Table II. Coordinates of the Heavier Atoms of 5

atom	*x*	*y*	*z*
Cl1	0.21926 (6)	0.01325 (8)	0.04100 (4)
Cl2	0.04780 (6)	0.29197 (8)	0.06547 (3)
O1	0.2496 (1)	−0.0939 (2)	−0.23057 (10)
O2	0.0756 (2)	0.1700 (2)	−0.44231 (9)
O3	0.0096 (1)	−0.2083 (2)	−0.32703 (8)
O4	−0.489 (2)	−0.4403 (2)	−0.28476 (10)
N1	0.1863 (2)	0.0433 (2)	−0.3412 (1)
C1	0.0565 (2)	0.0974 (2)	−0.1734 (1)
C2	0.1287 (2)	0.0349 (2)	−0.1094 (1)
C3	0.1267 (2)	0.0939 (3)	−0.0363 (1)
C4	0.0515 (2)	0.2149 (3)	−0.0255 (1)
C5	−0.0219 (2)	0.2751 (3)	−0.0876 (1)
C6	−0.0196 (2)	0.2179 (3)	−0.1610 (1)
C7	0.0549 (2)	0.0272 (2)	−0.2536 (1)
C8	0.1761 (2)	−0.0158 (3)	−0.2703 (1)
C9	0.2865 (2)	0.0111 (4)	−0.3779 (2)
C10	0.0890 (2)	0.1221 (3)	−0.3770 (1)
C11	0.0068 (2)	0.1398 (2)	−0.3202 (1)
C12	−0.1215 (2)	0.1184 (4)	−0.3561 (2)
C13	−0.1879 (2)	0.0179 (3)	−0.3100 (2)
C14	−0.1415 (2)	−0.0958 (3)	−0.2645 (1)
C15	−0.0149 (2)	−0.1289 (2)	−0.2578 (1)
C16	−0.0098 (2)	−0.3656 (2)	−0.3328 (1)
C17	0.0246 (2)	−0.4282 (3)	−0.4046 (1)

(89 mmol) of 1-acetoxybutadiene (Aldrich), 0.5 g of hydroquinone, and 200 mL of chloroform was heated under reflux for 2 days. An additional 5 g of diene was added and reflux was continued for an additional day. The volatiles were removed at reduced pressure to give a tacky, brown solid. Recrystallization from 2-propanol gave 12.3 g (74.4% yield) of straw-colored crystals: mp 146–148 °C; ^{1}H NMR δ 7.36–7.80 (m, 3 H, aromatic), 5.73–6.08 (m, 2 H, vinyl), 5.39 (d, J = 5.5Hz, 1 H, HCOAc), 3.27 (d of d, J = 9.9, 4.5 Hz, 1 H, H-2), 3.00 (s, 3H, NCH_3), 1.90 (s, 3 H, Ac); IR (KBr), 1778 (m), 1731 (s, ester), 1699 cm^{-1} (s, imide); mass spectrum, m/e 367 (9%, M$^+$), 325 (24, M-CH_2CO), 256 (83, $C_{11}H_7Cl_2NO_2$ + H$^+$), 112 (88, M-$C_{11}H_7Cl_2NO_2$), 70 (100, 112 - CH_2O).

Anal. Calcd for $C_{17}H_{15}Cl_2NO_4$: C, 55.45; H, 4.11; Cl. 19.26; N, 3.80. Found: C, 55.67; H, 4.17; Cl, 19.37; N, 3.81.

X-ray Crystal Structure of 5. The crystals were monoclinic, space group $P2_1/n$ (centrosymmetric). The cell dimensions, based on measurements for 24 strong reflections, are as follows: a = 11.694 (1) Å, b = 8.408 (1) Å, c = 17.566 (2) Å, β = 99.58 (1)°. The calculated density is 1.44 g cm^{-3} for one molecule in the asymmetric unit. Three-dimensional data collection on a CAD4 diffractometer with graphite monochromatized Cu Kα radiation gave 3510 independent reflections to a maximum 2θ of 150.0°. Of these 2574 were classified as observed by the criterion $I(h) > 3.0\sigma I(h)$.

The structure was solved by direct methods with the set of normalized structure factors $E(h) > 1.9$. An E map gave the positions of 18 atoms. The remaining atoms, including the hydrogens, were located in succeeding difference Fourier synthesis.

The structure was refined by the full-matrix least-squares method with isotropic hydrogen atoms. The final discrepancy factor was R = 0.041. The atomic parameters are listed in Tables II, III, and IV (Tables III and IV, supplementary material). The bond distances and angles are given in Table V (supplementary material).

Acknowledgment. The spectral data were obtained by Dr. W. E. Gore and staff. The elemental analyses were performed by Mr. L. M. Brancone and staff. The X-ray determination was carried out by the Molecular Structure Corp., College Station, TX. We thank Dr. Allan Wissner of Lederle Laboratories for adapting the Hückel program to run on the American Cyanamid DEC-10 computer.

Registry No. 1, 95-76-1; 2, 930-88-1; 3, 79722-40-0; 4, 1515-76-0; 5, 79735-26-5.

Supplementary Material Available: Table III containing anisotropic temperature factors, Table IV containing hydrogen coordinates and isotropic temperature factors, and Table V containing bond distances and angles (4 pages). Ordering information is given on any current masthead page.

Spectroscopic and Photochemical Properties of Diastereoisomeric α,α'-Disubstituted Bis[(9-anthryl)methyl] Ethers

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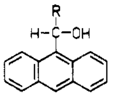
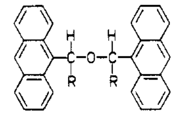
Received July 22, 1981

During their attempts to prepare 9-vinylanthracene from methyl(9-anthryl)carbinol (1), both Fieser and Hartwell and subsequently Hawkins noted the formation of a dimeric product which, on the basis of elemental analysis and infrared data, was presumed to be bis[α-(9-anthryl)ethyl] ether (3).[1,2] Most recently, bis[α-(9-anthryl)benzyl] ether (4) was reported to be formed, among other products, from (9-anthryl)benzyl hexachloroantimonate by treatment with potassium *tert*-butoxide.[3] Remarkably, in none of these reports has the problem of stereoisomerism of α,α'-disubstituted bis[(9-anthryl)methyl] ethers been mentioned. Bis[(9-anthryl)methyl] ethers 3 and 4 are characterized by having two like asymmetric carbon atoms and could, therefore, have been obtained as a mixture of isomers, namely, the *dl* form and the meso compound.



1: $R=CH_3$
2: $R=C_6H_5$



3: $R=CH_3$
4: $R=C_6H_5$
a: meso-form
b: dl-form

Inspection of Dreiding molecular models of α,α'-disubstituted bis[(9-anthryl)methyl] ethers suggests the molecular geometry of the meso form to be very much different from that of the *dl* form because the sterically demanding α-substituents always should be aligned more favorably out of the plane of the anthracene. The conformational consequences with respect to the mutual orientation of the two molecular halves could be dramatic. In the sterically possible conformation of the meso form, electronic interactions between the two anthracene moieties may be formidable, as fully overlapping alignment of the aromatic π systems (see Figure 1a) is possible in conjunction with rotation about the 9-anthryl–alkyl–ether bonds. By contrast, the molecular geometry of the *dl* form may be far less conducive to intramolecular π-orbital interaction. Model considerations lead to the conclusion that a conformational arrangement of perfectly overlapping anthracene moieties is not possible for steric reasons (see Figure 1b).

We have now found that α,α'-disubstituted bis[(9-anthryl)methyl] ethers can be prepared conveniently by reaction of the corresponding secondary 9-anthrylcarbinols with potassium hydrogen sulfate and that they indeed exist in diastereoisomeric meso and *dl* forms. For example, keeping methyl(9-anthryl)carbinol (1, 1.78 g) in the presence of $KHSO_4$ (35 mg) at 140 °C for 5 min gives a mixture (approximate ratio 1:1) of diastereoisomeric bis[α-(9-anthryl)ethyl] ethers (3) in 84% yield. Separation into the meso form **3a** and the *dl* racemate **3b** was accomplished

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(1) Fieser, L. F.; Hartwell, J. L. *J. Am. Chem. Soc.* **1938**, *60*, 2555.
(2) Hawkins, E. G. E. *J. Chem. Soc.* **1957**, 3858.
(3) Takagi, M.; Ogata, F.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2948.

0022-3263/82/1947-0354$01.25/0

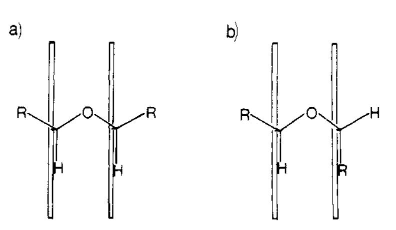


Figure 1. Schematic view of parallel aligned anthracene moieties in α,α'-disubstituted bis[(9-anthryl)methyl] ethers: a, meso form; b, *dl* diastereoisomers.

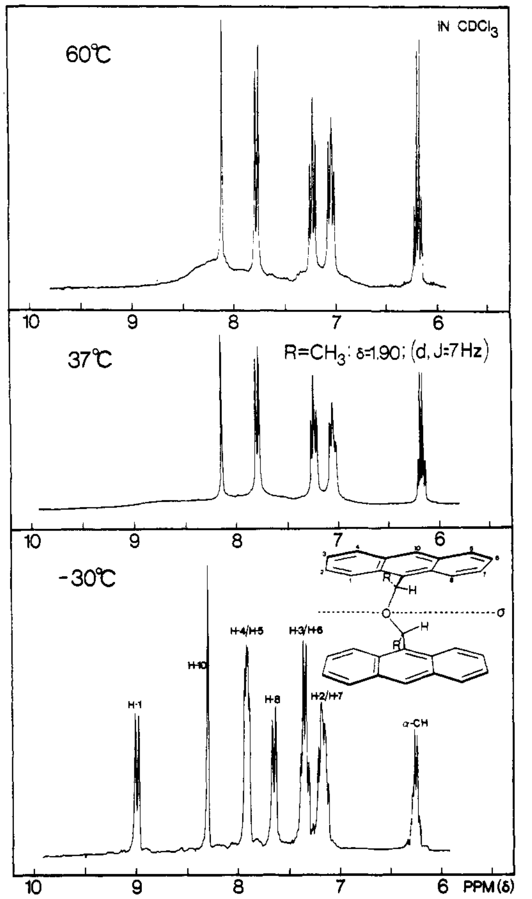


Figure 2. 270-MHz ^{1}H NMR spectra of meso compound **3a** at various temperatures.

by fractional crystallization. Diastereoisomeric meso and *dl*-bis[α-(9-anthryl)benzyl] ethers (**4**) were prepared from phenyl(9-anthryl)carbinol (**2**) in the same fashion in 91% yield.

The conformational differences between the meso and *dl* diastereoisomers discussed above are indeed borne out in their characteristically different spectral properties, and we believe that their structures can be deduced unequivocally from their ^{1}H NMR and UV absorption spectra. For example, in the ^{1}H NMR spectrum of the diastereoisomer which we consider to be *meso*-bis[(9-anthryl)methyl] ether (**3a**), H-10 gives rise to a singlet at δ 8.10, and the chemically equivalent aromatic protons of a molecular half are pairwise magnetically equivalent and give rise to a doublet (δ 7.80, $J \approx 8$ Hz), a triplet (δ 7.24, $J \approx 8$ Hz), and a slightly broadened triplet (δ 7.05, $J \approx 8$ Hz) which we attribute to H-4/H-5, H-3/H-6, and H-2/H-7, respectively (see Figure 2). Obviously missing in the room-temperature NMR spectrum of the meso compound **3a** is a signal due to the inner peri protons H-1/H-8. At 60 °C, a broad absorption around δ 8.2 becomes discernible, and a sharpening of the upfield triplet is noticeable. We believe these phenomena to be explicable by a molecular geometry of the meso form in which H-1 and H-8 may have different chemical shifts as long as rotation around the aryl–methyl single bond is impaired by the α-substituent. The low-temperature ^{1}H NMR spectrum fully supports this view. At −30 °C, conformational changes of **3a** have come nearly to a standstill, and H-1 and H-8 are distinguishable by well-defined doublets at δ 8.92 and 7.61, respectively ($J \approx 8$ Hz, in both cases). This difference in chemical shifts for chemically equivalent protons is remarkably large but is readily understood in terms of a molecular conformation (see Figure 2) which may be characterized by mirror plane symmetry (σ) and in which H-1, but not H-8, will be affected by the proximity of the ether oxygen and, consequently, give rise to the downfield doublet at δ 8.92.

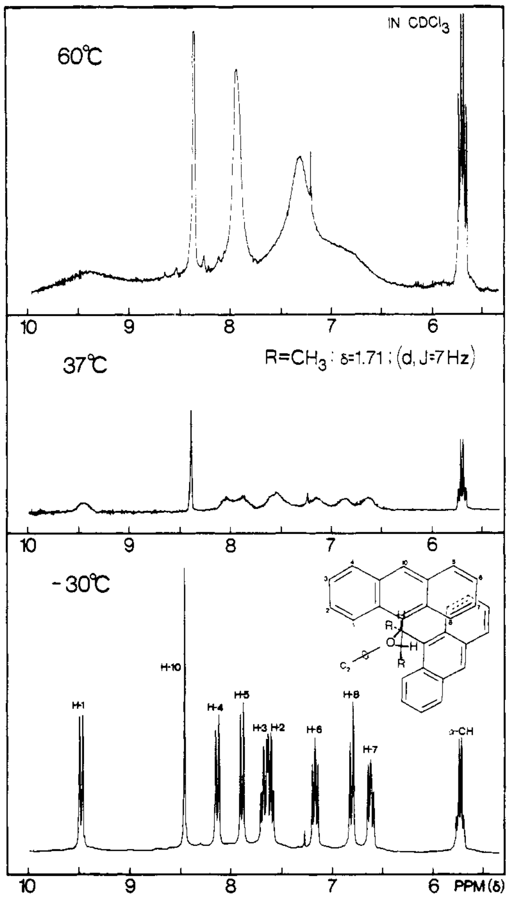


Figure 3. 270-MHz ^{1}H NMR spectra of *dl* diastereoisomeric **3b** at various temperatures.

The ^{1}H NMR spectrum of the *dl* form **3b** at 37 °C is unusual in several respects. Of the nine aromatic protons, only H-10 gives rise to a sharp signal (δ 8.39), while the absorptions by the other aromatic protons appear as a set of seven broad humps, ranging in chemical shift from δ 6.5 to 9.5 (see Figure 3). Apparently, the intramolecular mobility of the *dl* isomers is greatly impaired even at room temperature, and, therefore, all the protons of the anthracene system may differ in chemical shift. In accord with this interpretation, at 60 °C the number of broad signals decreases by way of coalescence, and at −30 °C all nine aromatic protons give rise to sharp and, significantly, well-separated absorptions. Since we can with reasonable certainty assign all the signals, the low-temperature ^{1}H NMR spectrum in conjunction with model considerations provides a fairly detailed picture of the actual conformation of **3b** in solution at −30 °C. In the sterically favored molecular geometry of the *dl* diastereoisomers, the α,α'-substituents will be oriented out of the plane of the anthracenes, and mutual interference by the α,α'-substituents will

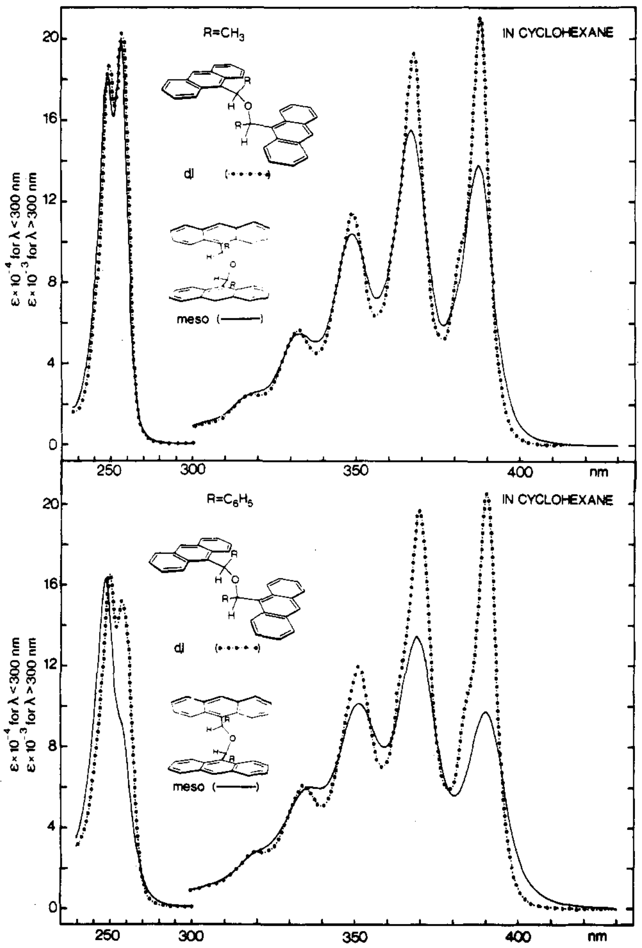


Figure 4. Electronic absorption spectra of *meso*- and *dl*-bis[(9-anthryl)methyl] ethers **3** and **4**.

be minimized by appropriate rotation around the alkyl–ether bonds. We thus obtain a conformer in which the long axes of the two anthracene moieties form an angle of 60°, and, interestingly, the molecular geometry is now characterized by a twofold axis of symmetry (see Figure 3). Of the two inner peri hydrogens, H-1 will be greatly affected by the proximity of the ether oxygen and will be shifted downfield to 9.46 ppm. Its chemical counterpart, H-8 of the other lateral ring, will be shifted upfield to δ 6.78 because of shielding by its C_2 equivalent ring system. The assignment of the remaining aromatic protons has been verified by the appropriate decoupling experiments. In principle, the ^{1}H NMR spectra of diastereoisomeric bis[(9-anthryl)methyl] ethers **4a** and **4b** exhibit the same type of temperature dependence as those of **3a** and **3b** (see Experimental Section), but the aromatic protons are more difficult to assign because of the phenyl substituent.

The electronic absorption spectra of *dl* diastereoisomeric bis[(9-anthryl)methyl] ethers **3b** and **4b** are characterized by well-resolved vibrational bands of the S_0–S_1 transition. The effect of geometrically feasible intramolecular π-orbital interaction in ground-state *meso*-bis[(9-anthryl)methyl] ethers **3a** and **4a** is such as to noticeably lower the excitation energy of the S_0–S_1 transition by broadening of the typical anthracene spectrum (see Figure 4).

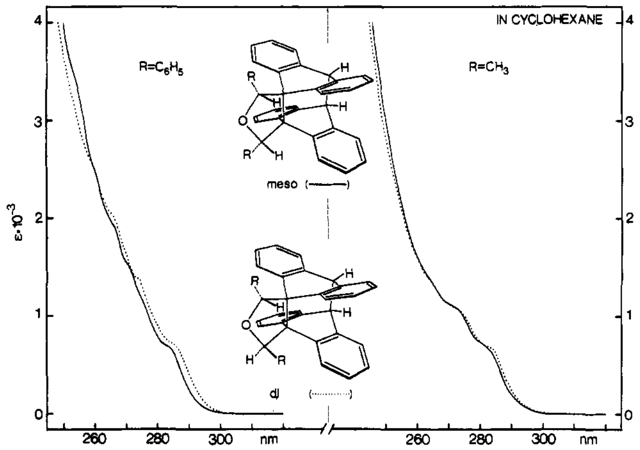
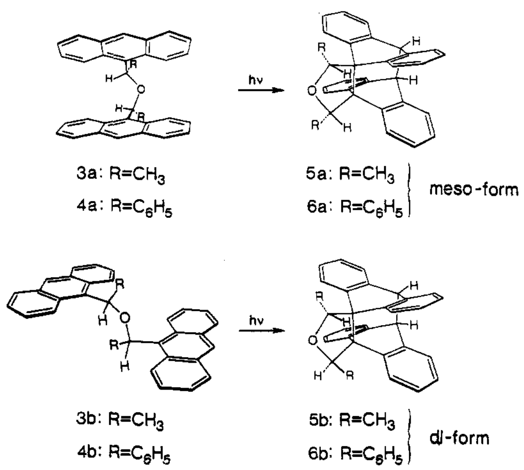


Figure 5. Electronic absorption spectra of meso and *dl* photoisomers **5** and **6**.

Upon photoexcitation, α,α'-disubstituted bis[(9-anthryl)methyl] ethers **3** and **4** undergo valence isomerization in the same fashion as has been described for the parent bis[(9-anthryl)methyl] ether,[4] i.e., by intramolecular, symmetrical [$4_\pi + 4_\pi$] cycloaddition to give the annelated dianthracenes **5** and **6**. The UV spectroscopically detectable differences between the meso and *dl* photoproducts are just as subtle as are their structural differences (see Figure 5). In the meso photoproducts **5a** and **6a** the substituents may be accommodated more easily "above" the dihydroanthracene systems than is the case in the *dl* photoproducts **5b** and **6b** whose UV absorption spectra are slightly broadened. As for their ^{1}H NMR spectra, the diastereoisomeric photoproducts are distinguishable by using a chiral shift reagent. For example, in the presence of [tris[3-(trifluoromethyl)hydroxymethylene]-*d*-camphor]europium(III), the α-protons in the spectrum of racemic **5b**, but not those in the spectrum of meso form **5a**, give rise to two overlapping quartets. We are grateful to a referee for suggesting these experiments.



Interestingly, meso and *dl*-bis[(9-anthryl)methyl] ethers undergo the intramolecular photochemical cyclization with about equal quantum efficiency. Thus, both **3a** and **3b** photoisomerize with a quantum yield of about 0.25.[5] Apparently, at room temperature the ground-state differences in molecular geometry are easily overcome by electronic excitation. However, as far as their radiative deactivation is concerned, electronically excited *meso*-bis[(9-anthryl)methyl] ethers are distinguishable from *dl* diastereoisomers. Thus, the meso compounds **3a** and **4a** are virtually nonfluorescent.[6] By contrast, photoexcited

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(4) Castellan, A.; Lacoste, J.-M.; Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 411.

(5) The photoisomerization of the unsubstituted bis[(9-anthryl)methyl] ether proceeds with a quantum yield of 0.32 in methylcyclohexane at room temperature (cf. ref 4).

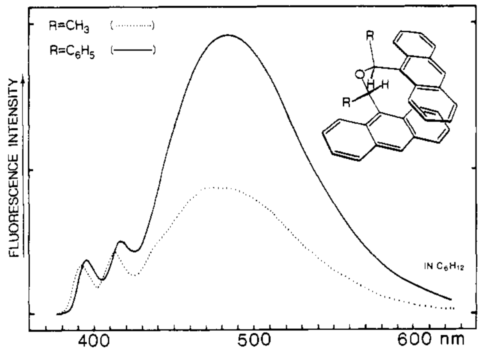

Figure 6. Dual emission spectra of *dl*-bis[(9-anthryl)methyl] ethers **3b** and **4b**.

dl compounds **3b** and **4b** deactivate radiatively from both their locally excited state and, more prominently, from an excimer state as evidenced by a structureless emission around 480 nm (see Figure 6). This result is of particular interest with respect to the relationship between molecular geometry and excimer luminescence. Molecular model considerations discussed above suggest that the geometry of the emitting excimer state of *dl*-bis[(9-anthryl)methyl] ethers deviates from the perfect sandwich structure and may be one in which the two anthracene moieties are only partially overlapping and are in an angular arrangement.[7]

Significantly, at room temperature the quantum yield of excimer luminescence from *dl*-bis[(9-anthryl)methyl] ethers is only about 1–3%.[8] Thus, both the meso and *dl* diastereoisomers deactivate to the ground state predominantly, and equally efficiently, by a nonradative decay process.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed by NOVO Microanalytical Laboratory. ^{1}H NMR spectra were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Electronic absorption spectra were recorded on a Varian Cary 210 spectrophotometer, and the emission spectra were obtained on an Aminco SPF 500 (corrected spectra) spectrofluorometer.

Photochemical Experiments. Preparative photoisomerizations of bis[(9-anthryl)methyl] ethers were carried out in a water-cooled Pyrex immersion well apparatus at 10 °C under nitrogen by using a Philips HPK 125-W high-pressure mercury lamp. Quantum yields of photoisomerizations were determined in an optical bench arrangement and are based on the quantum yield of photoisomerization of 1,2-bis(9-anthryl)ethane (0.26).[9] Quantum yields of emission are based on the quantum yield of fluorescence of the parent bis[(9-anthryl)methyl] ether (0.03).[4]

Methyl(9-anthryl)carbinol (1) was prepared according to ref 1.

Phenyl(9-anthryl)carbinol (2). Commercially available phenyllithium (23 mL; 16.8% in benzene–ether, 70:30) was added to a stirred solution of 9-anthraldehyde (3.72 g, 18 mmol) in benzene (150 mL) under nitrogen. The reaction was quenched after 30 min by addition of aqueous ammonium chloride (5%, 40 mL). The crude residue obtained from the organic layer of the usual workup was purified by column chromatography (SiO_2/CH_2Cl_2) to give 3.92 g (77%) of **2**, mp 112–114 °C (after recrystallization from methylene chloride/*n*-hexane) (lit.[10] mp 114 °C).

Bis[α-(9-anthryl)ethyl] Ether (3). Crystalline potassium hydrogen sulfate (35 mg) was added to molten carbinol **1** (1.78 g) at 140 °C. After 5 min at 140 °C, the reaction mixture solidified. Column chromatography on SiO_2 (CH_2Cl_2) afforded a 55:45 mixture (by ^{1}H NMR analysis) of meso and *dl* ethers **3** (1.41 g, 84%) which were separated by fractional crystallization from methylene chloride/*n*-hexane solution. The first fraction of pale yellow crystals (450 mg, 26%; mp 247–248 °C) was found to be the *dl* racemate **3b**. This melting point is in good agreement with that of the ether $C_{32}H_{26}O$ described by Fieser and Hartwell.[1] Anal. Calcd for $C_{32}H_{26}O$ (mol wt 426.53): C, 90.10; H, 6.14. Found: C, 90.46; H, 6.13.

The last fraction of pale yellow crystals (427 mg, 25%; mp 157–161 °C) was found to be the meso compound **3a**. It is more soluble in *n*-hexane than the *dl* racemate **3b**. Anal. Calcd for $C_{32}H_{26}O$ (mol wt 426.53): C, 90.10; H, 6.14. Found: C, 90.63; H, 6.14.

Bis[α-(9-anthryl)benzyl] Ether (4). The dehydration of carbinol **2** (2.27 g) in the presence of $KHSO_4$ (35 mg) was carried out for 20 min in the same manner as described for carbinol **1**. Column chromatography on $SiO_2(CH_2Cl_2)$ gave a 1:1 mixture (by ^{1}H NMR analysis) of meso and *dl* ether **4** (2.01 g, 91%). Slow crystallization from a methylene chloride/*n*-hexane mixture gave colorless needle-shaped crystals together with big, prismatic yellow crystals. Separation was accomplished manually. The yellow crystals (689 mg, 31%; mp 218–222 °C) were found to be the meso compound **4a**: ^{1}H NMR (in $CDCl_3$ at 60 °C) δ 7.85 (d, *J* = 8 Hz, 4, H-1/H-8), 7.77 (s, 2, H-10), 7.54 (d, *J* = 8 Hz, 4, H-4/H-5), 7.53 (d, *J* = 8 Hz, 4), 7.30 (s, 2, α-CH), 7.30–7.18 (m, 6), 7.07 (t, *J* = 8 Hz, 4, H-3/H-6), 6.78 (t, *J* = 8 Hz, 4, H-2/H-7). Anal. Calcd for $C_{42}H_{30}O$ (mol wt 550.71): C, 91.60; H, 5.49. Found: C, 91.92; H, 5.44.

The needle-shaped, colorless crystals (886 mg, 40%) had a melting point of 275–279 °C and were found to be the *dl* racemate **4b**: ^{1}H NMR (in $CDCl_3$ at 60 °C) δ 8.45 (s, 2, H-10), 7.94 (d, *J* = 8 Hz, 4), 7.41–6.80 (br hump, m, 22), 6.68 (s, 2, α-CH). Anal. Calcd for $C_{42}H_{30}O$ (mol wt 550.71): C, 91.60; H, 5.49. Found: C, 91.99; H, 5.44.

Photoisomerization of 3a To Give 5a. Irradiation of **3a** (300 mg) in *n*-hexane (100 mL) for 30 min gave **5a** as colorless crystalline product: mp 210–228 °C dec; yield 193 mg (64%, after recrystallization from methylene chloride by addition of methanol); ^{1}H NMR (in $CDCl_3$ at 37 °C) δ 7.36 (m, 2), 7.04 (m, 4), 6.89 (m, 4), 6.82–6.71 (m, 6), 5.19 (q, *J* = 7 Hz, 2), 4.42 (s, 2), 1.75 (d, *J* = 7 Hz, 6). Anal. Calcd for $C_{32}H_{26}O$ (mol wt 426.53): C, 90.10; H, 6.14. Found: C, 90.12; H, 6.09.

Photoisomerization of 3b To Give 5b. Irradiation of **3b** (750 mg) in benzene (80 mL) for 30 min, followed by the usual workup and recrystallization (CH_2Cl_2/CH_3OH), gave 530 mg (71%) of colorless crystalline **5b**. When this compound is heated, the crystal morphology of **5b** changes around 210 °C, and the substance melts around 244 °C: ^{1}H NMR (in $CDCl_3$ at 37 °C) δ 7.59 (m, 2), 7.13 (m, 2), 6.93–6.73 (m, 12), 5.57 (q, *J* = 7 Hz, 2), 4.39 (s, 2), 1.89 (d, *J* = 7 Hz, 6). Anal. Calcd for $C_{32}H_{26}O$ (mol wt 426.53): C, 90.10; H, 6.14. Found: C, 90.24; H, 6.11.

Photoisomerization of 4a To Give 6a. A solution of **4a** (200 mg) in benzene (80 mL) was irradiated for 10 min. Vacuum evaporation of solvent gave a colorless crystalline residue which was recrystallized from methylene chloride solution by addition of methanol: yield 140 mg (70%); mp 245–252 °C; ^{1}H NMR (in $CDCl_3$ at 37 °C) δ 7.40–6.24 (m, 28), 4.49 (s, 2). Anal. Calcd for $C_{42}H_{30}O$ (mol wt 550.71): C, 91.60; H, 5.49. Found: C, 91.40; H, 5.44.

Photoisomerization of 4b To Give 6b. Irradiation of **4b** (200 mg) in benzene (80 mL) for 10 min, followed by a workup as described above for **6a**, afforded 160 mg (80%) of colorless crystals. Upon being heated, the photoisomer turns yellow above 200 °C and melts at 284 °C: ^{1}H NMR (in $CDCl_3$ at 37 °C) δ 7.40–6.40 (m, 28), 4.42 (s, 2). Anal. Calcd for $C_{42}H_{30}O$ (mol wt 550.71): C,

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(6) The meso compound **3a** was found to fluoresce with a quantum yield of 4×10^{-3}. No emission was detectable from meso compound **4a** ($\phi \ll 10^{-4}$).

(7) A "staggered excimer" geometry has been proposed for 1,3-bis(9-anthryl)-1,1,3,3-tetramethyldisiloxane which, however, undergoes unsymmetrical intramolecular photocyclization: (a) Felix, G.; Lapouyade, R.; Bouas-Laurent, H.; Clin, B. *Tetrahedron Lett.* **1976**, 2277. (b) Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Nouv. J. Chim.* **1979**, 231. (c) Ferguson, J.; Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1981**, 446.

(8) The quantum yield of emission from **3b** is 0.014, and that of **4b** is 0.03.

(9) Livingston, R.; Wei, K. S. *J. Am. Chem. Soc.* **1967**, *89*, 3098.

(10) Julian, P. L.; Cole, W.; Diemer, G.; Schafer, J. G. *J. Am. Chem. Soc.* **1949**, *71*, 2058.

91.60; H, 5.49. Found: C, 91.80; H, 5.45.

Acknowledgment. We are indebted to Mr. Jan-Erik Löfroth and Dr. Kjell Sandros for recording the emisson spectra and to Mr. Reine Torberntsson for carrying out the ^{1}H NMR experiments.

Registry No. **1**, 7512-20-1; **2**, 72948-52-8; **3a**, 79916-87-3; **3b**, 79916-88-4; **4a**, 79916-89-5; **4b**, 79916-90-8; **5a**, 79916-91-9; **5b**, 79916-92-0; **6a**, 79916-93-1; **6b**, 79916-94-2; 9-anthraldehyde, 642-31-9.

Bromine Chloride from *N*-Chlorosuccinimide Oxidation of Bromide Ion. Electrophilic Addition Reactions in Protic and Aprotic Solvents

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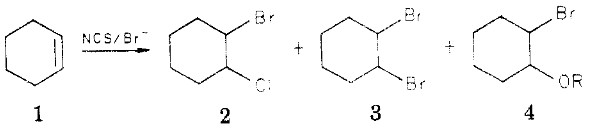
Bromine chloride can be prepared by condensing chlorine gas into liquid bromine.[2] However, applications of this method of bromine chloride formation to millimolar or smaller scale reactions is limited because of the difficulty in quantitating the amounts of each halide added. Bromine chloride may presumably by formed more conveniently from the reaction of compounds containing electrophilic halogens (Br^+ or Cl^+) and the appropriate halide ion.[3] Surprisingly, very few investigations of this method of bromine chloride formation have been reported in the literature.[4,5]

A desire to explore methods of generating electrophilic brominating agents in situ[6] led to an investigation of the formation of bromine chloride from *N*-chlorosuccinimide (NCS) and bromide ion. We now report on the reaction products obtained from the reaction of cyclohexene with what appears to be bromine chloride[7] formed from NCS and lithium bromide in a variety of solvents.

Results and Discussion

Reaction of cyclohexene **1** with NCS/Br^- in aprotic solvents at room temperature yielded two major addition products. These reaction products were shown to be 1-bromo-2-chlorocyclohexane (**2**) and 1,2-dibromocyclohexane (**3**) by gas chromatography/mass spectrometric analysis. Reaction of **1** in protic solvents also yielded **2** and **3**; however, the major product was that of the addition of one bromine atom and a molecule of solvent, **4**. As might be expected, a change in the concentration of reactants in solution changed the relative proportions of products observed (Table I). An increase in the concentration of reactants in protic solvents increased the percentage of **2** and **3** and decreased the percentage of **4**. This is what might be expected for a reaction which involved a bromonium ion intermediate, where an increase in reactant concentration increases the availability of halogen anion for attack of the brominium ion. Likewise, an increase in the concentration of reactants in aprotic solvents also increased the percentage of **2** and **3** present. In these examples however, the increases observed were accompanied by a decrease in the amount of products other than **2** and **3**.[8] Hageman and Havinga[4] have demonstrated that the reaction of bromine chloride with substituted cyclohexenes in methylene chloride yields the trans diaxial addition products. Although different solvents were used in this investigation, the same stereochemical and regiochemical reaction course would be expected.



1 2 3 4

Table I. Cyclohexene Addition Products[a]

solvent	% composition[b] 2	3	4	other
MeOH[c]	5.3	7.4	86.3	1.0
MeOH[d]	18.5	22.1	57.9	1.4
EtOH[c]	13.4	10.5	75.3	0.8
EtOH[d]	36.3	30.3	31.7	1.7
CH_3CN[c]	25.4	55.8		18.8
CH_3CN[d]	39.5	59.3		1.2
THF[c]	63.5	21.1		15.3
THF[d]	75.6	22.3		2.1
DME[c]	74.1	13.2		12.7
DME[c]	66.4	30.4		3.2

[a] Composition determined by GC analysis. [b] Values not corrected for FID response factors. [c] Concentration of NCS and $Br^- \cong 6 \times 10^{-2}$ M. [d] Concentration of NCS and $Br^- \cong 6 \times 10^{-1}$ M.

None of the dichloride addition product was detected by GC/MS analysis of the product mixtures. In contrast to this, Beger and Thielmann[9] found that the reaction of cyclopentene with bromine chloride gave approximately equal quantities of dibromo adduct and dichloro adduct in both methylene chloride and methanol. the presence of equal quantities of dibromo and dichloro addition products in that investigation can be readily explained by the disproportionation of BrCl in solution (eq 1).[10] However, to explain the substantial amounts of dibromo adduct **3** and total absence of dichloro adduct observed in this investigation, it must be assumed that if BrCl is formed, it does not disproportionate under the reaction conditiions employed. Since BrCl is stabilized by an association of chloride ions in solution (eq 2),[11] it can be surmised that other anionic species such as bromide ions (eq 3) or the nitrogen anion of succinimide might also have the same effect. Evidence for such in situ stabilization of BrCl can be obtained from an investigation by de la Mare and Galandauer[12] where BrCl (from Br_2 and Cl_2) was added to propene in 1 M HCl. In their investigation they also observed no dichloro adduct. Additionally, Surles and Popov[13] have noted the stabilization of BrCl with nitrogen

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(1) Graduate Research Assistant, 1980–1981.

(2) de la Mare, P. B. D., "Electrophilic Halogenation"; Cambridge University Press: New York, 1976; p 23.

(3) Reference 2, p 150.

(4) Hageman, H. J.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1141–1150.

(5) Ziegler, J. B.; Shabica, A. C. *J. Am. Chem. Soc.* **1952**, *74*, 4891–4894.

(6) Our interest was in finding methods which could be applied to radiobrominations. Radiobromine is obtained as bromide, and its conversion to an electrophilic brominating agent in situ is the most convenient and yields the highest radiochemical yields.

(7) It can only be presumed that bromine chloride is formed in situ. However, the fact that the reaction solution turns to a deep yellow-orange color when NCS and bromide are mixed might be taken as evidence for the presence of dihalide.

(8) Several minor peaks were observed in most chromatograms. Although these peaks were not identified, they had retention times identical with those observed in the reaciton of NCS and cyclohexene.

(9) Beger, J.; Thielmann, C. *J. Prakt. Chem.* **1980**, **322**, 809–815.

(10) Popov, A.; Mannion, J. J. *J. Am. Chem. Soc.* **1952**, *74*, 222–224.

(11) Jolles, Z. E., Ed., "Bromine and its Compounds"; Academic Press: New York, 1966; p 25.

(12) de la Mare, P. B. D.; Galandauer, S. *J. Chem. Soc.* **1958**, 36–43.

(13) Surles, T.; Popov, A. I. *Inorg. Chem.* **1969**, *8*, 2049–2052.