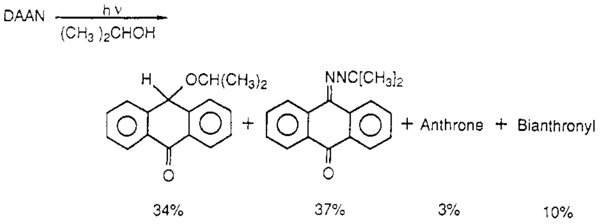
[19] Eisenthal, K. B.; Turro, N. J.; Moss, R. A. *Science (Washington, D.C.)* **1984**, *225*, 1439.

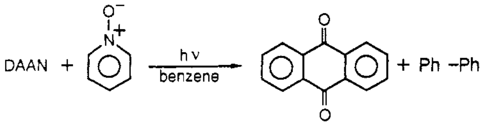


(6)

analysis of its competition for the triplet carbene with styrene. The absorbance at 352 nm 13 μs after the laser pulse for solutions that contain both alcohol and styrene is due exclusively to ANH• formed from hydrogen atom abstraction by the triplet carbene from the alcohol (there is no radical formed in the absence of alcohol). When the relative yield of ANH• is combined with the rate of reaction of ^{3}AN with styrene (see above), calculations analogous to eq 4 give $k_{IPA} = 1.7 \pm 0.3 \times 10^7$ M^{-1} s^{-1}, Figure 3.

Irradiation (350 nm) of DAAN in deoxygenated *tert*-butyl alcohol (83% conversion) gives the *tert*-butyl ether in 33% yield. The rate constant for this reaction of ^{3}AN ($k_{t\text{-BuOH}}$) was determined also by competition with α-methylstyrene to be $6.1 \pm 0.13 \times 10^6$ M^{-1} s^{-1}. It is significant that *tert*-butyl alcohol, which has only primary hydrogens bound to carbon, reacts more slowly with ^{3}AN than does isopropyl alcohol.

(F) Reaction of AN with Pyridine *N*-Oxide. Irradiation of DAAN in a benzene solution containing 0.9 M pyridine *N*-oxide (PYO) gives anthraquinone (92%) and biphenyl (from reaction of ^{3}AN with benzene,[9] 6%), eq 7.



(7)

When a solution of DAAN in benzene containing 0.25 M α-methylstyrene is irradiated, the yield of the cyclopropane is 93%, the yield of biphenyl is 0.1%, and the yield of anthraquinone is only 2%. It is important to recall that the experiments with β-deuterio-α-methylstyrene (see above) reveal that the cyclopropane formed under these conditions originates exclusively from reaction of the triplet carbene. When a solution of DAAN in benzene containing both PYO (0.9 M) and α-methylstyrene (0.25 M) is irradiated, the yield of cyclopropane is 31%, that of anthraquinone is 53%, and no biphenyl can be detected. The formation of anthraquinone from the reaction of PYO with AN has previously been assumed to be a reaction of the singlet state of this carbene.[9] If this is so, then these experiments show that, in the absence of the styrene, ^{3}AN can reform ^{1}AN and then react with PYO.

We examined the reaction of ^{3}AN with PYO spectroscopically on a nanosecond time scale. As the PYO concentration in a benzene solution of DAAN increases, the triplet carbene absorption at 354 nm decreases due to competitive absorption by PYO at the excitation wavelength (337 nm). No change in the lifetime of ^{3}AN can be detected when PYO is added to benzene solutions of DAAN and the rate constant for reaction of the carbene with α-methylstyrene is not changed by the presence of PYO. These experiments indicate that the chemical properties of ^{3}AN are unaffected by the presence of PYO and that if ^{3}AN reacts directly with PYO, then this rate constant must be small in comparison with the abstraction of hydrogen from benzene.

The rate constant for conversion of ^{3}AN to ^{1}AN can be put on a quantitative basis by analysis of a competition between the reaction of the triplet carbene with a low concentration of α-methylstyrene and its reversion to the singlet and subsequent capture by PYO. Solution of the kinetic scheme for this competition gives the relationship between the yield of anthraquinone (Φ_{ANO}) and the styrene concentration shown in eq 8. This relationship indicates

$$\Phi_{ANO} = \frac{k_{pyo}[PYO]}{k_{pyo}[PYO] + k_{ST}} \left[1 + \frac{k_{TS}}{k_{TS} + k_{\alpha MS}[\alpha MS]} \right] \quad (8)$$

that a plot of Φ_{ANO} against the reciprocal of the α-methylstyrene concentration at fixed PYO concentration will yield a straight line whose intercept to slope ratio is equal to $[1 + (k_{\alpha MS}/k_{TS})]$, where k_{TS} is the rate constant for conversion of ^{3}AN to ^{1}AN. Figure 5 shows such a plot for samples containing 0.93 M PYO with α-methylstyrene concentrations ranging from 0.019 to 0.094 M. With the previously determined value of $k_{\alpha MS}$, this experiment gives $k_{TS} = 2.3 \pm 1.0 \times 10^6$ s^{-1}.

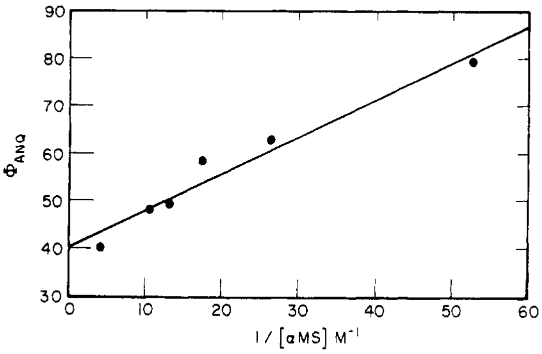


Figure 5. Plot of the absolute yield of anthraquinone from the photolysis of diazoanthrone in benzene solution at constant [PYO] (0.93 M) vs the reciprocal of [α-methylstyrene].

(4) Estimation of ΔG_{ST} of AN. The free-energy difference between the singlet and the triplet states of AN can be estimated from the kinetic data described above. This analysis requires that the reaction mechanism used to define the meaning of the rate constants obtained is correct. In the present case, the assumed mechanism requires both reaction of ^{1}AN with methanol at the diffusion-controlled rate and that PYO reacts exclusively with ^{1}AN to form anthraquinone. Both of these assumptions are reasonable and are well-precedented.[7,9] The kinetic measurements give k_{TS} and k_{ST}, which represent the forward and reverse reactions in the equilibration of the singlet and triplet carbenes. Division gives the equilibrium constant (K_{EQ}) = $1.3 \pm 0.8 \times 10^4$, which corresponds to $\Delta G_{ST} = 5.8 \pm 0.6$ kcal/mol.

Some additional confidence in the estimate of ΔG_{ST} may be obtained by comparison of this value with one obtained from a MINDO/3 calculation,[20] Figure 6. We have shown previously that MINDO/3 gives consistent estimates of ΔG_{ST} for rigid, aryl-substituted carbenes.[21] The correlation revealed in Figure 6 shows that the relative (if not the absolute) value of ΔG_{ST} obtained in this work for AN follows the trend of structural and electronic effects defined by the series of other similar carbenes.

Conclusion

The ground state of AN is a triplet that reacts rapidly with oxygen to form a carbonyl oxide, with olefins to form cyclopropanes with complete loss of stereochemistry, and with hydrocarbons by hydrogen atom abstraction. The singlet state of AN is ca. 5.8 kcal/mol above its triplet state. Under most circumstances, a gap of this magnitude

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(20) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(21) Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1988**, *53*, 1273.

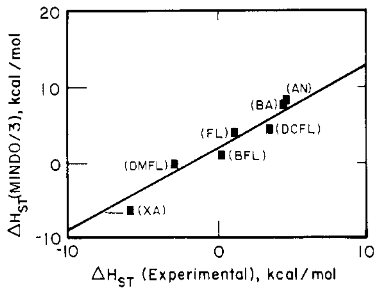

Figure 6. Plot of ΔH_{ST} calculated (MINDO/3) vs experimentally determined values: XA (9-xanthylidene); DMFL (3,6-dimethoxyfluorenylidene); BFL (2,3-benzofluorenylidene); FL (fluorenylidene); DCFL (2,7-dichlorofluorenylidene); BA (9-mesityl-9,10-dihydro-9-boraanthrylidene); AN (anthronylidene).

is too large to permit reformation of the singlet carbene from the triplet before the lower state is consumed by bimolecular reactions. However, in relatively inert solvent (benzene, for example) in the presence of a reagent specific for the singlet carbene (for, example PYO) equilibration with and reaction from the upper state does occur.

Experimental Section

General. Proton (^{1}H NMR) and carbon (^{13}C NMR) magnetic resonance spectra were recorded on a Varian Associates XL-200 (200 MHz, FT) spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with Varian MAT CH-5 and 731 mass spectrometers. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 1320, an IBM Instruments, Inc., IR/32 FT-IR, and a Nicolet Model 7199 FT-IR instrument. Steady-state ultraviolet–visible (UV–vis) absorption spectra were recorded on a Perkin-Elmer Model 552 spectrometer and are expressed as λ_{max} in nm (log ϵ). Electron spin resonance (ESR) spectra were recorded on a Varian Associates E-4 (X-band) spectrometer with a liquid nitrogen Dewar insert. Gas–liquid partition chromatography (GLPC) analyses were performed on a Varian 3700 instrument equipped with flame-ionization detector (helium carrier gas) and a Hewlett-Packard 5900 integrator. Analytical high-performance liquid chromatography (HPLC) was performed with an IBM 9560 instrument equipped with a 5 μm, 4.5 × 250 mm, octadecyl column with 40% water in acetonitrile as eluant at 1.5 mL/min. Direct photolyses were performed in a Rayonet photochemical reactor equipped with 350-nm lamps. Melting points were determined in sealed Pyrex capillary tubes. Spinning-disk chromatographic separations were performed on a Harrison Research Model 7924 T chromatotron.

Materials. Acetonitrile (Aldrich Gold Label) for laser spectroscopy was refluxed over CaH_2 and distilled under nitrogen through a 3-m vacuum-jacketed column packed with glass helices. Benzene was shaken in turn with sulfuric acid and water, then dried with sodium sulfate, and distilled from sodium-benzophenone ketyl under nitrogen. Prior to use, methanol, isopropyl alcohol, *tert*-butyl alcohol, and cyclohexane were refluxed over CaH_2 and then distilled. 2-Methyltetrahydrofuran was refluxed over sodium (paraffin dispersion) and distilled; α-methylstyrene and styrene were distilled at reduced pressure. Pyridine *N*-oxide was distilled: bp 102 °C (0.45 mm). (*E*)-α-Methyl-β-deuteriostyrene was >95% isotopic purity (79% isomeric purity) as determined by ^{1}H NMR and mass spectroscopy. All other materials were used as received.

10-Diazoanthrone (DAAN). The diazo compound was prepared in 95% yield by the method of Regitz.[11] Recrystallization from dioxane afforded red needles: mp 130 °C dec; IR (CCl_4) 2055.6 (C=N$_2$), 1649.2 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.36–7.48 (m, 4 H, Ar), 7.69–7.78 (m, 4 H, Ar), 8.55–8.60 (d, 2 H, Ar); UV (solvent) λ_{max} (log ϵ) (CH_3CN), 415 (4.04); (MTHF), 408.5 (4.02), (C_6H_6), 412.4 (4.16); (*t*-BuOH), 417; (*i*-PrOH), 417.5.

Bianthronyl. This material was prepared in 58% yield according to the procedure of Barnett and Matthews[22] by refluxing a mixture of anthracene, glacial acetic acid, and concentrated nitric acid. Trituration of the resulting yellow solid with benzene followed by ethanol afforded the desired material: UV (C_6H_6) λ_{max} (log ϵ) 350 (3.74); ^{1}H NMR ($CDCl_3$) δ 4.78 (s, 1 H), 6.84–6.87 (m, 2.0 H), 7.37–7.44 (m, 4 H), 7.91–7.96 (m, 2 H).

Nanosecond Laser Flash Photolysis. The laser flash photolysis apparatus has been described previously.[23] A nitrogen laser (337 nm) was used for excitation. Concentrations of DAAN (ca. 3 × 10^{-3} M) were adjusted so that a significant portion of the laser light was absorbed. Solutions were placed in a 1.0-cm quartz fluorescence cell equipped with a stir bar and Teflon-brand stopcock. Oxygen was removed by purging the solutions with dry nitrogen, and the solutions were stirred between laser firings. The pseudo-first-order rate constants (k_{obsd}) for the decay of the transients were determined by least-squares fit.

General Procedure for the Photolysis of DAAN in the Presence of Trapping Agents. Unless specified otherwise, DAAN (ca. 1 × 10^{-4} M) was dissolved in solutions containing the carbene trapping reagents in a volumetric flask. Equal volume aliquots were placed in oven-dried, foil-covered, round-bottomed flasks and sealed with a rubber serum cap. After purging each solution for 1 h with dry nitrogen, a UV spectrum of each sample was obtained. The two flasks, keeping the control reaction flask covered with foil, were photolyzed, with stirring, in the Rayonet. The progress of the decompositions was periodically monitored by UV spectroscopy; after photolysis, the percent decompositions were calculated. Removal of the volatile materials first by rotary evaporation and then at ca. 1 Torr gave material that was analyzed by quantitative (*p*-dioxane internal standard) ^{1}H NMR spectroscopy. The identity of each product was confirmed by isolation and comparison with authentic materials. No reaction was ever observed (UV and NMR) in the control flask.

Photolysis of DAAN in Alkenes. (a) In 5.0 M Styrene. DAAN (56 mg, 0.25 mmol) and styrene (26 g, 0.25 mol) were diluted to 50 mL with benzene and the two 25-mL aliquots were treated as described above. Photolysis to 98% completion afforded the anticipated cyclopropane quantitatively: mp 153.5–154 °C [lit.[9] mp 153–154 °C]; ^{1}H NMR ($CDCl_3$) δ 2.58 (d, J = 9 Hz, 2 H, cyclopropyl), 3.16 (t, J = 9 Hz, 1 H, cyclopropyl), 6.46 (d, J = 8.3 Hz, 1 H, Ar), 6.97–7.72 (m, 10 H, Ar), 8.37 (dd, J_1 = 8.7 Hz, J_2 = 1.1 Hz, 1 H, Ar), 8.45 (dd, J_1 = 9.3 Hz, J_2 = 1.6 Hz, 1 H, Ar); MS (10 eV), *m/e* (relative abundance) 296 (100), 218 (37); molecular ion calcd for $C_{22}H_{16}O$ *m/e* 296.12011, found 296.12010.

(b) In 1.0 M α-Methylstyrene. DAAN (52 mg, 0.24 mmol) and α-methylstyrene (6.0 g, 51 mmol) were diluted to 50 mL with benzene and the two 25-mL aliquots were treated as described above. Photolysis to 99% completion yielded the anticipated cyclopropane in 97% yield; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 3 H, methyl), 2.37 (d, J = 6.9 Hz, 1 H, cyclopropyl), 2.65 (d, J = 6.9 Hz, 1 H, cyclopropyl), 6.51 (d, J = 7.9 Hz, 1 H, Ar), 6.80–7.64 (m, 10 H, Ar), 8.13 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H, Ar), 8.32 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1 H, Ar); MS (10 eV), *m/e* (relative abundance), 310 (100), 295 (65); molecular ion calcd for $C_{23}H_{18}O$ *m/e* 310.13576, found 310.13574.

(c) In 0.99 M (*E*)-α-Methyl-β-deuteriostyrene. DAAN (8.8 mg, 0.04 mmol) and (*E*)-α-methyl-β-deuteriostyrene (0.35 g, 3.0 mmol)[7] were diluted to 3.0 mL with benzene, placed in a 1.0-cm quartz fluorescence cell, and treated as described above. Photolysis to 98% completion, followed by bulb-to-bulb distillation of the solvent and unreacted α-methylstyrene, afforded the desired cyclopropane. The ^{1}H NMR spectrum of the cyclopropane was essentially the same as for the undeuteriated sample except that the cyclopropyl protons appeared as equal area singlets, δ ($CDCl_3$) 2.37 (s, 0.5 H), 2.65 (s, 0.5 H), indicating that the cyclopropanation reaction was nonstereospecific. The ^{1}H NMR spectrum of the recovered α-methylstyrene showed that it had not been isomerized.

Photolysis of DAAN in Alcohols. (a) In Isopropyl Alcohol. DAAN (18 mg, 0.084 mmol) was dissolved in 25 mL of 2-propanol. Photolysis to 56% completion afforded bianthronyl (14%), anthrone (25%), unsymmetrical azine (31%), and ether (33%).

Anthraquinone isopropylidenehydrazone (unsymmetrical azine): mp 125–126 °C; ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3 H, methyl), 2.26 (s, 3 H, methyl), 7.65 (m, 4 H, Ar), 8.43 (m, 4 H, Ar); ^{13}C NMR

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[22] Barnett, E. B.; Matthews, M. A. *J. Chem. Soc.* **1923**, *123*, 380.

[23] Horn, K. A.; Schuster, G. B. *Tetrahedron* **1982**, *38*, 1095.

(CDCl$_3$) δ 19.3, 25.1, 125.8, 126.7, 127.7, 129.7, 130.4, 130.6, 130.8, 131.2, 132.5, 132.7, 133.2, 137.4, 143.4, 157.9, 183.8; IR (CCl$_4$) 1669.5 (C=O) cm^{-1}; MS (70 eV), *m/e* (relative abundance) 138 (100), 193 (100), 199 (100); molecular ion calcd for $C_{17}H_{14}N_2O$ *m/e* 262.1106, found 262.1105.

Isopropyl ether: ^1H NMR (CDCl$_3$) δ 1.07 (d, J = 6.0 Hz, 6 H, methyl), 3.76 (m, J = 6.0 Hz, 1 H, methine), 5.74 (s, 1 H, CHOR).

(b) In *tert*-Butyl Alcohol. DAAN (55 mg, 0.25 mmol) was dissolved in 50 mL of *tert*-butyl alcohol; two 25-mL aliquots were treated as described above. Photolysis to 83% completion afforded bianthronyl (39%), anthrone (<1%), unsymmetrical azine (7%), and the expected *tert*-butyl ether (33%) as determined by ^1H NMR spectroscopy.

tert-Butyl ether: ^1H NMR (CDCl$_3$) δ 1.46 (s, 9 H, methyl), 5.73 (s, 1 H, CHOR).

Photolysis of DAAN in Hydrocarbons. (a) In Cyclohexane. DAAN (16 mg, 0.075 mmol) was dissolved in 25 mL of cyclohexane. Photolysis to 98% completion afforded bianthronyl (61%), anthrone (1%), and 10-cyclohexylanthrone (12%) as determined by ^1H NMR spectroscopy.

10-Cyclohexanthrone: ^1H NMR (CDCl$_3$) δ 0.6–2.0 (m, 11 H, cyclohexyl), 4.10 (d, J = 4 Hz, 1 H, anthronyl), 7.48 (m, 6 H, Ar), 8.22 (dd, 2 H, Ar); [lit.[9] δ (CDCl$_3$) 4.05 (d)]; MS (10 eV), *m/e* (relative abundance) 276 (2.51), 195 (15.11), 194 (100); molecular ion calcd for $C_{20}H_{20}O$ *m/e* 276.1514, found 276.1511.

Irradiation of DAAN in a 6.5:1 Mixture of Cyclohexane-d_{12} and Cyclohexane. A stock solution of DAAN (8.9×10^{-3} M) in benzene was prepared. A mixture containing 1.0 mL of the stock solution, 1.3 mL of C_6D_{12}, and 0.20 mL of C_6H_{12} was placed in a 1.0-cm quartz fluorescence cell, equipped with a stir bar; the mixture was purged with dry nitrogen for 7 min. A second solution, 1.0 mL of stock and 1.5 mL of C_6H_{12}, was similarly prepared. The two solutions were irradiated (Rayonet) for 45 min and then concentrated. Appropriate analysis by mass spectrometry (CI) of the 10-cyclohexylanthrone and the deuteriated sample revealed that crossover product (30%) was formed.

(b) In Benzene. DAAN (29 mg, 0.13 mmol) was dissolved in 25 mL of benzene and two 10-mL aliquots were treated as previously described. Photolysis to 98% completion afforded bianthronyl (42, 45%) and anthrone (5, 6%), determined via ^1H NMR, and biphenyl (27, 25%), determined by GLPC using dodecane as an internal standard (6 ft × 0.125 in. glass column containing 10% OV-101 on Chrom W-H.P., 100/120 mesh).

Irradiation of DAAN in Benzene at >385 nm in the Presence of α-Methylstyrene and/or Pyridine *N*-Oxide; Run I. Four samples were prepared in Pyrex cells, each containing DAAN (4.8×10^{-3} M). Each sample was purged with dry nitrogen for 10 min and irradiated for 45 min at >385 nm (450-W mercury lamp with ferric chloride filter). Sample 2 also contained α-methylstyrene (0.25 M), while sample 3 contained pyridine *N*-oxide (0.88 M). Sample 4 contained both α-methylstyrene (0.25 M) and pyridine N-oxide (0.91 M). The conversion (100% for each run) was determined by monitoring the diazo absorption at 2056 cm^{-1}. The volatiles were removed from the samples by rotary evaporation at reduced pressure and the products analyzed by ^1H NMR (200 MHz) spectroscopy and GLPC (undecane internal standard).

Run II. Six samples were prepared in quartz cells, each containing DAAN (2.0×10^{-3} M); samples 1–5 also contained pyridine *N*-oxide (0.931 M). Each sample contained α-methylstyrene (1, 0.094 M; 2, 0.075 M; 3, 0.066 M; 4, 0.038 M; 5–6, 0.019 M). The samples were purged with dry nitrogen (10 min) and irradiated to completion (15 min) as described in run I. The anthraquinone yields were determined by analytical HPLC, anthracene internal standard, (sample no., yield: 1, 48; 2, 49; 3, 58; 4, 63; 5, 80; 6, 14).

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Synthesis and Reactions of Iodo Lactams[†]

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The synthesis of a series of iodo lactams has been achieved by a new cyclization method that depends on generating *N,O*-bis(trimethylsilyl)imidate derivatives as intermediates. Treatment of an unsaturated amide with trimethylsilyl triflate in pentane and then iodine in tetrahydrofuran gives the iodo lactam. Some reactions of this new difunctional group with bases, nucleophiles, and Michael acceptors leading to functionalized or elaborated lactams are presented. In general, iodo lactams undergo direct S_N2 reactions with reactive (but weakly basic) nucleophiles like azide and triphenylphosphine and elimination or decomposition in the presence of bases or basic nucleophiles. Sodium hydride may be used to generate an *N*-acylaziridine intermediate, which can be opened with azide to deliver an azido lactam with overall retention of stereochemistry. Silver-assisted solvolysis of iodo lactams gives the hydroxy lactams with retention of configuration, probably also because of participation by the lactam nitrogen. The sodium salt of 5-(iodomethyl)-2-pyrrolidinone (3), generated at −20 °C, undergoes an annulation reaction with unsaturated esters (but not sulfones), leading to pyrrolizidine derivatives.

We recently reported a method for the synthesis of iodo lactams from the corresponding unsaturated amides, illustrated below by the conversion of 4-pentenamide (1) to 5-(iodomethyl)-2-pyrrolidinone (3).[1] Whereas 1 cannot be cyclized to 3 directly,[2-5] prior conversion of 1 to its *N,O*-bis(trimethylsilyl) derivative 2 allows a cyclization process analogous to the familiar and useful iodolactonization reaction.[6,7] The resulting iodo lactams constitute a new class of difunctional compounds, one whose chemistry is expected to reflect the close interaction of the two groups. In this paper, we describe the exper-

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[†] This paper is dedicated to Prof. Jerrold Meinwald on the occasion of his 60th birthday.

(1) Knapp, S.; Rodriques, K. E.; Levorse, A. T.; Ornaf, R. M. *Tetrahedron Lett.* **1985**, *26*, 1803.

(2) Treatment of 1 with a solution of iodine in THF gave the iodo lactone 6 as the only cyclization product after aqueous workup. A similar result was observed by Ganem, who attempted to reproduce a literature report of the synthesis of 3. Biloski, A. J.; Wood, R. D.; Ganem, B. *J. Am. Chem. Soc.* **1982**, *104*, 3233 (see footnote 8 therein).

(3) Intentional O-iodocyclization of unsaturated amides to give lactones: (a) Corey, E. J.; Shibasaki, M.; Knolle, J. *Tetrahedron Lett.* **1977**, 1625. (b) Tamaru, Y.; Mizutani, M.; Furukawa, Y.; Kawamura, S.; Yoshida, Z.; Yanagi, K.; Minobe, M. *J. Am. Chem. Soc.* **1984**, *106*, 1079.

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