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Synthesis and Photochemical Isomerization of 1,2-Di-9-anthrylethanol and 1,2-Di-9-anthrylethanone

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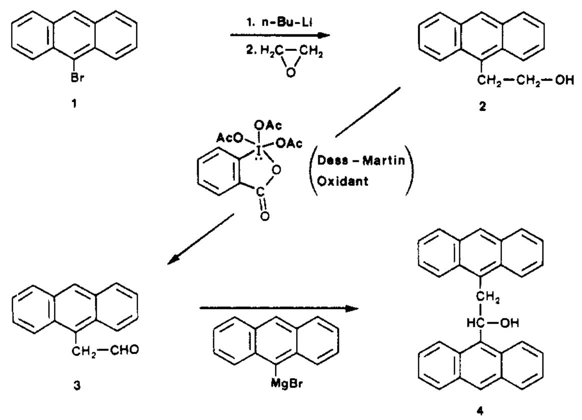
1,2-Di-9-anthrylethanol has been synthesized by Grignard reaction of 9-anthrylmagnesium bromide with 9-anthrylacetaldehyde which, in turn, was obtained by oxidation of 9-anthrylethanol with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one ("Dess–Martin periodinane"). This oxidant also was found to be the reagent of choice for the conversion of dianthrylethanol into 1,2-di-9-anthrylethanone. The photochemical isomerization of dianthrylethanol in benzene solution proceeds with a quantum yield of 0.34 by intramolecular [4 + 4] cycloaddition involving the excited singlet state. Remarkably, the course of photochemical isomerization of 1,2-di-9-anthrylethanone is dependent on the substrate concentration, affording mainly intramolecular [4 + 2] cyclomers in dilute (0.00001 M) solution but the intramolecular [4 + 4] cycloadduct in concentrated (0.01 M) solution. The proposed triplet state pathway for the formation of intramolecular Diels–Alder products from dianthrylethanone is supported by oxygen quenching results and sensitization experiments with biacetyl. The photochemical isomerization of di-9-anthryl ketone and 1,3-di-9-anthrylpropan-1-one gives rise to intramolecular [4 + 2] (Φ = 0.0003) and [4 + 4] (Φ = 0.65) cycloadducts, respectively. The differences in quantum yields and modes of cycloaddition are attributed to differences in molecular geometry.

Some years ago, in conjunction with an investigation dealing with the effects of molecular geometry on the photochemical and photophysical properties of bichromophoric anthracenes such as *cis*-1,2-di-9-anthrylethylene,[1] we realized that the compound in the literature[2] described to be 1,2-di-9-anthrylethanol (4) actually is a derivative of 9,10-dihydroanthracene whose structure was established by X-ray diffraction analysis.[3,4] In order to investigate their photochemical isomerization, we have now prepared both dianthrylethanol and its corresponding ketone 1,2-di-9-anthrylethanone (5). The photochemistry of 1,2-di-9-anthrylethane has been the subject of numerous investigations,[5] but derivatives substituted in the ethane link have not been described before.

Scheme I



Results and Discussion

The four-step synthesis of dianthrylethanol 4 from anthracene in an overall yield of 47% was accomplished as outlined in Scheme I. Thus, 9-bromoanthracene (1), prepared in 87% yield from anthracene and cupric bromide,[6] was converted into 2-(9-anthryl)ethanol (2) via 9-anthryllithium.[7] The seemingly simple oxidative conversion of 2 into 9-anthrylacetaldehyde[8] (3) turned out to be a major obstacle because commonly used oxidants such as chromium trioxide–pyridine complex[9] or pyridinium chlorochromate[10] (PCC) afforded only low yields (20–30%) and resulted in the concomitant formation of side products such as anthraquinone. However, oxidation of 2-(9-anthryl)ethanol with the recently[11] described 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one ("Dess–Martin periodinane") gave 9-anthrylacetaldehyde in synthetically useful yields of 73%. Dianthrylethanol 4 was then accessible in 92% yield by reaction of 9-anthrylacetaldehyde with 9-anthrylmagnesium bromide. The temperature-dependent ^{1}H NMR spectra of dianthrylethanol shown in Figure 1 indicate hindered rotations about the two 9-anthrylmethyl bonds.[12]

The oxidation of dianthrylethanol with chromium trioxide–pyridine complex, or with PCC gave mixtures of 9-anthraldehyde and 9-anthrylacetaldehyde. By contrast, the Dess–Martin oxidant smoothly converted 4 into the desired 1,2-di-9-anthrylethanone (5) in 93% yield. The syntheses of 9-anthrylacetaldehyde and dianthrylethanone thus attest to the usefulness of the periodinane as oxidant

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(1) (a) Becker, H.-D. *Pure Appl. Chem.* **1982**, *54*, 1589. (b) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1981**, *46*, 5419. (c) Becker, H.-D.; Sandros, K.; Andersson, K. *Angew. Chem.* **1983**, *95*, 507; *Angew. Chem. Suppl.* **1983**, 609–619; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 495.

(2) Schreiber, K. C.; Emerson, W. *J. Org. Chem.* **1966**, *31*, 95.

(3) Becker, H.-D.; Sandros, K.; Arvidsson, A. *J. Org. Chem.* **1979**, *44*, 1336.

(4) Becker, H.-D.; Sandros, K.; Skelton, B. W.; White, A. H. *J. Phys. Chem.* **1981**, *85*, 2930.

(5) (a) Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098. (b) Becker, H.-D.; Elebring, T.; Sandros, K. *J. Org. Chem.* **1982**, *47*, 1064. (c) Manring, L. E.; Peters, K. S.; Jones, G., II; Bergmark, W. R. *J. Am. Chem. Soc.* **1985**, *107*, 1485 and references cited therein.

(6) House, H. O.; Ghali, N. I.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 1807.

(7) Mikhailov, B. M. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.* **1948**, 420; *Chem. Abstr.* **1949**, *43*, 208g.

(8) A convenient synthetic route to 9-anthrylacetaldehyde has not been reported before, though the compound has recently been obtained by photolysis of 9,10-ethano-9,10-dihydroanthran-11-yl nitrite: Rajan-Babu, T. V.; Eaton, D. F.; Fukunaga, T. *J. Org. Chem.* **1983**, *48*, 652.

(9) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.

(10) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(11) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

(12) From the observed coalescence temperatures of 273 K and 213 K, energy barriers of 12 and 10 kcal/mol, respectively, were calculated according to the method of Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc. D* **1971**, 656. The barrier of internal rotation about the ethane bond may be about 5 kcal/mol (cf. Castellan, A.; Desvergne, J.-P.; Lesclaux, R.; Soulignac, J.-C. *Chem. Phys. Lett.* **1984**, *106*, 117).

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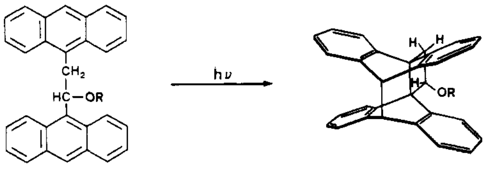
4: R = 9-Anthryl
6: R = Phenyl

5: R = 9-Anthryl
7: R = Phenyl

for anthryl-substituted primary and secondary alcohols. In a corollary experiment, we found that 2-(9-anthryl)-1-phenylethanol (**6**) is converted into the corresponding ethanone **7** in 89% yield by oxidation with Dess–Martin periodinane. PCC oxidation of **6** afforded **7** in only 35% yield.

The electronic absorption spectrum of dianthrylethanol resembles that of the parent dianthrylethane as regards the position of the longest wavelength absorption band and its molar extinction coefficient.[5b] The broadness of the spectrum of dianthrylethanone, by comparison, is in line with absorption by a bichromophoric system (see Figure 2). The fluorescence quantum yield (Φ_F) of dianthrylethanol in benzene solution was found to be 0.04. This value is considerably lower than that of the parent dianthrylethane (Φ_F 0.20).[5a] As for dianthrylethanone, it is virtually nonfluorescent in solution, suggestive of efficient singlet–triplet intersystem crossing involving the carbonyl moiety (vide infra).

Upon photoexcitation in benzene ($\lambda > 340$ nm) under argon, dianthrylethanol isomerizes by [4 + 4] cycloaddition to give **9**, which was isolated in 78% yield. The quantum yield of the cyclization, measured in degassed benzene, was found to be 0.34. The acetate **8** of dianthrylethanol (Φ_F 0.03) cyclizes photochemically to give **10** with equally high efficiency (Φ 0.35). It is worth noting that these reaction quantum yields markedly exceed that found for the [4 + 4] cycloaddition of the parent dianthrylethane (Φ 0.26)[5a] and those of its 10-substituted derivatives.[5b]



4: R = H
8: R = Ac

9: R = H
10: R = Ac

The photochemistry of dianthrylethanone **5** was of particular interest to us since we had found recently[13] that the photochemical isomerization of 1,2-di-9-anthrylethane can be triplet-sensitized to proceed by [4 + 2] cycloaddition, while direct excitation of dianthrylethane results in [4 + 4] cycloaddition via the excited singlet state.[5a] For directly excited dianthrylethanone, interestingly, the in-

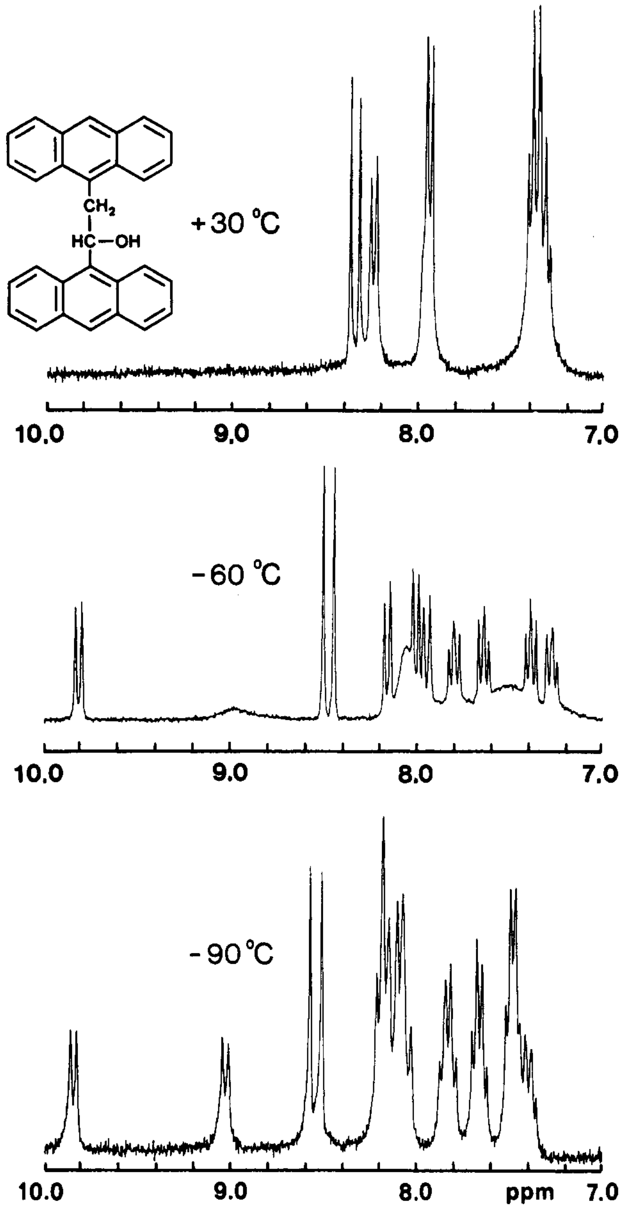
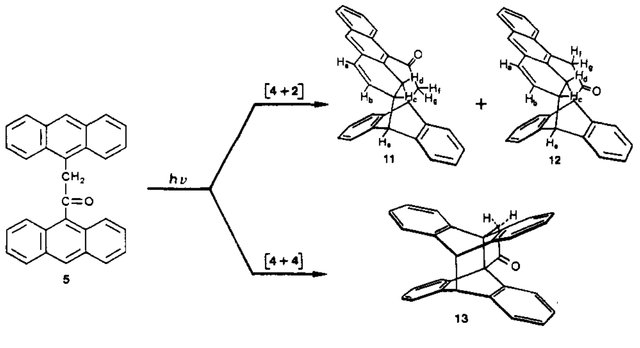


Figure 1. ^{1}H NMR spectra (270 MHz) of 1,2-di-9-anthrylethanol in CD_2Cl_2/acetone-d_6 at various temperatures.

volvement of both singlet and triplet state pathways to cycloaddition products is apparent from the formation of [4 + 4] and [4 + 2] cyclomers, respectively. Thus, photoexcitation of **5** in dilute solution (0.00003 M in degassed benzene; $\lambda > 400$ nm) affords mainly (80%) the isomers **11** and **12** (ratio 3:1) formed by intramolecular Diels–Alder addition but only 20% of the isomer **13** formed by [4 + 4] cycloaddition.[14] Unexpectedly, however, the photoproduct composition markedly depends on the initial concentration of dianthrylethanone (cf. Table I). The more concentrated the dianthrylethanone solution, the more [4 + 4] cycloaddition product is formed at the ex-



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(13) Becker, H.-D.; Andersson, K. *Tetrahedron Lett.* **1985**, *26*, 6129.

(14) As for the structural assignments of the different dianthrylethanone photoisomers, the distinction between Diels–Alder adducts **11** and **12**, and the [4 + 4] cyclomer **13** can conveniently be made on the basis of their characteristic electronic absorption spectra. The conjugation of the carbonyl chromophore in **11** is borne out in the bathochromic shift of the 2-vinylnaphthalene absorption relative to that of Diels–Alder adduct **12** (see ref 13). Moreover, the differences between isomers **11** and **12** are unequivocally reflected in their ^{1}H NMR spectra. Deshielding of one "naphthalene" proton by the carbonyl group in **11** gives rise to a downfield doublet at 9.34 ppm (cf. Experimental Section). The structure of the [4 + 4] cycloadduct **13** was established by its preparation from the dianthrylethanol photoproduct **9** by PCC oxidation.

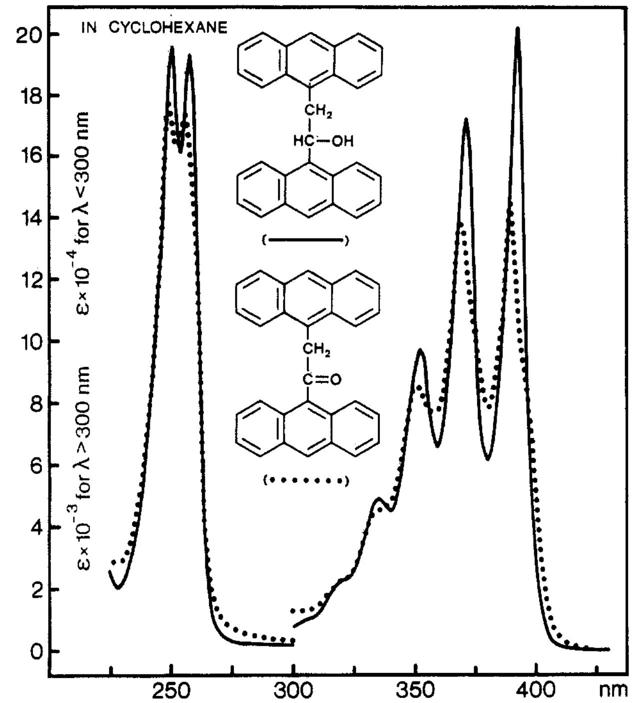


Figure 2. Electronic absorption spectra of 1,2-di-9-anthrylethanol and 1,2-di-9-anthrylethanone in cyclohexane.

Table I. Photochemical Isomerization of 1,2-Di-9-anthrylethanone. Concentration Dependent Product Composition (%)

concn (M)	[4 + 2] adduct 11	[4 + 2] adduct 12	[4 + 4] adduct 13
0.0000066	64	20	16
0.00003	60	20	20
0.00013	44	14	42
0.00053	29	9	62
0.001	12	4	84
0.0034	7		93
0.0075	2		98

pense of the [4 + 2] isomers. In 0.0075 M solution, dianthrylethanone isomerizes upon photoexcitation to give 98% of the [4 + 4] cycloadduct **13** and only 2% of Diels–Alder adducts **11** and **12** (^{1}H NMR analysis). Apparently, [4 + 4] cycloaddition involving the excited singlet state becomes predominant because of triplet quenching in concentrated solution.[15] Triplet–triplet annihilation[16] as a mode of quenching does not seem to be of importance, as we find the efficiency of quenching to be independent of the light intensity.

The biacetyl-sensitized photochemical isomerization of **5** (0.000 63 M in benzene) gives 97% of [4 + 2] cycloadducts **11** and **12** (ratio 75:22) but only 3% of the [4 + 4] cycloadduct **13**. The quantum yield for the biacetyl-sensitized disappearance of dianthrylethanone (0.000 019 M) in benzene solution is 15%. We conclude, therefore, that the intramolecular Diels–Alder reaction, but not the [4 + 4] cycloaddition, observed upon direct photoexcitation also proceeds from the excited triplet state. Indeed, irradiation ($\lambda > 400$ nm) of dianthrylethanone (0.000 056 M) in air-saturated benzene, so as to quench triplet excited **5**, does not give any of the [4 + 2] cycloadducts **11** and **12** but affords the [4 + 4] cycloadduct **13**. The quantum yield for the disappearance of dianthrylethanone under these conditions, i.e., by cycloaddition via the excited singlet state, is 3.6%. In degassed, dilute solution (0.000 03 M in benzene), by contrast, the quantum yield of dianthrylethanone disappearance was found to be as high as 11%. We conclude from these results that intersystem crossing to the excited triplet state represents a major deactivation mode of singlet-excited dianthrylethanone which proceeds with an estimated quantum yield of about 0.6,[17] and it is from this state that [4 + 2] cycloaddition occurs.

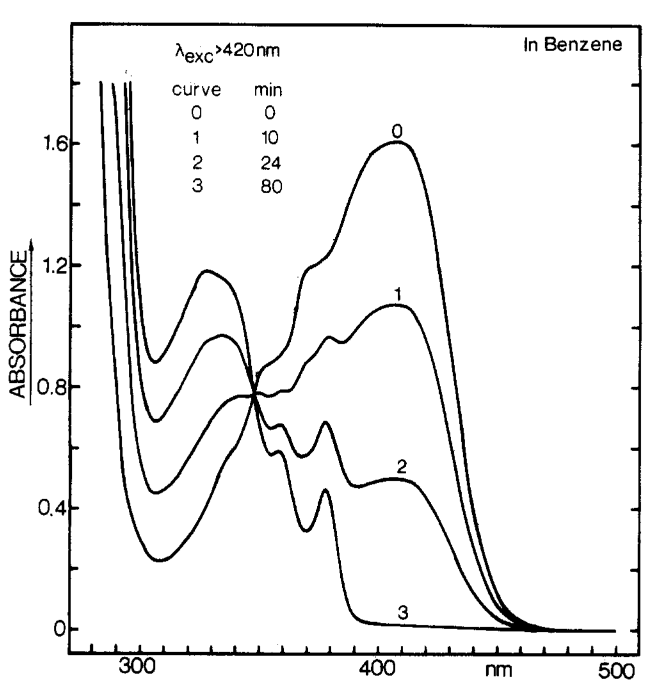
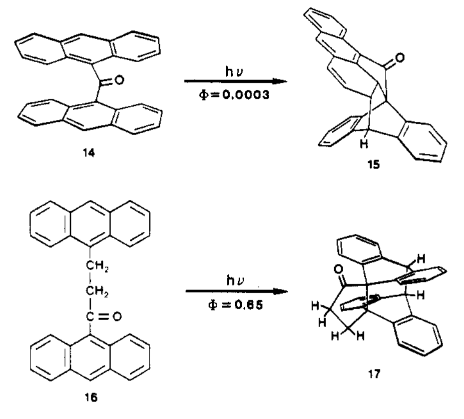


Figure 3. Electron spectral changes associated with the photochemical isomerization of di-9-anthryl ketone (0.000 044 M in degassed benzene; pathlength 3 cm; $\lambda > 420$ nm; 1000-W high-pressure xenon/mercury lamp).

For comparison purposes, we have included two homologues of dianthrylethanone, viz., di-9-anthryl ketone (**14**) and 1,3-di-9-anthrylpropan-1-one (**16**) into the present investigation. Dianthryl ketone **14** is nonfluorescent, and upon direct photoexcitation in degassed benzene (0.000 03 M) it isomerizes exclusively by [4 + 2] cycloaddition (Φ 0.0003) to give **15** (see Figure 3). The biacetyl-sensitized photochemical isomerization of **14** also affords the [4 + 2] cyclomer **15**, but with far higher quantum yield (Φ 0.005).



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(15) Chapman, O. L.; Wampfler, G. *J. Am. Chem. Soc.* **1969**, *91*, 5390.

(16) Cf. Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978; p 343.

(17) The quantum yield of intersystem crossing has been estimated as follows. The optimal quantum yield of disappearance of dianthrylethanone by direct excitation is 0.11, and we assume that the Diels–Alder products (80%) formed in this reaction derive from the excited triplet state. Consequently, the quantum yield of triplet state product formation by direct excitation is 0.088. Since the quantum yield for the formation of triplet state products in the biacetyl-sensitized reaction is 0.15, the quantum yield of intersystem crossing should then be 0.59.

The observed difference in quantum yields suggests that singlet-excited dianthryl ketone may deactivate efficiently by internal conversion.[18] By contrast, the geometrically less constrained 1,3-di-9-anthrylpropan-1-one (**16**) isomerizes both upon direct photoexcitation[19] and by biacetyl sensitization with identical quantum yields of 0.65. In both cases, the isomerization of **16** involves the excited triplet state (as is evident from oxygen quenching experiments) and leads to the formation of the [4 + 4] cyclomer **17**. This result is in line with the previous conclusion[13] that the photochemical isomerization of triplet-excited dianthrylalkanes should proceed with high quantum efficiency by [4 + 4] rather than by [4 + 2] cycloaddition whenever their molecular geometry facilitates the overlap of the aromatic π-systems.

Experimental Section

^{1}H NMR spectra were obtained on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Absorption and emission spectra were recorded on a Kontron Uvikon 810 and an Aminco SPF 500 (corrected spectra) spectrometer, respectively. Melting points (uncorrected) were taken on hot-stage microscope. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark.

Actinometric Measurements. The quantum yields of emission are based on the fluorescence quantum yield of 9,10-diphenylanthracene (Φ 0.83).[20] Quantum yields of cyclization by direct excitation were determined in an optical bench arrangement equipped with a monochromator to select the 366-nm line of a 1000-W high-pressure xenon/mercury lamp and by using the cyclization of 1,2-di-9-anthrylethane (Φ 0.26)[5a] as actinometer. Quantum yields of biacetyl-sensitized isomerizations of dianthrylethanone were determined by using biacetyl and substrate concentrations of 0.01 M and 0.000 02 M, respectively, and by selective excitation of biacetyl at 436 nm. As actinometer for the triplet-sensitized reactions, the quantum yield for the cyclization of 1,3-di-9-anthrylpropan-1-one (0.65) was used which, in turn, is based on the potassium ferrioxalate actinometer. In the quantum yield measurement of the biacetyl-sensitized cyclization of dianthryl ketone, selective excitation of the sensitizer was accomplished by using wavelengths >455 nm (cut-off filter ORIEL LP-470).

Materials. Benzene and diethyl ether were freshly distilled from benzophenone ketyl sodium. Methylene chloride was distilled from calcium hydride. Dess–Martin periodinane was prepared from 2-iodobenzoic acid[21] according to the literature.[11] Pyridinium chlorochromate was prepared according to ref 10. 9-Bromoanthracene was prepared according to ref 6 and purified by sublimation at 110 °C/0.05 mmHg. It was obtained in 87% yield, and its mp was 98–101 °C (lit.[6] mp 98–99 °C).

2-(9-Anthryl)ethanol (2). Commercially available *n*-butyllithium (9 mL, 1.6 M) was added over a 5-min period to an ice-cold solution of 9-bromoanthracene (3 g, 11.7 mmol) in ether (100 mL) under argon or nitrogen blanketing. After the resulting yellow-orange colored suspension had been stirred for 30 min, an ice-cold solution of ethylene oxide (3 g, 68 mmol) in ether (16 mL) was added to it. After the mixture had been stirred for 1 h, water (70 mL) and ether (50 mL) were added to it. The ether layer was separated, and the aqueous layer was extracted with methylene chloride (100 mL). The combined organic extracts were washed with water to remove residual base and dried over sodium sulfate. Vacuum evaporation of solvents gave a yellow crystalline residue which was purified by flash chromatography (silica gel/methylene chloride) to give 2.1 g (81%) of 2-(9-anthryl)ethanol (2) as pale yellow crystals, mp 106–108 °C (lit.[7] mp 106.5–107.5 °C); ^{1}H NMR ($CDCl_3$) δ 8.38 (s, H-10), 8.32 ("d", J = 8.4 Hz, 2), 8.01 ("d", J = 8.9 Hz, 2), 7.55–7.43 (m, 4), 4.10 (t, J = 6.5 Hz, 2), 3.94 (t, J = 6.5 Hz, 2).

9-Anthrylacetaldehyde (3). A solution of **2** (2.22 g, 10 mmol) in dry methylene chloride (35 mL) was added to a stirred mixture of Dess–Martin oxidant (6.36 g, 15 mmol) in methylene chloride (60 mL). After 50 min, the reaction mixture was diluted with ether (100 mL) and poured onto 1.3 M aqueous sodium hydroxide (100 mL). After 10 min, the ether layer was separated and extracted with 1.3 M NaOH (50 mL). The ether layer was washed with water to pH 7 and dried. Vacuum evaporation of solvent gave crude **3** as a yellow crystalline residue. It was purified by flash chromatography (silica gel/methylene chloride) or recrystallization (methylene chloride/hexane) to give 1.6 g (73%) of 9-anthrylacetaldehyde as light green crystals, mp 144–145 °C: ^{1}H NMR ($CDCl_3$) δ 9.78 (t, J = 2.4 Hz, CHO), 8.47 (s, H-10), 8.16 ("d", J = 8.5 Hz, 2), 8.05 ("d", J. = 8.5 Hz, 2), 7.59–7.47 (m, 4), 4.67 (d, J = 2.4 Hz, 2); IR (KBr) 1700 cm^{-1} (CO); UV (cyclohexane) ($\epsilon \times 10^{-3}$) 388 (9), 368 (9.6), 350 (6.1), 333 (3.1), 256 (160) nm.

1,2-Di-9-anthrylethanol (4). 1,2-Dibromoethane (0.94 g, 5 mmol) was added over a period of 8 h to a refluxing mixture of magnesium (365 mg, 15 mmol) and 9-bromoanthracene (2.57 g, 10 mmol) in ether (50 mL). The Grignard solution was then diluted with ether (100 mL), and 9-anthrylacetaldehyde (660 mg, 3 mmol) was Soxhlet-extracted into the Grignard solution. Refluxing was continued overnight. Workup by hydrolysis with saturated ammonium chloride, separation and washing to pH 7 of the ether layer, drying, and vacuum evaporation of solvent gave a crystalline yellow residue. It was purified by flash chromatography (silica gel/methylene chloride) and recrystallized from methylene chloride/hexane to give 1.1 g (92%) of **4** as pale yellow crystals, mp 255–258 °C: ^{1}H NMR (in $CDCl_3$ at 30 °C) δ 8.41 (s, H-10), 8.37 (s, H-10′), 8.35–8.31 (m, 2), 8.02–7.97 (m, 4), 7.52–7.42 (m, 8), 6.65 (dd, J = 8.2, 5.0 Hz, 1), 4.86 (dd, J = 14.6, 8.2 Hz, 1), 4.27 (dd, J = 14.6, 5.0 Hz, 1), 2.23 (s, OH). Anal. Calcd for $C_{30}H_{22}O$: C, 90.42; H, 5.56. Found: C, 90.46; H, 5.57.

1,2-Di-9-anthrylethanone (5). The periodinane[11] (1.27 g, 3 mmol) was added in one portion to a solution of 1,2-di-9-anthrylethanol (0.8 g, 2 mmol) in dry methylene chloride (50 mL). The reaction mixture was stirred for 50 min, then diluted with ether (50 mL), and poured onto 25 mL of 1.3 M aqueous NaOH. The organic layer was separated, extracted with 25 mL of 1.3 M NaOH, washed with water to pH 7, and dried. The yellow crystalline residue obtained on vacuum evaporation of solvent was recrystallized from methylene chloride/ethanol to give 0.74 g (93%) of **5** as pale yellow crystals, mp 230–231 °C: ^{1}H NMR ($CDCl_3$) δ 8.42 (s, H-10), 8.36 (s, H-10′), 8.08–8.05 (m, 2), 7.97–7.72 (m, 4), 7.69–7.65 (m, 2), 7.43–7.29 (m, 8), 5.36 (s, 2). Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08. Found: C, 90.71; H, 5.07.

2-(9-Anthryl)-1-phenylethanol (6).[22] A Grignard solution of phenylmagnesium bromide was prepared from magnesium (0.48 g, 20 mmol) and bromobenzene (3.14 g, 20 mmol) in ether (10 mL) and subsequently diluted with 150 mL of ether. 9-Anthrylacetaldehyde (1.1 g, 10 mmol) was transferred into the Grignard solution by means of Soxhlet extraction. After the mixture had been refluxed for 20 h, the reaction was terminated by addition of aqueous ammonium chloride. Conventional workup, followed by flash chromatography (silica gel/toluene), gave a pale yellow crystalline product which was recrystallized from ether/hexane to yield 1.03 g (69%) of **6** as yellow crystals, mp 117–118 °C: ^{1}H NMR ($CDCl_3$) δ 8.41 (s, 1), 8.33 ("d", J = 9.5 Hz, 2), 8.04–8.0 (m, 2), 7.54–7.30 (m, 9), 5.22–5.17 (m, 1), 4.12 (dd, J = 14.5, 9.0 Hz, 1), 3.96 (dd, J = 14.5, 4.3 Hz, 1), 1.84 (d, J = 2.5 Hz, OH). When the sample is treated with deuterium oxide, the doublet at 1.84 ppm disappears and the multiplet centered at 5.19 ppm is changed into a doublet of doublets (J = 9.0, 4.3 Hz). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 87.78; H, 5.95.

2-(9-Anthryl)-1-phenylethanone (7). Dess–Martin periodinane[11] (1.3 g, 3 mmol) was added in one portion to a stirred nitrogen-purged solution of 2-(9-anthryl)-1-phenylethanol (597 mg, 2 mmol) in anhydrous methylene chloride (50 mL). After

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[18] Analogous inefficient photochemistry in conjunction with lack of fluorescence had been noted in the case of *cis*-1,2-di-9-anthrylethylene; (cf. ref 1). Both dianthryl ketone and *cis*-dianthrylethylene are characterized by having the two anthryl moieties in close proximity facing each other.

[19] Becker, H.-D.; Andersson, K. *J. Org. Chem.* **1983**, *48*, 4542.

[20] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 103.

[21] Wachter, W. *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 1744.

[22] This compound has recently been obtained in the reaction of 9-anthrylmethyl carbanion with benzaldehyde, but no physical data were reported: Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1984**, *24*, 4645.

50 min, the suspension was diluted with diethyl ether (50 mL) and poured onto 50 mL of 1.3 M aqueous sodium hydroxide solution. The mixture was stirred vigorously for 10 min, and the ether phase was separated, then extracted again with 50 mL of 1.3 M sodium hydroxide solution, and washed with water until neutral. The ether layer was dried over magnesium sulfate, and the residue obtained on vacuum evaporation of solvent was purified by column chromatography (silica gel/methylene chloride) to give 525 mg (89%) of **7**, mp 240 °C (from methylene chloride/cyclohexane) (lit.[23] mp 240–241 °C): ^{1}H NMR ($CDCl_3$) δ 8.46 (s, 1), 8.23–8.00 (m, 6), 7.58–7.44 (m, 7), 5.34 (s, 2).

1-Acetoxy-1,2-di-9-anthrylethane (8). A solution of **4** (100 mg) in a mixture of acetic anhydride (7 mL) and pyridine (6 drops) was kept at 120 °C for about 3 min. When the solution had cooled to room temperature, **8** crystallized. Conventional workup by decomposing excess of acetic anhydride with ethanol and recrystallization of the crude product from methylene chloride/ethanol gave 107 mg (97%) of **8** as pale greenish-yellow crystals, mp 242–245 °C: ^{1}H NMR ($CDCl_3$) δ 8.38 (s, 1), 8.30 (s), 8.24–8.21 (m, 2), 7.96–7.91 (m, 4), 7.65 (dd, 1, J = 7.9 Hz, J = 6.1 Hz), 7.42–7.34 (m, 10), 4.87 (dd, 1, J = 14.6 Hz, J = 6.1 Hz), 4.37 (dd, 1, J = 14.6 Hz, J = 7.9 Hz), 1.89 (s, 3). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49. Found: C, 86.89; H, 5.48.

Photochemical Isomerization of Dianthrylethanol To Give 9. A solution of **4** (200 mg) in benzene (150 mL) was irradiated for 3 h under argon (immersion well apparatus; 125-W high-pressure mercury lamp; 340-nm cut-off filter sleeve; 12 °C). Vacuum evaporation of solvent gave a solid residue which was washed with ether. Recrystallization from methylene chloride/methanol gave 155 mg (78%) of **9** as colorless crystals, mp 250–260 °C dec: ^{1}H NMR ($CDCl_3$) δ 7.97 ("d", J = 9.1 Hz, 1), 7.14–6.72 (m, 15), 5.72 (td, J = 9.6, 3.9 Hz, 1), 4.49 ("s", 2 bridgehead H), 3.41 (dd, J = 12.4, 9.9 Hz, 1), 3.21 (dd, J = 12.4, 9.2 Hz, 1), 2.20 (d, J = 3.9 Hz, OH). Anal. Calcd for $C_{30}H_{22}O$: C, 90.42; H, 5.56. Found: C, 90.65; H, 5.58.

Photochemical Isomerization of Acetate 8 To Give 10. A solution of **8** (110 mg) in methylene chloride (75 mL) was irradiated under argon for 1 h (immersion well apparatus, 340-nm cut-off filter, 125-W high-pressure mercury lamp, 12 °C). Vacuum evaporation of solvent gave an oily residue which crystallized upon treatment with ether. Recrystallization from a mixture of methylene chloride and ethanol gave 85 mg (77%) of **10** as colorless crystals, mp 242–246 °C dec: ^{1}H NMR ($CDCl_3$) δ 7.77–7.74 (m, 1), 7.28–6.74 (m, 15), 6.58 ("t", 1, J = 9.5 Hz), 4.51 (d, 1, J = 10.9 Hz), 4.50 (d, 1, J = 10.9 Hz), 3.43 (dd, 1, J = 12.7 Hz, J = 9.7 Hz), 3.30 (dd, 1, J = 12.7 Hz, J = 9.1 Hz), 2.24 (s, 3). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49. Found: 86.87; H, 5.50.

Photochemical Isomerization of 1,2-Di-9-anthrylethanone (5) To Give 11, 12, and 13. A. By Direct Excitation. A 0.0014 M solution of 1,2-di-9-anthrylethanone (100 mg) in benzene (175 mL) was irradiated for 2 h under argon in an immersion well apparatus, using light of λ > 400 nm (Philips high-pressure mercury lamp HPK 125 W; 1-cm path length of filter solution containing 150 g of potassium nitrite in 200 mL of water; 15 °C). Workup by vacuum evaporation of solvent gave a residue which was subjected to column chromatography on silica gel/methylene chloride. From two identical experiments, 130 mg (65%, after recrystallization from methylene chloride/methanol) of the cyclobutanone **13** were obtained, which was identical in every respect with the compound obtained by PCC oxidation of the cyclobutanol **9**. In addition, 9 mg (4.5%) of the [4 + 2] cyclomer **11** were isolated (vide infra). The presence of the [4 + 2] cyclomer **12** in the crude photoproduct was ascertained by ^{1}H NMR, but it was difficult to separate from cyclobutanone **13** by recrystallization. Cyclomer **12** is prepared conveniently by triplet-sensitized isomerization of **5** described below.

B. By Triplet-Sensitized Excitation. An argon-saturated, stirred solution of **5** (20 mg) and biacetyl (300 mg) in benzene (80 mL) was irradiated for 30 min in an optical bench arrangement with light of λ > 440 nm (1000-W high-pressure xenon/mercury lamp; cut-off filter). Vacuum evaporation of solvent and biacetyl gave a residue which, according to ^{1}H NMR analysis, consisted of **11** (75%), **12** (22%), and **13** (3%). Combined workup of four identical experiments by column chromatography (silica gel/methylene chloride) gave two fractions, the first of which consisted of a mixture of **12** and **13**, while the slower moving fraction consisted of pure **11**. Isomer **11** (32 mg, 40% yield) forms pale yellow crystals (from methylene chloride/methanol). It undergoes cycloreversion upon melting (215–216 °C). The separation of **12** (12 mg, colorless needle-shaped crystals, mp 211–212 °C) and **13** (1 mg, colorless cubic crystals) was accomplished by fractional crystallization from methylene chloride/hexane.

11: ^{1}H NMR of **11** ($CDCl_3$) δ 9.34 (d, J = 8.7 Hz, 1), 7.60–6.72 (m, 12), 6.30 (dd, J = 9.8, 2.0 Hz, Ha), 5.99 (dd, J = 9.8, 4.5 Hz, Hb), 4.25 (d, J = 1.1 Hz, He), 3.98 (d, J = 18.5 Hz, 1 methylene H), 3.80 (d, J = 18.5 Hz, 1 methylene H), 3.76 (d, J = 11.4 Hz, Hd), 3.25 ("dddd", J = 11.4, 4.5, 2.0, 1.1 Hz, Hc). Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08. Found, C, 90.85; H, 5.07.

12: high-resolution mass spectrum, m/z calcd for $C_{30}H_{20}O$ 396.1515, found 396.1505; ^{1}H NMR of **12** ($CDCl_3$) δ 8.00–6.49 (m, 13), 6.23 (dd, J = 9.9, 2.1 Hz, Ha), 5.85 (dd, J = 9.9, 3.8 Hz, Hb), 4.69 (d, J = 17.1 Hz, 1 methylene H), 4.35 (d, J = 2.1 Hz, He), 3.93 (d, J = 17.1 Hz, 1 methylene H), 3.88 (d, J = 11.7 Hz, Hd), 3.36 ("dddd", J = 11.7, 3.8, 2.1, 2.1 Hz, Hc). Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08. Found: C, 90.34; H, 5.19. Coupling constants (in Hz) pertinent to the structural assignments of **11** and **12** are as follows:

isomer	J_{ab}	J_{ac}	J_{bc}	J_{cd}	J_{ce}	J_{fg}
11	9.8	2.0	4.5	11.4	1.1	18.5
12	9.9	2.1	3.8	11.7	2.1	17.1

Oxidation of Cyclobutanol 9 To Give Cyclobutanone 13. Cyclobutanol **9** (315 mg, 0.8 mmol) was added in one portion to a stirred mixture of PCC (185 mg, 0.86 mmol) in dry methylene chloride (25 mL). After 1 h, more PCC (70 mg) was added, and stirring was continued for additional 1.5 h. The reaction mixture was then filtered through a 10-cm column of silica gel. Column chromatography (silica gel/methylene chloride) of the residue obtained after vacuum evaporation of solvent from the filtrate, followed by recrystallization from methylene chloride/methanol gave 250 mg (63%) of **13** as colorless crystals, mp 228–231 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.08–6.79 (m, 16), 4.64 (d, J = 11.2 Hz, 1), 4.58 (d, J = 11.2 Hz, 1), 4.04 (s, 2). Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08. Found: C, 91.20; H, 5.10.

Di-9-anthryl Ketone (14). Dianthryl ketone[24] was obtained according to a modified procedure for the synthesis of its 10-chloro derivative.[25] 9-Anthracenecarbonyl chloride was prepared by refluxing a solution of 9-anthracenecarboxylic acid (2.22 g, 10 mmol) in thionyl chloride (10 mL) for 1 h, and an excess of thionyl chloride was then removed by vacuum distillation. The anthracenecarbonyl chloride thus obtained and anthracene (1.34 g, 7.5 mmol) were dissolved in methylene chloride (200 mL). After addition of aluminum chloride (2.0 g, 15 mmol), the reaction mixture was refluxed for 12 h. Conventional workup by addition of ice–water, washing, and separation of the organic layer, followed by vacuum evaporation of solvent gave a dark-colored solid residue. It was dissolved in toluene and purified by repetitive column chromatography on silica gel/toluene. After three consecutive purification steps, and one final recrystallization from boiling toluene, there was obtained 610 mg (21%) of **14** as lemon-yellow, needle-shaped crystals, mp 269–272 °C (lit.[26] mp 266–267 °C): ^{1}H NMR ($CDCl_3$) δ 8.63 (s, H-10, 2), 8.14 ("d", J = 9.0 Hz, 4), 8.04 ("d", J = 8.5 Hz, 4), 7.46–7.26 (m, 8).

Photochemical Isomerization of Di-9-anthryl Ketone (14) To Give 15. A solution of dianthryl ketone (100 mg) in benzene (150 mL) was irradiated at 10 °C (125-W high-pressure mercury lamp) under argon atmosphere for 48 h with wavelengths > 400 nm (1-cm filter solution of 150 g sodium nitrite in 200 mL of water). The residue obtained on vacuum evaporation of solvent

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[23] Kirrstetter, R. G. H.; Vagt, U. *Chem. Ber.* **1981**, *114*, 630.

[24] Di-9-anthryl ketone has previously been obtained as a byproduct in the synthesis of 9-anthryl carboxylic acid by reaction of anthracene with oxalyl chloride (Latham, H. G., Jr.; May, E. L.; Mosettig, E. *J. Am. Chem. Soc.* **1948**, *70*, 1079; footnote 11).

[25] Blum, J.; Oppenheimer, E.; Bergmann, E. D. *J. Am. Chem. Soc.* **1967**, *89*, 2338.

[26] Weinshenker, N. M.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 506.

was purified by column chromatography on silica gel/methylene chloride to give 77 mg (77%) of **15** as pale yellow crystals, mp 200–206 °C (recrystallized from ether/methanol): ^{1}H NMR ($CDCl_3$) δ 8.81 (d, J = 8.5 Hz, 1), 8.08 ("d", J = 7.2 Hz, 1), 7.72 (d, J = 8.2 Hz, 1), 7.63–7.57 (m, 1), 7.46–7.13 (m, 6), 6.92–6.86 (m, 1), 6.71–6.61 (m, 2), 6.26 (dd, J = 10.0, 2.6 Hz, Ha), 5.91 (dd, J = 10.0, 3.6 Hz, Hb), 4.42 (d, J = 3.0 Hz, He), 4.12 (d, J = 12.5 Hz, Hd), 3.28 ("dddd", J = 12.5, 3.6, 3.0, 2.6 Hz, Hc).

Photochemical Isomerization of Dianthrylpropanone 16 To Give 17. This reaction has been described in ref 19.

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Registry No. **1**, 1564-64-3; **2**, 54060-73-0; **3**, 84332-58-1; **4**, 4709-80-2; **5**, 102725-05-3; **6**, 88920-58-5; **7**, 77312-81-3; **8**, 68975-27-9; **9**, 102725-06-4; **10**, 102725-07-5; **11**, 102735-75-1; **12**, 102725-08-6; **13**, 102725-09-7; **14**, 102725-10-0; **15**, 102725-11-1; ethylene oxide, 75-21-8; Dess–Martin oxidant, 87413-09-0; 9-anthracenecarboxylic acid, 723-62-6; 9-anthryl chloride, 16331-52-5; anthracene, 120-12-7.

Dicyclopenta[*ef*,*kl*]heptalene (Azupyrene) Chemistry. Jutz Synthesis Byproducts. Synthesis and Thermal Isomerization of 1-Methylazupyrene[1]

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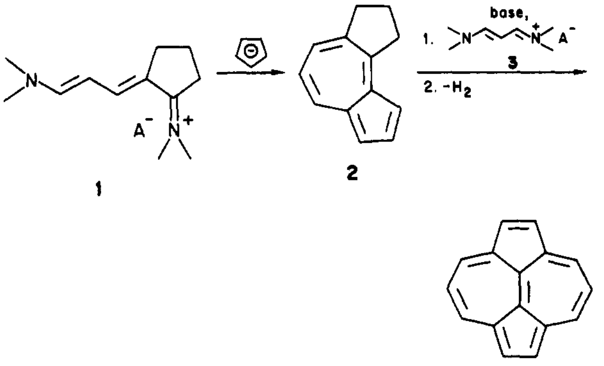
The Jutz synthesis of azupyrene (4) has been found to form chloro-, methyl-, and dimethylazupyrene byproducts in the final step. Perchlorate and methoxide ions were shown to cause the chlorination and methylation, respectively. Temperature control at 200–205 °C reduced the chlorination and the use of ethoxide virtually eliminated the alkylation. 1-Methylazupyrene (7) was synthesized. The thermal isomerization of 7 to methylpyrenes was carried out and the products were found to be those predicted by certain of the mechanisms proposed for the azulene to naphthalene isomerization.

After the first synthesis of dicyclopenta[*ef*,*kl*]heptalene (azupyrene, **4**) had established the stability and physical aromatic character of this 4n π electron structure,[3] a report by Jutz and Schweiger of a more direct route[4] contained a footnote which indicated a high yield conversion of 2,3-dihydro-1*H*-cyclopent[*e*]azulene (**2**) to **4**. Procedures for this latter route were then developed in our laboratories which closely approximated those subsequently reported[5] except that the tetrafluoroborate ion replaced perchlorate ion in the intermediate salt **1** and, initially, as the anion of the immonium reagent **3** for the formation of the second seven-membered ring (eq 1). The yield of **2** (31%) with the tetrafluoroborate salt was satisfactory. However, the yield of **4** from **2** was quite low (≲12%)[6] compared to ca. 40–50% obtained with the perchlorate salt of **3**.



(1)

Scheme I

$$\text{dihydro-4} + ClO_4^- \rightarrow 4 + ClO_3^- + H_2O$$
$$\text{dihydro-4} + ClO_3^- \rightarrow 4 + HClO_2 + OH^-$$
$$\text{dihydro-4} + HClO_2 \rightarrow 4 + HClO + H_2O$$
$$4 + HClO \rightarrow Cl\text{-}4 + H_2O$$

Although **4** as isolated melted sharply in the correct range, difficulties were encountered in obtaining analytically pure samples of derivatives subsequently prepared. High resolution GC/MS analysis showed that **2** was free of chlorination and methylation impurities but samples of **4** contained up to 4% methylazupyrene, 1% dimethylazupyrene, and up to 12% chloroazupyrene. The byproducts were therefore formed in the conversion of **2** to **4**. The azupyrene obtained when **3** (A = BF_4) was used contained no chloro impurities and the crude product had twice as much (ca. 40%) of the 1,2-dihydroazupyrene. The perchlorate ion was therefore the source of the chloro impurities and acted to oxidize 1,2-dihydroazupyrene to azupyrene. The reactions proposed for these processes are shown in Scheme I. Hypochlorite is a known reagent for the chlorination of aromatic compounds,[7] and it was shown that calcium hypochlorite effected the chlorination of **4**.

These findings led to further study of the conversion of **2** to **4**. Measurement of the evolution of dimethylamine (a product of each of two main steps involved in forming the new ring) showed that the alkylation of **2** by **3** occurred below 100 °C but that ring closure required ≳200 °C. The

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(1) Presented in part at the 39th Northwest Regional Meeting of the American Chemical Society, Moscow, ID, June 13–15, 1984.

(2) Ph.D. Theses of Daugs, E. D., 1985; Kao, L. G., 1981, M.S. Thesis of Wang, J-F., 1976, University of Washington.

(3) Anderson, A. G., Jr.; MacDonald, A. A.; Montana, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 2993. Anderson, A. G., Jr.; Masada, G. M.; Montana, A. F. *J. Org. Chem.* **1973**, *38*, 1439. Anderson, A. G., Jr.; Montana, A. F.; MacDonald, A. A.; Masada, G. M. *Ibid.* **1973**, *38*, 1445.

(4) Jutz, C. J.; Schweiger, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 808.

(5) Jutz, C. J.; Schweiger, E. *Synthesis* **1974**, 193. Prof. Jutz kindly provided some details prior to publication: personal communication, June 1973.

(6) The low yields from the BF_4^- salt were possibly due to the instability of the 1,2-dihydro-4 which was shown (GC/MS) to be present early in the final heating in larger amounts (ca. 40%) in the absence of ClO_4^-. Prof. Jutz reported similar findings in analogous reactions to us: personal communication, Sept 1973.

(7) See: March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 477.

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