pentane (−78 °C) to give 60 mg of yellow crystalline **8** (67%): mp 86–87 °C; ^{1}H NMR δ 2.63 (2 H, d, J = 13.4 Hz), 2.00–1.60 (10 H, m), 1.60 (6 H, s), 1.45 (2 H, d, J = 11.2 Hz); ^{13}C NMR δ 93.10 (s), 41.92 (d), 36.48 (t), 32.97 (t), 31.12 (t), 27.91 (d), 26.36 (d), 24.65 (q); MS, m/e 208.1463 (M^+, 208.1463 calcd for $C_{13}H_{20}O_2$).

1-Acetyl-2-methyl-2-adamantanol (9). To an O_2-saturated solution of 88 mg (0.50 mmol) of **6** in 10 mL of CH_2Cl_2 and 0.50 mL each of TFA and TFAA at −78 °C was added dropwise 1.20 mL of a 7.60 mM solution of $4^+SbCl_6^-$ (9.1 μmol) in CH_2Cl_2 to give a persistent green solution. The reaction was quenched with ether and warmed to room temperature, and the solvent was evaporated to give 110 mg of crude **9**. Column chromatography using 10% EtOAc/hexane gave 73 mg of **9** (70%): mp 94–95 °C; ^{1}H NMR δ 4.11 (1 H, s), 2.35 (2 H, m), 2.17 (3 H, s), 2.05–1.40 (11 H, m), 1.28 (3 H, s); ^{13}C NMR δ 217.68 (s), 74.02 (s), 52.47 (s), 39.57 (d), 37.23 (t), 36.53 (t), 35.71 (t), 33.67 (t), 32.09 (t), 27.95 (d), 27.30 (q), 27.19 (d), 24.56 (q); MS, m/e 208.1465 (M^+, 208.1463 calcd for $C_{13}H_{20}O_2$), 193.1229 ($M^+ - CH_3$), 190.1366 ($M^+ - H_2O$), 165.1308 ($M^+ - CH_3CO$); IR ($CHCl_3$) 3475, 1678.

Cleavage of 8 to Dione 10. To an O_2-saturated solution of 26.3 mg (0.15 mmol) of **6** in 5 mL of CH_2Cl_2 and 23 μL each of TFA and TFAA was added 1.1 mL of a 2.4 mM solution of $4^+SbCl_6^-$ (2.6 μmol) in CH_2Cl_2 to give a persistent green solution. The reaction was quenched with 0.5 mL of Et_3N, diluted with pentane, and extracted with saturated Na_2CO_3. The organic phase was extracted once with 10% HCl, and then saturated Na_2CO_3, dried with K_2CO_3, filtered, and evaporated to give 50 mg of oil. Immediate spectroscopic observation indicated the presence of **10**: ^{1}H NMR δ 2.53 (2 H, m), 2.15 (6 H, s), 2.00–1.50 (10 H, m), 1.43 (2 H, t, J = 3.5 Hz); IR ($CHCl_3$) 1707.

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Registry No. **6**, 103241-27-6; **7**, 103241-28-7; **8**, 103241-29-8; **9**, 58773-73-2; **10**, 103241-30-1; O_2, 7782-44-7; homoadamantane-4,5-dione, 26775-76-8.

Photochemical Isomerization and Dimerization of 1-(9-Anthryl)-2-nitroethylene

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Photoexcited nitroalkenes may undergo a variety of molecular transformations that are governed by the nature of the ethylene substituents. For example, *trans*-1-phenyl-2-nitroethylene in cyclohexane solution upon irradiation through Pyrex undergoes geometrical isomerization to give the cis compound in an apparently rather inefficient reaction, as is suggested by the long irradiation times reported for preparative conversions.[1,2] By contrast, *trans*-2-nitro-1-(9-phenanthryl)propene in dioxane solution undergoes photochemical geometric isomerization with a quantum yield of 0.50.[3] The cis isomer does not regenerate the trans isomer ($\Phi < 0.001$) upon photoexcitation but yields both 2-methylphenanthro[9,10-*b*]furan and 9-phenanthraldehyde. Spectroscopically detectable transients are attributed to the formation of labile intramolecular cycloaddition products.[3,4] As for α-nitro-substituted arylethylenes, their photochemistry is characterized by far more complex reaction patterns involving both cyclization, rearrangement, and cleavage reactions.[5,6]

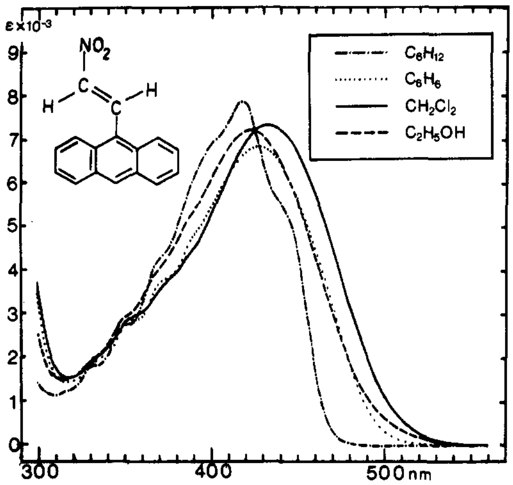

Figure 1. Electronic absorption spectra of **1** in cyclohexane, benzene, methylene chloride, and ethanol.

Within the scope of a study dealing with the effects of molecular geometry on the excited-state properties of 9-anthryl-substituted alkenes,[7] we have now investigated the photochemistry of *trans*-1-(9-anthryl)-2-nitroethylene (**1**). Commercially available "9-(2-nitrovinyl)anthracene" is of unspecified geometry, and it has been used as such in a previous photochemical investigation of light-induced viscosity changes of micellar solutions of substituted anthracenes.[8] The melting point of the commercial product suggests the material to consist mainly of the trans isomer. For the present study, we have prepared *trans*-1-(9-anthryl)-2-nitroethylene in excellent yield by piperidine-catalyzed condensation of 9-anthraldehyde with nitromethane in methylene chloride solution. The trans substitution of the ethylene bond in the product prepared this way is supported by its ^{1}H NMR spectrum in which the ethylene protons are characterized by a coupling constant of 14 Hz (see Experimental Section).

In accordance with earlier spectroscopic studies on nitro-substituted ethylenes,[9,10] the electronic absorption spectrum of **1** is characteristically affected by solvent polarity. Thus, the onset of absorption is shifted bathochromically in the solvent order cyclohexane, benzene, and ethanol, whose $E_T(30)$[11] values are 31.2, 34.5, and 51.9 kcal/mol, respectively. Remarkably, the largest bathochromic shift of the absorption maximum of **1** is observed in methylene chloride ($E_T(30)$ = 41.1 kcal/mol), suggesting unique solvent–solute interactions in this particular case (see Figure 1).

When dilute solutions of **1** in benzene are briefly exposed to ordinary laboratory light, drastic absorption spectral changes are noticeable. Upon irradiation in benzene so-

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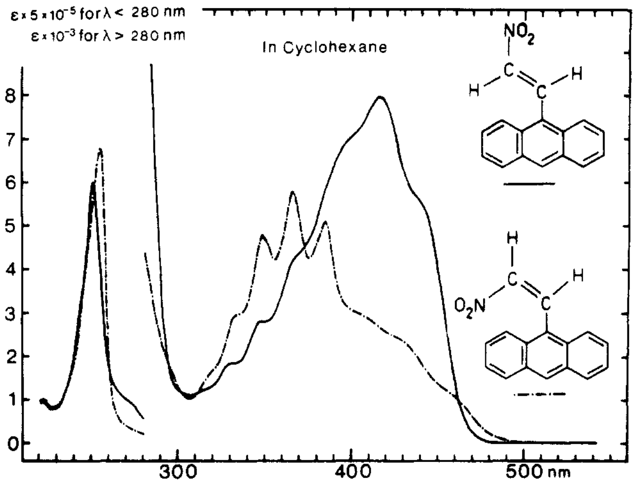
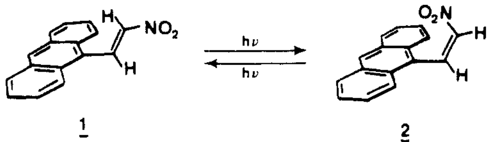


Figure 2. Electronic absorption spectra of 1 and 2 in cyclohexane.

Table I. Solvent Effect on the Quantum Yield of the Photochemical Isomerization of 1 and 2

solvent	trans → cis	cis → trans
cyclohexane	0.017	0.011
benzene	0.20	0.021
methylene chloride	0.008	0.005
ethanol	0.014	0.004

lution, using an immersion well apparatus equipped with a 125-W mercury high-pressure lamp and using wavelengths > 400 nm, 1 is smoothly converted into the heretofore unknown cis isomer 2, which was isolated in 84% yield. The cis substitution of 2 is evident from its ^1H



1 2

NMR spectrum by the 9-Hz coupling constant associated with the ethylenic protons (see Experimental Section). The decreased conjugation of the nitrovinyl moiety with the anthracene π-system in 2 is borne out in the more pronounced fine structure which characterizes its electronic absorption spectrum in comparison with that of the trans isomer (see Figure 2). Similar effects of molecular geometry on the absorption spectra of 9-anthrylalkenes have been discussed previously, and the bathochromically shifted onset of absorption of the cis-isomer 2 relative that of the trans-isomer 1 parallels the spectroscopic differences of *cis*- and *trans*-1-(9-anthryl)-2-benzoylethylenes.[7]

Quantum yield measurements for the geometrical isomerization of 1 and 2, summarized in Table I, were carried out in cyclohexane, benzene, methylene chloride, and ethanol. Thus, in all four solvents, the photostationary state favors the cis isomer, but there are drastic differences in the quantum yield of geometrical isomerization. In benzene solution, the trans → cis isomerization proceeds with a quantum yield of 0.20, but in cyclohexane, though its solvent properties resemble those of benzene as far as polarity is concerned, the corresponding quantum yield has decreased by one order of magnitude. In methylene chloride, the quantum yield of trans → cis isomerization is as low as 0.008.

For preparative photochemical conversions of *trans*-1-(9-anthryl)-2-nitroethylene into its cis isomer, benzene is the obvious solvent of choice. However, when the isomerization of 1 in benzene is carried out at concentrations >0.01 M, the competing formation of dimeric products becomes noticeable. Upon irradiation of 1 at high concentration (>0.1 M) in those solvents in which the quantum efficiency of geometrical isomerization inherently is low, dimerization reactions actually are predominant. For example, at an initial concentration of about 0.3 M in methylene chloride, the quantum yield for the disappearance of 1 by dimerization was found to be 0.087. Remarkably, however, the photochemical dimerization of 1 does not proceed by 4π + 4π cycloaddition, as is typical of most anthracene derivatives including 9-vinylanthracene,[12] but by 4π + 2π and 6π + 6π cycloadditions to give products 3 (56%), 4 (17%), and 5 (12%). ^1H NMR spectroscopic analysis of the crude photoproduct mixture revealed that the cis-isomer 2 was present in only 3%.

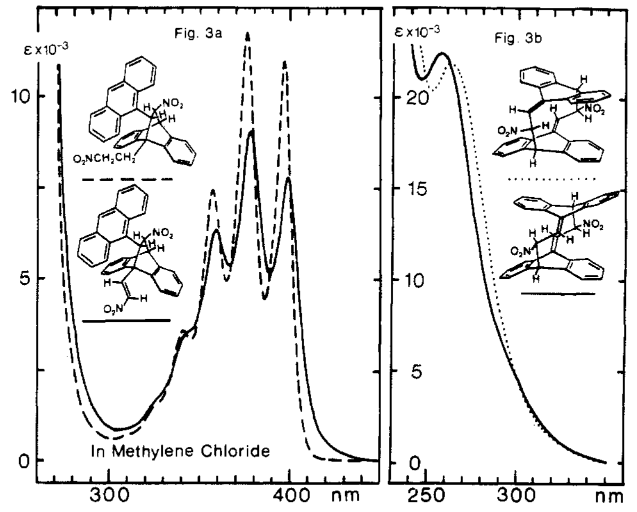
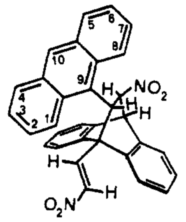


Figure 3. Electronic absorption spectra of dimers 3–5 and of reduction product 6 in methylene chloride.

The spectroscopic properties of dimers 3–5 are in agreement with the assigned structures. The formation of the major product 3 is rationalized by a Diels–Alder addition of the vinyl moiety of 1 to the diene system of the anthracene. Analogous to the Diels–Alder dimerizations of 9-(phenylethynyl)anthracene and *trans*-1-(9-anthryl)-2-phenylethylene, only that one of the two conceivable regioisomers is formed, whose precursor orientation complex is characterized by maximal π-orbital overlap.[13,14] In the 270-MHz ^1H NMR spectrum of 3, shielding



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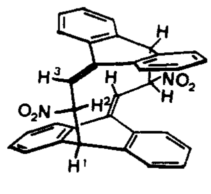

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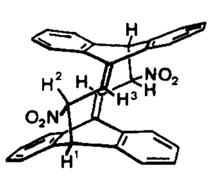

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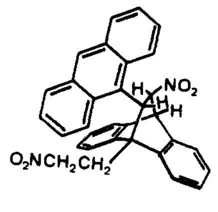

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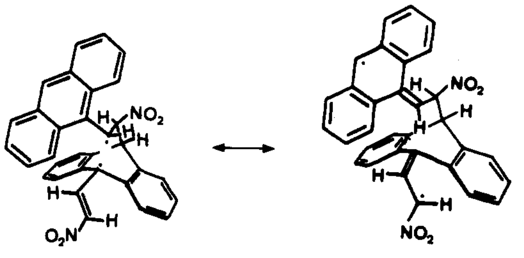
of H-1 of the anthracene moiety by the underlying aromatic π-system is indicated by an upfield doublet at 5.94 ppm. Similar shielding of one aromatic proton was also observed in the ^{1}H NMR spectrum of the dihydro derivative **6** which was prepared from **3** by sodium borohydride reduction. The presence of the anthracene π-system in both **3** and **6** is evident from their electronic absorption spectra (see Figure 3a).

Selective photoexcitation of **1** at wavelengths > 435 nm was found to be prerequisite for the preparation of dimer **3** because of its own photolability. The quantum yield for the disappearance of **3** upon excitation at 366 nm in methylene chloride is 0.3, and the major process was found to be cycloreversion to give **1**. According to ^{1}H NMR analysis of the photolysis mixture, **1**, **2**, **4**, and **5** were formed in 75%, 9%, 5%, and 11% yield, respectively. The Diels–Alder dimer of *trans*-1-(9-anthryl)-2-phenylethylene is characterized by similar photolability.[14] The thermolysis of **3** in refluxing toluene was found to give nitrovinylanthracene **1** (79%) besides isomers **4** (18%) and **5** (3%). In the thermal reaction, dissociation of the triaryl ethane bond in **3** probably gives biradical **7**, which may undergo β-cleavage to give **1**, or rebond to give **4** and **5**. We presume the C_2-symmetrical compound **4** for steric reasons to be thermodynamically favored over the more rigid centrosymmetrical isomer **5**.



7

Dimers **4** and **5** are formally derived from **1** by $6\pi + 6\pi$ cycloaddition. Their electronic absorption spectra (see Figure 3b) are characteristic of the benzenoid chromophore, and the differentiation between the C_2-symmetrical and centrosymmetrical dimers is based on ^{1}H NMR spectroscopic evidence. We deduce from inspection of Dreiding molecular models that only in the centrosymmetrical dimer **5** is the dihedral angle between the bridgehead proton H^1 and the adjacent H^2 about 120° so as to agree with the observed coupling constant of 2.3 Hz. No coupling is detectable for the corresponding protons in the C_2-symmetrical dimer **4** in which the dihedral angle between H^1 and H^2, according to model considerations, should be about 90°.

Concerning the mechanism of the photochemical dimerizations of nitrovinylanthracene **1**, we believe that the formation of $4\pi + 2\pi$ and $6\pi + 6\pi$ cycloaddition products in conjunction with the virtual absence of the "normal" $4\pi + 4\pi$ cycloadduct typical of singlet excited anthracenes is explicable by the existence of ground-state aggregates. Indeed, we find that the electronic absorption spectra of **1** are concentration dependent. The deviation from Beer's law with increasing concentration of **1** in methylene chloride solution is apparent by hyperchromicity and by the bathochromic shift of the end absorption. By assuming the deviations from Beer's law to be due to an equilibrium between monomeric **1** and an associative ground-state dimer D, ($2\mathbf{1} \rightleftarrows \mathrm{D}$), the association constant K was calculated from the concentration dependence of the molar extinction coefficient of **1** at 540 nm ($\epsilon_1 = 37\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$; $\epsilon_\mathrm{D} = 155\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). Thus, at high concentration of **1**, the absorption of light by D is considerable.

$$K = [\mathrm{D}]/[\mathbf{1}]^2 = 0.93$$

Table II. Concentration Dependence of Quantum Yield of Dimerization of 1 in Methylene Chloride[a]

$[\mathrm{A}]/\mathrm{M}^b$	$[\mathrm{D}]/\mathrm{M}$	F^c	Φ_dim	Φ_dim/F
0.015	0.00020	0.027	0.0045	0.167
0.094	0.0063	0.134	0.0210	0.157
0.298	0.0423	0.284	0.0435	0.153

[a] λ_exc 436 nm. [b] Initial analytical concentration of 1. [c] F is the fraction of the incident light absorbed by D at 436 nm. Its estimation is based on the assumption that the molar extinction coefficient of D at 436 nm is twice as large as that of 1.

Significantly, the results summarized in Table II reveal that the concentration-dependent quantum yield of dimer formation is directly proportional to the fraction of light absorbed by the ground-state aggregates D. We conclude, therefore, that the dimerization of **1** by $4\pi + 2\pi$ and $6\pi + 6\pi$ cycloaddition involves electronic excitation of aggregates. In support of this conclusion, we find that photoexcitation ($\lambda > 435$ nm) of **1** (0.097 M) in the presence of anthracene (0.140 M) in methylene chloride gives a mixture of **2** (12%), **3** (60%), **4** (16%), and **5** (12%), but there is no mixed cycloaddition product of **1** with anthracene detectable by ^{1}H NMR analysis.

Experimental Section

Electronic absorption spectra were recorded on a Uvicon 810 instrument. ^{1}H NMR spectra were obtained on a Bruker 270 spectrometer, and chemical shifts are reported in parts per million downfield from $\mathrm{Me_4Si}$. Melting points were taken on a hot-stage microscope and are uncorrected. High-resolution mass spectra were obtained at 60 eV with a VG Analytical ZAB/HF instrument (acceleration voltage 8000 V; 500 μA; temperature 150–180 °C).

Photochemical Measurements. Quantum yields of isomerization were measured in an optical bench arrangement equipped with a 125-W high-pressure mercury lamp and a Corning narrow-band-pass filter (7-83) for the 366-nm mercury line. The measurements were conducted at conversions of 10%. The photochemical isomerization of 1,2-di(9-anthryl)ethane ($\Phi = 0.26$)[15] served as actinometer.

Quantum yields of dimerization of **1** were measured in an optical bench arrangement equipped with a 1000-W high-pressure xenon/mercury lamp and by using an interference filter for 436 nm. Conversions of **1** were about 5%, and the quantum yields are based on the potassium ferrioxalate actinometer.

***trans*-1-(9-Anthryl)-2-nitroethylene (1).** A solution of 9-anthraldehyde (2.06 g; 10 mmol), nitromethane (0.54 mL; 10 mmol), and piperidine (0.20 mL) in methylene chloride (20 mL) was refluxed for 9 h. Vacuum evaporation of solvent from the deep red reaction mixture gave a residue, which was subjected to flash chromatography on silica gel/toluene to give 1.87 g of red crystalline **1** and 0.42 g of 9-anthraldehyde. Based on consumed anthraldehyde, the yield of **1** is 94%. When it is recrystallized from methylene chloride by precipitation with hexane, **1** melts at 162–164 °C. The literature melting point of **1** varies between 142,[16] 145–148,[17] 155,[18] and 157–160 °C:[19] ^{1}H NMR ($\mathrm{CDCl_3}$) δ 9.00 (d, J = 14 Hz, 1 ethylene H), 8.54 (s, H-10), 8.20–8.60 (m, 2 H), 8.06–8.03 (m, 2 H), 7.62–7.50 (m, 5 H). In order to ascertain the chemical shifts of both ethylenic H, the ^{1}H NMR spectrum of **1** was also recorded in acetone-d_6: δ 8.96 (d, J = 14 Hz, 1 ethylene H), 8.66 (s, H-10), 8.30–8.26 (m, 2 H), 8.14–8.10 (m, 2 H), 7.74 (d, J = 14 Hz, 1 ethylene H), 7.66–7.54

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(m, 4 H). IR (KBr) 1310, 1480 cm^{-1}.

***cis*-1-(9-Anthryl)-2-nitroethylene (2).** A solution of **1** (250 mg; 1 mmol) in benzene (150 mL) under argon at 20 °C was irradiated for 1 h with a high-pressure mercury lamp (Philips HPK 125 W) in an immersion well apparatus equipped with a 400-nm cutoff filter solution (75 g of potassium nitrite in 100 mL of water; 1-cm path length). Workup by vacuum evaporation of solvent, followed by flash chromatography on silica gel/toluene and recrystallization from methylene chloride gave 210 mg (84%) of orange-red crystals: mp 187–192 °C (upon melting, **2** isomerizes to give **1**); ^{1}H NMR (CDCl$_3$) δ 8.50 (s, H-10), 8.06-8.01 (m, 2 H), 7.93–7.89 (m, 2 H), 7.70 (d, J = 9 Hz, 1 H), 7.61 (d, J = 9 Hz, 1 H), 7.53–7.46 (m, 4 H). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.08; H, 4.49; N, 5.60; IR (KBr) 1340, 1500 cm^{-1}.

Photochemical Dimerization of 1 To Give 3–5. A solution of **1** (410 mg, 1.64 mmol) in methylene chloride (4 mL), placed in a cylindrical quartz cell of 1-cm path length and degassed by three freeze–thaw cycles, was irradiated for 6 h with a 1000-W xenon/mercury lamp in optical bench arrangement equipped with an Oriel LP 480 filter (cutoff at 435 nm). Partly, the dimers precipitated during the irradiation. According to ^{1}H NMR analysis, the reaction mixture consisted of starting material **1** (12%), its cis-isomer **2** (3%), Diels–Alder dimer **3** (56%), C_2-symmetrical dimer **4** (17%), and centrosymmetrical dimer **5** (12%). By addition of hexane, 50 mg of centrosymmetrical dimer **5** precipitated from the reaction mixture. It was washed with boiling methylene chloride (10 mL) to give 27 mg (7%) of **5** as colorless crystalline residue, melting with decomposition at 255–263 °C.

The solid residue obtained on vacuum evaporation of solvent from the original filtrate was washed with ether (5–10 mL) in order to dissolve **1** and **2**. From the residue, 191 mg (47%) of **3** and 25 mg (6%) of **4** were obtained by fractional crystallization from methylene chloride/hexane. The Diels–Alder dimer **3** forms lemon-yellow crystals, which melt with decomposition around 190 °C. The C_2-symmetrical dimer **4** forms colorless crystals, which decompose upon melting between 242 and 245 °C.

3: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1583; IR (KBr) 1340, 1520, 1540 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.46 (s, H-10), 8.07–6.73 (m, 15 Ar H), 7.62 (obscured d, J = 14.3 Hz, 1 ethylenic H), 6.82 (d, J = 14.3 Hz, 1 ethylenic H), 5.94 (d, J = 9.2 Hz, 1 Ar H), 5.88 (dd, J = 6.9, 2.5 Hz, 1), 5.64 (d, J = 6.9 Hz, 1), 5.32 (d, J = 2.5 Hz, 1).[20] Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45. Found, C, 76.94; H, 4.40.

4: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1578; IR (KBr) 1340, 1540 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.39–7.02 (m, 8), 6.39, (d, J = 10.4 Hz, H-2), 5.56 (d, J = 10.4 Hz, H-3), 4.84 (s, H-1). Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45; N, 5.62. Found, C, 77.10; H, 5.04; N, 5.22.

5: high-resolution mass spectrum, m/z calcd for $C_{32}H_{22}N_2O_4$ 498.15806, found 498.1590; IR (KBr) 1340, 1530 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.58–7.12 (m, 8), 5.72 (dd, J = 11.2, 2.3 Hz, H-2), 5.40 (d, J = 11.2 Hz, H-3), 4.84 (d, J = 2.3 Hz, H-1). Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.10; H, 4.45; N, 5.62. Found, C, 76.88; H, 4.40; N, 5.44.

Sodium Borohydride Reduction of Dimer 3 To Give 6. Sodium borohydride (20 mg, 0.53 mmol) was added to a stirred solution of **3** (125 mg, 0.25 mmol) in a mixture of methylene chloride (5 mL) and methanol (5 mL). After 10 min, when the yellow color of the solution had faded, the methylene chloride was removed by vacuum evaporation, and the remaining reaction mixture was diluted with water (10 mL) and extracted with five 25-mL portions of ether. The ether solution was dried over magnesium sulfate, and the residue obtained on vacuum evaporation of solvent was purified by flash chromatography on silica gel/toluene to give an oily substance, which gave pale yellow crystals upon addition of ether: yield, 90 mg (72%); mp 200–202 °C; ^{1}H NMR (CDCl$_3$) δ 8.42 (s, H-10), 8.22-6.71 (m, 15), 5.96 (d, J = 9.1 Hz, 1 Ar H), 5.79 (dd, J = 7.1, 2.3 Hz, 1), 5.46 (d, J = 7.1 Hz, 1), 5.21 (d, J = 2.3 Hz, 1), 4.44 (br m, 1), 4.24 (br m, 1), 3.11–2.97 (m, 1), 2.84–2.70 (m, 1). Anal. Calcd for $C_{32}H_{24}N_2O_4$: C, 76.79; H, 4.83; N, 5.60. Found: C, 77.19; H, 4.81; N, 5.33. High-resolution mass spectrum, m/z calcd for $C_{32}H_{24}N_2O_4$ 500.1736, found 500.1705; IR (KBr) 1350, 1530 cm^{-1}.

Thermolysis of 3 in Toluene. A solution of **3** (8 mg) in toluene (5 mL) was refluxed for 2 h. The residue obtained on vacuum evaporation of solvent was dissolved in deuterated chloroform and analyzed by ^{1}H NMR.

Registry No. 1, 55446-60-1; 2, 102781-65-7; 3, 102781-66-8; 4, 102781-67-9; 5, 102850-00-0; 6, 102781-68-0; 9-anthraldehyde, 642-31-9; nitromethane, 75-52-5.

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[20] The doublet at 5.64 ppm is attributed to the methine proton adjacent to the 9-anthryl substituent in **3**. The corresponding signal in the ^{1}H NMR spectrum of compound **6** appears at 5.46 ppm. The remarkable downfield position most likely is due to deshielding by the adjacent nitro group. In the ^{1}H NMR spectrum of the Diels–Alder dimer of *trans*-1-(9-anthryl)-2-phenylethylene[14] the corresponding proton gives rise to a doublet at 4.92 ppm.

The Cine-Substitution Reaction of 5-Bromopyrimidines by Lithium Reagents

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In the 1970s we reported a useful synthetic transformation of 5-bromo-4-(methylthio)pyrimidines **1** (Scheme I; R^1 = H, OMe, SMe, NMe$_2$; R^2 = SMe) into 4,5′-bipyrimidines **7** upon treatment with 0.5 equiv of *n*-BuLi.[1] The reaction has been applied in the preparation of a series of biologically important, [(dimethylamino)ethyl]thio-substituted 4,5′-bipyrimidines.[2] The mechanism of this transformation was only briefly investigated, and, since quenching of the reaction mixture of **1b** with D_2O produced 5-deuterio-2,2′,4′,6-tetrakis(methylthio)-4,5′-bipyrimidine (**7b**), it was suggested (erroneously) that the respective 5-lithio derivative **2b** was the intermediate product[1a] in this cine-substituted reaction of the bromine atom. As an extension of our studies on this transformation we investigated the reactions of two closely related pyrimidines **1a** and **1b** with lithium reagents. We present evidence that the cine-substitution reaction of 4-(alkylthio)-5-bromopyrimidines involves a σ-adduct, such as **3**, between the 5-bromopyrimidine and a lithium compound.

Treatment of 5-bromo-2-(methylthio)pyrimidine (**1a**) in THF with 1 equiv of *n*-BuLi at −80 °C resulted in a bromine–lithium exchange reaction, because on quenching with D_2O, 5-deuterio-2-(methylthio)pyrimidine[3] was obtained as a sole product. When 0.5 equiv of *n*-BuLi was used and the reaction mixture was allowed to warm up to −20 °C and then quenched with water, another major compound was formed in a 72% yield. The product was air stable and had the empirical formula $C_{10}H_{11}BrN_4S_2$. It was positively identified as 5-bromo-2,2′-bis(methylthio)-3,4-dihydro-4,5′-bipyrimidine (**4a**) on the basis of the ^{1}H NMR NOE difference spectra (see the Experimental Section) and the spectral comparison with known 5-bromo-4-ethyl-2-(methylthio)-3,4-dihydropyrimidine.[4]

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