On the Relationship between Molecular Geometry and Photochemical Properties of 1,2-Substituted 1,2-Di-9-anthrylethylenes

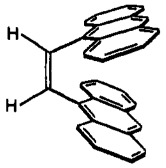
Hans-Dieter Becker* and Kjell Andersson

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

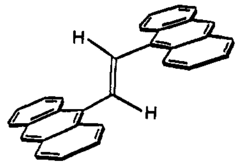
Received April 13, 1987

Starting from either 1,2-di-9-anthrylethanone or di-9-anthrylcyclopropenone, a series of cis–trans isomeric 1,2-di-9-anthrylethylenes substituted at the central ethylene bond has been synthesized, and their photochemical properties in terms of geometric isomerization and intramolecular cycloaddition have been investigated. By substitution of the ethylene bond with methoxy and methyl, the quantum yields of both photochemical trans → cis isomerization and intramolecular [4 + 4] cycloaddition of the cis isomers are greatly increased. Substituents such as formyl and methoxycarbonyl apparently enhance intersystem crossing so as to induce isomerization by [4 + 2] cycloaddition. Photochemical isomerization of 1,2-di-9-anthryl-1-hydroxypropene proceeds by hydrogen shift and results in the dearomatization of one anthracene moiety. Monosubstituted *cis*-dianthrylethylenes in solution are nonfluorescent. The fluorescence of *cis*-1-methoxy-2-methyl-1,2-di-9-anthrylethylene is suggested to originate from an intramolecular excimer state. For the corresponding trans isomer, the fluorescence is found to be dependent on solvent polarity as is typical of a twisted intramolecular charge-transfer state.

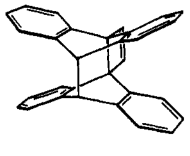
Photoexcited *cis*-1,2-di-9-anthrylethylene (**1a**) undergoes both geometric isomerization and intramolecular cycloaddition with remarkably low quantum efficiency, and "normal" anthracene photochemistry in terms of [4 + 4] cycloaddition to give **3** is insignificant ($\Phi < 0.00007$) in comparison to the isomerization by [4 + 2] cycloaddition leading to **4** ($\Phi = 0.0007$). The quantum yield for the geometric isomerization of **1a** to give the trans compound **2a** is equally low (0.0007) in cyclohexane solution, though it is markedly higher in benzene ($\Phi = 0.007$) and chloroform ($\Phi = 0.015$).[1,2] On the other hand, all attempts to bring about the photochemical geometric isomerization of *trans*-1,2-di-9-anthrylethylene (**2a**) to give **1a** have been unsuccessful. Several other examples of photochemical "one-way" cis–trans isomerization of anthryl-substituted ethylenes have become known in recent years.[3,4]



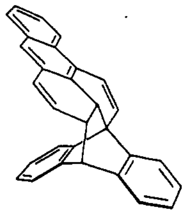
1



2

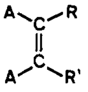


3

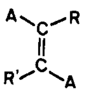


4

It is obvious that *cis*-dianthrylethylene **1a** cannot assume a molecular geometry in which the ethylene and anthracene moieties are coplanar. However, also *trans*-1,2-di-9-anthrylethylenes such as **2a** are nonplanar molecules. Their molecular geometry as known from crystal structure analyses is such as to have the planes of the two anthracene systems twisted out of the plane of the ethylene by about 55–60°.[5,6] The twists about the two 9-anthrylethylene single bonds in either conrotatory or disrotatory fashion relieve steric interaction between the ethylenic hydrogens and those attached to the 1- and 8-carbons of the anthracene moieties. As for the molecular geometry of *cis*-1,2-di-9-anthrylethylene (**1a**), crystal structure data are not available. The predominant formation of the [4 + 2] adduct **4** over that of the [4 + 4] adduct **3** suggests that the geometry of the cis isomer **1a** undergoing the intramolecular photochemical Diels–Alder reaction could be characterized by C_2 rather than mirror symmetry.



1a-f



2a-f

1;2	R	R'
a	H	H
b	H	OCH_3
c	H	CHO
d	H	$COOCH_3$
e	CH_3	OCH_3
f	CH_3	OH

A = 9-anthryl

The present paper deals with the synthesis and photochemical properties of previously unknown 1,2-di-9-anthrylethylenes **1b–f** and **2b–f**, which are substituted at the central ethylene bond. In these dianthrylethylenes, the substituents R and R′ should affect the molecular geometry of both the cis and trans isomers by increasing the angle between the plane of the ethylenic double bond and the planes of the anthracene moieties.

We also report about the photophysical repercussions of substitution as borne out in the emission spectral properties of cis–trans isomeric dianthrylethylenes.

Results and Discussion

Syntheses. One approach we have used to prepare substituted 1,2-di-9-anthrylethylenes **1** is based on the

---

[1] Becker, H.-D. Hansen, L.; Andersson, K. *J. Org. Chem.* 1981, *46*, 5419.

[2] Becker, H.-D.; Sandros, K.; Andersson, K. *Angew. Chem.* 1983, *95*, 507.

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

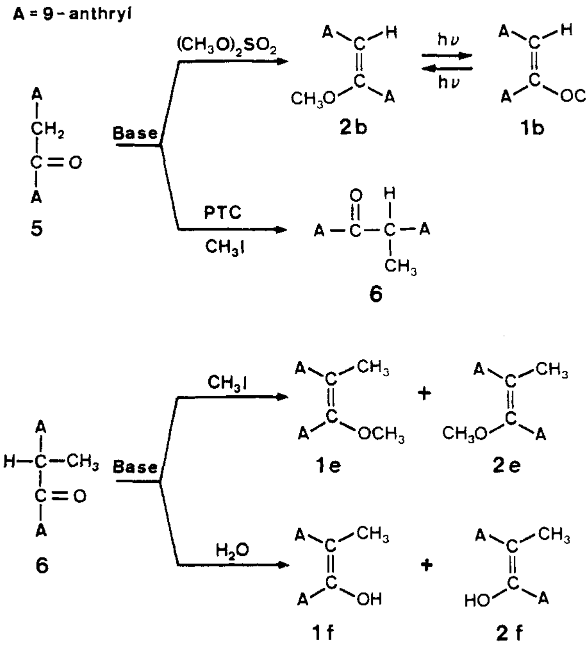
[4] Karatsu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* 1985, *115*, 9.

[5] Becker, H.-D.; Engelhardt, L. M.; Hansen, L.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* 1984, *37*, 1329.

[6] Becker, H.-D.; Hansen, L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1985, *38*, 809.

0022-3263/87/1952-5205$01.50/0 © 1987 American Chemical Society

Scheme I



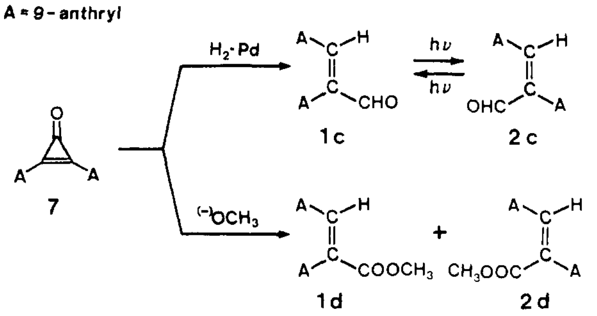
enolization and alkylation of 1,2-di-9-anthrylethanone[7] (**5**; see Scheme I). Thus, reaction of **5** in dimethylformamide (DMF) with sodium methoxide gives the deep red colored enolate ion, which is converted into the trans dianthryl enol methyl ether **2b** (85% yield) by alkylation with dimethyl sulfate. The corresponding cis isomer **1b** can be prepared from **2b** by irradiation in methylene chloride solution (vide infra). Surprisingly, column chromatography of **2b** on neutral alumina/toluene also results in geometric isomerization to give **1b**.

C-Methylation of dianthrylethanone **5** to give 1,2-di-9-anthrylpropanone (**6**; about 60% yield) was accomplished by phase-transfer-catalyzed (PTC) alkylation with methyl iodide in methylene chloride. Enolization of dianthrylpropanone **6** with potassium *tert*-butoxide in DMF followed by alkylation with methyl iodide gives mainly (66%) the cis-substituted dianthrylethylene **1e**, i.e., (*E*)-1,2-di-9-anthryl-1-methoxypropene. The corresponding trans isomer **2e** was isolated from the reaction mixture in 16% yield.

When the 1,2-dianthrylpropanone enolate is protonated by addition of water or dilute hydrochloric acid, a 2:1 mixture of *cis*- and *trans*-ethenols **1f** and **2f** precipitates from the reaction mixture. Attempts to separate the two enols by fractional crystallization have failed because of the lability of the cis isomer in solution. However, treatment of the cis–trans isomer mixture in methylene chloride solution containing a trace of hydrochloric acid smoothly gives the stable trans isomer **2f**. Remarkably, the conversion of 1,2-dianthrylpropanone **6** into the crystalline *trans*-enol **2f** also can be accomplished by treatment with excess sodium borohydride in a mixture of methylene chloride and methanol.

The formation of a stable enol from 1,2-dianthrylpropanone **6** is interesting because most other stable simple enols are mesityl-substituted, and have to be synthesized by Grignard additions to dimesitylketene.[8] Moreover, for the present investigation, enol, **2f** is synthetically useful, as its methylation with methyl iodide in DMF in the presence of potassium *tert*-butoxide provides the most convenient route to the 1-methoxy-2-methyl-substituted *trans*-dianthrylethylene **2e**. Significantly, there is no cis isomer **1e** formed in the alkylation of **2f**. We conclude, therefore, that thermal trans–cis equilibration of **2f** enolate ion is negligible, and the favored formation of the *cis*-dianthrylethylene **1e** by methylation of dianthrylpropanone **6** under phase-transfer conditions is indicative of the preferential formation of the *cis*- rather than *trans*-enolate.

Scheme II



As a second route to substituted *cis*-1,2-di-9-anthrylethylenes **1** we explored some transformations of di-9-anthrylcyclopropenone[9] (**7**) (see Scheme II) which is accessible from tetrachlorocyclopropene[10] by reaction with 2 molar equiv of anthracene in the presence of aluminum chloride. Catalytic hydrogenation of **7** over Pd in ethyl acetate resulted in the formation of the 1-formyl-substituted *cis*-dianthrylethylene **1c**, but inadvertent concomitant hydrogenation of the anthracene systems necessitated the rearomatization of the crude hydrogenation product with DDQ. Because of the extremely low solubility of cyclopropenone **7** in most solvents, the preparation of **1c** is rather tedious. The synthesis of the trans isomer **2c** was accomplished by irradiation of **1c**, though also this reaction is synthetically cumbersome because the cis isomer is favored at the photostationary state.

Ring opening of cyclopropenone **7** with sodium methoxide in DMF/methanol gave in 63% yield the 1-methoxycarbonyl-substituted *cis*-dianthrylethylene **1d** which was separated from concomitantly formed trans isomer **2d** (19% yield) by column chromatography on silica gel/toluene. The ring opening of **7** with base has ample precedence in the chemistry of diphenylcyclopropenone.[11,12]

Electronic Absorption Spectra. The ultraviolet absorption spectrum of the parent *cis*-dianthrylethylene **1a** around 380 nm is characterized by fine structure which is typical of the anthracene chromophore. The spectrum of the trans isomer **2a**, by contrast, is almost structureless and is shifted toward longer wavelengths (see Figure 1a). 1-Substitution of *cis*-dianthrylethylene **1** by methoxy, formyl, and methoxycarbonyl is borne out absorption spectroscopically by minor distortion of the anthracene-like spectrum. The repercussions of substitution on the absorption of the corresponding trans isomers are more clearly noticeable, as the spectra get increasingly structured and, significantly, shifted toward shorter wavelengths (see Figure 1b–d). This effect of substitution on electronic absorption is most pronounced for 1-methoxy-2-methyldianthrylethylenes: cis isomer **1e** is yellow, while the trans isomer **2e** is virtually colorless (see Figure 1e). Similarly,

---

[7] Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1986**, *51*, 2956.

[8] For some recent literature on stable simple enols, see: (a) Hart, H. *Chem. Rev.* **1979**, *79*, 515. (b) Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685. (c) Biali, S.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669.

[9] Wadsworth, D. H.; Donatelli, B. A. *Synthesis*, 1981, 285.

[10] Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2478.

[11] Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189.

[12] Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1.

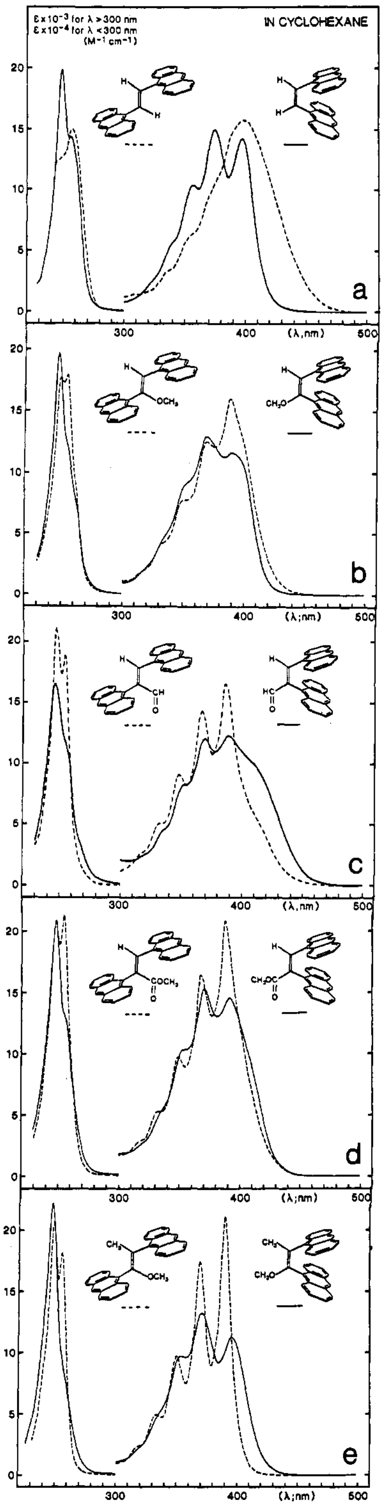
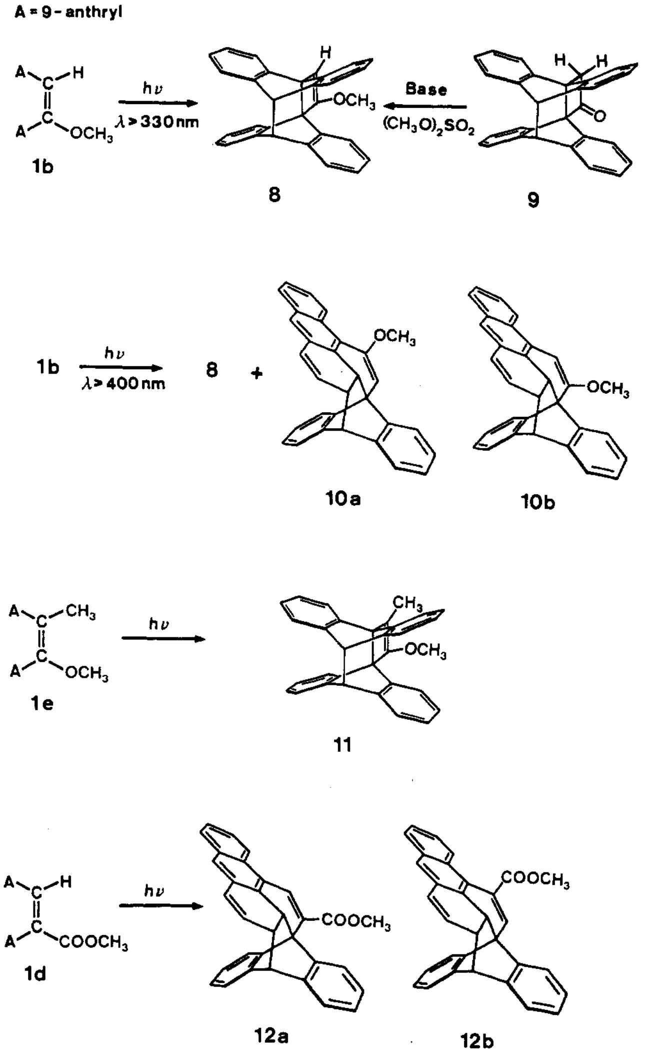


Figure 1. Electronic absorption spectra of cis-trans isomeric substituted dianthrylethylenes **1a**-**e** and **2a**-**e** in cyclohexane.

the absorption spectrum of the *trans*-ethenol **2f** is hypsochromically shifted relative to that of its precursor 1,2-dianthrylpropanone **6** and shows far more fine structure (cf. ref 19).

The short-wavelength absorption ($S_0 \rightarrow S_3$ transition) of dianthrylethylenes deserves comment. In the spectra of the cis isomers **1**, this absorption is characterized by one maximum around 248 nm and a shoulder around 256 nm. In the spectra of all the trans isomers, however, the absorption around 256 nm is enhanced so that the shoulder has developed into a well-resolved maximum. Thus, excepting the spectra of the parent pair **1a**/**2a**, two maxima due to the $S_0 \rightarrow S_3$ transition typically distinguish the absorption spectra of trans isomers from those of the cis isomers.

Scheme III



Photochemical Reactions of 1,2-Substituted Dianthrylethylenes (Cf. Scheme III). Different from the parent *trans*-dianthrylethylene **2a**, derivatives **2b**-**e** undergo photochemical geometric isomerization with such an efficiency as to give the corresponding cis isomers **1b**-**e** in preparatively useful yields. Significantly, the quantum yield ratios for the reversible geometric isomerization of 1-substituted dianthrylethylenes actually favor the formation of the cis rather than the trans isomers. Moreover, substitution of the ethylene double bond also markedly enhances the photochemical isomerization of *cis*-dianthrylethylenes by intramolecular cycloaddition. Thus, irradiation of the 1-methoxy derivative **1b** in cyclohexane results in its isomerization by cycloaddition with a quantum yield of 0.0012.[13] When the isomerization of **1b** is carried out on a preparative scale in toluene solution and when light of wavelengths >330 nm is used, the sole product was found to be the [4 + 4] cyclomer **8** (whose structure we have established by independent synthesis from 1,2-dianthrylethanone via its [4 + 4] cyclomer **9**, followed by enolization and subsequent methylation; see Experimental Section). When light of wavelengths >400

---

[13] The quantum yield of cycloaddition is solvent dependent. In methylene chloride solution, the quantum yield for the disappearance of **1b** is as low as 0.000 25.

Table I. Photochemical Isomerizations of Dianthrylethylenes 1 and 2 in Cyclohexane (λ_{exc} 366 nm)

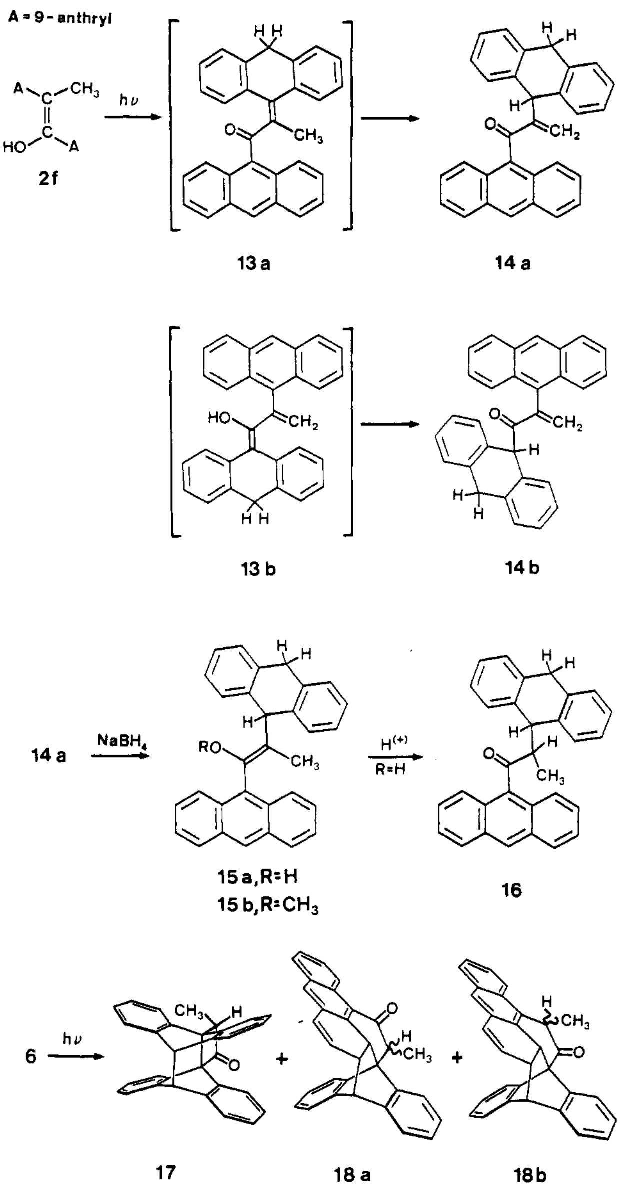
		reaction quantum yields			major mode of
R	R′	2 → 1	1 → 2	1 → cyclomer	cyclo-addtn
H	H	<<0.0001	0.0007	0.0007	4 + 2
H	CHO	0.22	0.015	<0.001	4 + 2
H	CH_3OCO	0.20	0.015	<0.001	4 + 2
H	CH_3O	0.088	0.053	0.0012	4 + 4
CH_3	CH_3O	?	<0.01	0.20	4 + 4

nm is employed, the additional formation of a [4 + 2] cyclomer of **1b** (approximate ratio 4:1) is noticeable.[14] Only one of the two possible Diels–Alder isomers of **1b** has been detected by ^{1}H NMR; as we assume the methoxyvinyl-substituted anthracene moiety of **1b** to be electron-rich, the [4 + 2] cyclomer should probably be assigned structure **10a**, rather than **10b**.

The photochemistry of **1b** suggests that double bond substitution of *cis*-dianthrylethylene both increases the quantum efficiency of trans → cis isomerization and enhances the efficiency of isomerization by [4 + 4] cycloaddition over that of [4 + 2] cycloaddition. This substitution effect is evident in the case of the 1-methoxy-2-methyl derivative **1e**, whose isomerization by intramolecular [4 + 4] cycloaddition to give isomer **11** proceeds with a quantum yield of 0.20![15] (Any isomerization of **1e** by [4 + 2] cycloadditon has not been detected). For the trans isomer **2e**, the quantum yield of disappearance is only 0.002. We believe, therefore, that the enhanced efficiency of cycloaddition observed for the 1,2-substituted cis isomer **1e** is a repercussion of its molecular geometry which predisposes the two anthracene moieties for the observed course of the photoreaction.[16]

Quantum yield data for both geometric isomerization and cycloaddition are summarized in Table I. The cycloaddition of the methoxycarbonyl derivative **1d**, exceptionally, proceeds exclusively as Diels–Alder reaction (Φ < 0.001). In view of previously reported examples of photochemical isomerizations of carbonyl-substituted linked anthracenes, the observed cycloaddition of **1d** may involve the excited triplet state.[17] Only one of the two possible [4 + 2] adducts **12a** and **12b** is formed from **1d**. Although a clear-cut distinction between these two structures is not possible on the basis of their ^{1}H NMR spectra, structure **12a** may be tentatively assigned to the photoproduct if we assume the carbonyl–vinyl conjugated anthracene to be the electron-deficient anthracene moiety of **1d** which reacts as dienophile.[18] The quantum yield for the photochemical isomerization by cycloaddition of the formyl derivative **1c** was found to be so low as to make preparative experiments impracticable. However, the absorption spectral changes associated with the photochemical reaction of **1c** at spectroscopic concentration (~0.0001 M) suggest the formation of a [4 + 2] rather than [4 + 4] adduct.

Scheme IV



The photochemical properties of the *trans*-dianthrylethenol **2f** turned out to be unexpected and unprecedented in anthracene photochemistry (see Scheme IV). Upon irradiation (λ > 400 nm) in methylene chloride solution, **2f** isomerizes with a quantum yield of 0.18 to give the 9-anthryl-substituted enone **14a**, whose formation is suggested to involve the photochemical ketonization of **2f** to give intermediate **13a**, which undergoes 1,3-hydrogen shift. On the basis of an erroneous interpretation of ^{1}H NMR data, we had first assigned the isomer structure **14b** to the photoproduct, and we believed the isomerization to involve **13b** as obvious intermediate.[19] However, ^{1}H NMR decoupling experiments and chemical evidence clearly confirm the correctness of structure **14a**. Thus, reduction of the **2f** photoisomer with sodium borohydride gives the isolable "simple" enol of structure **15a** which we find to undergo acid-catalyzed ketonization to give **16**. It is in ketone **16** that the position of the 9,10-dihydroanthryl moiety as being adjacent to the tertiary carbon (rather than to the carbonyl group) can be established by ^{1}H NMR.

---

(14) The [4 + 2] cyclomer **10** absorbs light in the region of 330–400 nm and undergoes photolytic cycloreversion (see ref 2) to regenerate **1b**, which, in turn, reenters the photochemical conversion cycle.

(15) For 1-methoxy-2-methyldianthrylethylene **1e**, the quantum yield of cycloaddition decreases from 0.20 in cyclohexane to 0.16 in methylene chloride.

(16) According to an X-ray diffraction analysis of crystalline **1e**, the angle between the plane of the ethylene double bond and the plane of the anthracene on the methyl-substituted carbon is 75°, and the corresponding angle between the ethylene and the anthracene on the methoxy-substituted carbon is as large as 84°. Details will be published in a comprehensive paper dealing with the results of a series of X-ray diffraction analyses of variously substituted anthryl-substituted ethylenes.

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

(18) Becker, H.-D.; Andersson, K. *Tetrahedron* **1986**, *42*, 1560.

(19) Becker, H.-D.; Andersson, K. *Tetrahedron Lett.* **1987**, *28*, 1323.

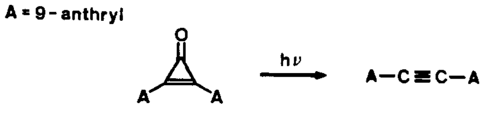
Table II. Emission Spectral Data for *trans*-Dianthrylethylenes 2

R	R′	solv	λ_{max}^{abs}	λ_{max}^{em}	Stokes shift	Φ_F
H	H	toluene	400	650	9600	0.0042
		CH_2Cl_2	400	660	9800	0.0041
H	CHO	C_6H_{12}	387	610	9400	0.0021
		CH_2Cl_2	389	610	9300	0.00026
H	CH_3OCO	C_6H_{12}	388	590	8800	0.0018
		CH_2Cl_2	390	590	9700	0.0004
H	CH_3O	C_6H_{12}	389	525	6600	0.0022
		CH_2Cl_2	391	565	7900	0.0009
CH_3	CH_3O	C_6H_{12}	389	450	3500	0.0014
		CH_2Cl_2	392	540	7000	0.0016
		CH_3CN	389	555	7700	0.0013

Without this NMR evidence, the positions of the 9-anthryl and dihydroanthryl moieties of the **2f**-photoisomer **14a** and in enol **15a** and its methyl ether **15b** remained ambiguous.

When we first observed the photochemical isomerization of enol **2f** by hydrogen shift (rather than cycloaddition), we did not expect the mode of excited-state ketonization to differ from that of the ground-state tautomerization.[20] We did ascertain that photoexcitation of **2f** does not result in ketonization to give 1,2-dianthrylpropanone **6**, which we find to undergo "normal" photochemical intramolecular cycloaddition reactions. The main photoproduct of **6** is the [4 + 4]cyclomer **17**, and at least two (of the four possible) Diels–Alder adducts **18** are detectable by ^1H NMR. We have also carried out the biacetyl-sensitized isomerization of dianthrylpropanone **6** and found that the triplet-state isomerization mainly leads to [4 + 2] adducts **18a** and **18b** (see Experimental Section).

The present investigation was extended to dianthrylcyclopropenone **7**, which upon irradiation in cyclohexane solution smoothly decarbonylates to give dianthrylacetylene **19**. Precedence for the observed decarbonylation exists in the photochemistry of diphenylcyclopropenone and its derivatives.[21] In cyclohexane, the formation of dianthrylacetylene proceeds with a quantum yield of 0.14, but for preparative purposes, the low solubility of dianthrylcyclopropenone necessitates the use of other solvents such as toluene or methylene chloride where decreased decarbonylation quantum yields of 0.02 and 0.01, respectively, were measured. Nevertheless, compared to other syntheses of dianthrylacetylene,[22] photolysis of dianthrycyclopropenone in toluene appears to be the method of choice.



7 **19**

Emission Spectroscopic Properties of Dianthrylethylenes. For photoexcited *cis*-dianthrylethylene **1a**, the virtual absence of both fluorescence and chemical reactivity suggests that the intramolecular proximity of the anthracene π-systems enhances radiationless deactivation to the ground state. As for the parent trans isomer **2a**, its fluorescence at room temperature is associated with a remarkably large Stokes shift of about 10 000 cm^{-1}, which is indicative of the large differences between the molecular geometry of the ground state and that of the fluorescent excited singlet state. When geometrical changes of **2a** are impaired by increasing solvent viscosity, the Stokes shift of the **2a** fluorescence decreases markedly.[23]

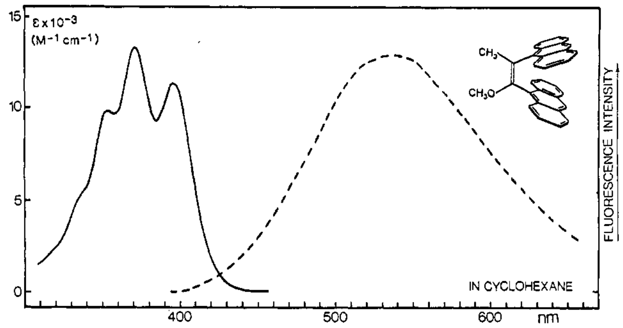


Figure 2. Absorption (solid line) and emission spectra (dashed line) of *cis*-1,2-di-9-anthrylethylene **1e**.

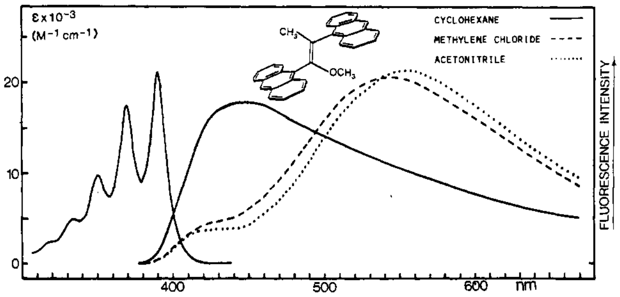


Figure 3. Absorption and emission spectra of *trans*-1,2-di-9-anthrylethylene **2e** in cyclohexane (solid line) and emission spectra in methylene chloride (dashed line) and acetonitrile (dotted line).

Monosubstituted *cis*-dianthrylethylenes **1b–d** in solution at room temperature were found to be nonfluorescent ($\Phi < 0.0001$). Disubstituted *cis*-dianthrylethylene **1e** in solution, by contrast, does fluoresce ($\Phi = 0.0018$, 0.0042, and 0.0064 in cyclohexane, methylene chloride, and acetonitrile, respectively). The fluorescence of **1e** (see Figure 2) is of particular interest in conjunction with the fairly high quantum yield of cyclomerization of **1e** discussed above. The molecular geometry[16] of **1e** suggests that the emission may originate from an intramolecular anthracene excimer, rather than from the locally excited anthracene fluorophore. The emission of **1e** is structureless, and is associated with a Stokes shift of about 6000 cm^{-1}. The nature of the solvent does not affect the Stokes shift.

Pertinent emission spectral data for the trans isomeric dianthrylethylenes are summarized in Table II. It is evident that the Stokes shift associated with the broad emission of substituted ethylenes decreases as the degree of substitution increases. Substitution of the ethylene double bond thus appears to have the same infringing

---

(20) Cf.: Hart, H.; Lin, L.-T. *Tetrahedron Lett.* **1985**, *26*, 575.

(21) Quinkert, G.; Opitz, K.; Wiersdorff, W. W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863. Cf. also: Quinkert, G. *Pure Appl. Chem.* **1964**, *9*, 607.

(22) Akiyama, S.; Nakasui, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2231.

(23) (a) Castel, N.; Fischer, E.; Bartocci, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1969. (b) Becker, H.-D.; Sandros, K.; Hansen, L. *J. Org. Chem.* **1981**, *46*, 821.

Table III. ^{1}H NMR Spectral Data (δ) of Dianthrylethylenes 1 and 2 in $CDCl_3$ (Chemical Shifts in ppm Downfield from Me_4Si)[a]

1/2	R	R′	Ar H	H-10/H-10′	R	R′
1a	H	H	8.21–7.02	8.05/8.05	8.03	8.03
2a	H	H	8.68–7.53	8.53/8.53	7.91	7.91
1b	H	CH_3O	8.39–7.00	8.01/7.91	>7.0	4.26
2b	H	CH_3O	8.75–7.47	8.59/8.45	6.49	3.21
1c	H	CHO	8.13–7.08	8.14/8.14	9.20	10.47
2c	H	CHO	8.63–7.54	8.55*/8.13*	8.16*	9.90
1d	H	CH_3OCO	8.14–7.00	8.03/8.00	9.37	3.81
2d	H	CH_3OCO	8.56–7.45	8.57*/7.88*	8.50*	3.16
1e	CH_3	CH_3O	8.47–7.06	7.88/7.80	2.69	3.48
2e	CH_3	CH_3O	8.75–7.52	8.60/8.47	1.74	2.99
1f	CH_3	OH	8.50–7.15	7.95/7.87	2.72	4.80
2f	CH_3	OH	8.71–7.54	8.59/8.57	1.84	4.68

[a] Assignments labeled with * may be interchangeable.

effect on the geometrical changes of photoexcited *trans*-dianthrylethylenes as has a solvent of high viscosity. Interestingly, the nature of the solvent markedly affects the Stokes shift in the case of methoxy-substituted *trans*-dianthrylethylenes. For the monosubstituted *trans*-dianthrylethylene **2b**, the Stokes shifts in cyclohexane ($\Phi = 0.0022$) and methylene chloride ($\Phi = 0.0009$) are 6600 and 7900 cm^{-1}, respectively. Similarly, for the disubstituted trans derivative **2e** in cyclohexane, methylene chloride, and acetonitrile the Stokes shifts are 3500, 7000, and 7700 cm^{-1}, respectively (see Figure 3). These fluorescence properties of **2e** are remarkable insofar as the broad emission in cyclohexane virtually extends through the entire visible spectral region. Moreover, the emission spectrum of **2e** in both methylene chloride and acetonitrile not only is characterized by the red-shifted maximum around 550 nm, but a residual low-intensity component is noticeable by a shoulder around 420 nm whose excitation spectrum agrees with the absorption spectrum of **2e**. Provided the short-wavelength contribution to the spectrum is not due to an impurity, the luminescence properties of *trans*-dianthrylethylene **2e** are reminiscent of the solvent-dependent fluorescence of 9,9′-bianthryl and related nonplanar bichromophoric compounds.[24] Thus, the short-wavelength component of the dual emission of **2e** could originate from the locally excited state, while the emission around 550 nm may be due to a twisted intramolecular charge-transfer (TICT) state. The highly structured absorption spectrum of **2e** indeed is indicative of large deviations from molecular planarity and lends support to this interpretation.

Conclusions. The spatial features of the molecular geometry of cis–trans isomeric dianthrylethylenes are borne out in their photochemical and photophysical properties. By appropriate substitution of the ethylene double bond, both the efficiency and the mode of photochemical intramolecular cycloadditions can be manipulated. The nature of the substituent on the ethylene double bond also may affect the excited-state chemistry of the anthracene chromophore, as the photochemical isomerization of carbonyl-substituted ethylenes, or the photoinduced H-shift of dianthrylethenol **2f** exemplify.

Experimental Section

Absorption and emission spectra were recorded on a Kontron Uvicon 810 and an Aminco SPF 500 (corrected spectra) spectrometer, respectively. ^{1}H NMR spectra were obtained in deuteriated chloroform with a Bruker 270 instrument. Chemical shifts (δ) are given in parts per million downfield from Me_4Si, and coupling constants (*J*) are given in Hz. ^{1}H NMR data of dianthrylethylenes 1 and 2 are summarized in Table III.[25] Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark, and Mikro Kemi AB, Uppsala, Sweden. Melting points (uncorrected) were taken on a hot-stage microscope.

Photochemical Experiments. Preparative-scale irradiations were performed under inert gas in a water-cooled Pyrex immersion well apparatus equipped with a cylindrical liquid filter arrangement of about 0.5-cm pathlength and by using a high-pressure mercury lamp (Philips HPK 125 W). The following filter solutions were employed: aqueous potassium nitrate (2 M), for wavelengths >333 nm; sodium nitrite (75 g) in water (100 mL) for wavelengths >400 nm; potassium chromate (380 mg) in water (100 mL) for wavelengths >420 nm.

Actinometric Experiments. Quantum yields of isomerization were determined in argon-purged solutions in an optical bench arrangement equipped with a 1000-W high-pressure xenon/mercury lamp, and a monochromator to select the 366-nm emission. The quantum yield data apply to conversions of <10%. The cyclization of 1,2-di-9-anthrylethane ($\Phi = 0.26$)[26] was used as actinometer. Fluorescence quantum yields are based on the fluorescence quantum yield of 9,10-diphenylanthracene ($\Phi = 0.83$).[27]

(*E*)-1,2-Di-9-anthryl-1-methoxyethene (1b). A. By Photochemical Isomerization of 2b. An argon-purged solution of **2b** (820 mg) in methylene chloride (170 mL) was irradiated for 1 h at 10 °C with light of wavelengths >400 nm. Vacuum evaporation of solvent gave a pale yellow crystalline residue, which was triturated with warm toluene (20 mL). The precipitate was removed by filtration and recrystallized from a boiling mixture of methylene chloride and toluene to give 370 mg of **1b** as pale yellow crystals, mp 243–245 °C. Flash chromatography of the combined mother liquors gave 180 mg of recovered **2b** and an additional 100 mg of **1b**. Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.53; H, 5.41.

B. By Isomerization of 2b on Aluminum Oxide. A saturated solution of **2b** (240 mg) in warm toluene was placed on a column of neutral aluminum oxide (2.5 × 40 cm) and "chromatographed" for 4 h with dry, freshly distilled toluene. The adsorbed substrate, which formed a broad (ca. 30 cm) greenish colored band, was subsequently eluted with ethyl acetate. Vacuum evaporation of solvent gave crude **1b** as a brownish crystalline residue, which was purified by column chromatography on silica gel/toluene (column dimensions 2.5 × 100 cm). The yield of **1b** was 110 mg (46%), mp 243–245 °C.

(*Z*)-1,2-Di-9-anthryl-1-methoxyethene (2b). Sodium methoxide (500 mg) was added to an argon-purged solution of dianthrylethanone **5** (420 mg) in DMF (40 mL) to give a deep purple colored reaction mixture. Addition of 20 drops of dimethyl

---

(24) Cf.: Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

(25) As noted previously in ref 1, cis–trans isomeric dianthrylethylenes 1 and 2 are distinguishable by their ^{1}H NMR spectra, in which the hydrogens on C-2/7 and C-3/6 of the cis isomers are shifted upfield due to shielding by the anthracene π-system. Cf. also: Geiger, J. H.; Mislow, K. *J. Org. Chem.* **1986**, *51*, 5471.

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

(27) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 103.

sulfate gave a light yellow colored suspension. After 10 min, the reaction mixture was slowly diluted with water (50 mL) to give first a clear yellow solution from which yellow crystalline **2b** precipitated. The precipitate was removed by filtration and purified by column chromatography on silica gel/toluene. Recrystallization from methylene chloride/hexane gave 420 mg (96%) of **2b**, mp 197–199 °C. Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.35; H, 5.41.

(*E*)-2,3-Di-9-anthrylpropen-1-al (1c). A rapidly stirred suspension of dianthrylcyclopropenone **7** (200 mg) and palladium on calcium carbonate (10%; 400 mg) in ethyl acetate (200 mL) was hydrogenated under ambient conditions for 24 h. Conventional workup of two identical experiments gave, after vacuum evaporation of solvent, a yellow solid residue. Subsequent column chromatography on silica gel/methylene chloride gave 278 mg of yellow crystalline material consisting mainly of a tetrahydro derivative of **1c** (^{1}H NMR analysis). The crude hydrogenation product was dissolved in methylene chloride (50 mL), DDQ (320 mg) was added, and the deep green reaction mixture was stirred for 16 h. Precipitated DD-hydroquinone was removed by filtration, and the filtrate was chromatographed on silica gel/methylene chloride to give 112 mg of yellow crystals. They were recrystallized from methylene chloride by addition of hexane: yield, 75 mg (19%) of **1c** as yellow crystals, mp 275–280 °C. High-resolution mass spectrum, *m/z* calcd for $C_{31}H_{20}O$ 408.1515, found 408.150. IR (KBr) 1688 cm^{-1} (C=O).

(*Z*)-2,3-Di-9-anthrylpropen-1-al (2c). A slution of **1c** (30 mg) in methylene chloride (150 mL) was irradiated with light of wavelengths >400 nm. After 1 h, when the photostationary state was established, the reaction was terminated. Workup of three identical experiments by vacuum evaporation of solvent and subsequent column chromatography on silica gel/methylene chloride gave (in addition to recovered **1c**) 6 mg of **2c** as yellow flaky crystals (from methylene chloride/methanol), which melt around 280 °C. High-resolution mass spectrum, *m/z* calcd for $C_{31}H_{20}O$, 408.1515, found 408.1514.

(*E*)- and (*Z*)-Methyl 2,3-Di-9-anthrylacrylate (1d and 2d). Sodium methoxide (500 mg) was added to a stirred suspension of dianthrylcyclopropenone **7** (500 mg) in DMF (50 mL) and methanol (10 mL). The reaction mixture was warmed to 50 °C to give, after 10 min, a clear solution. After 15 min, the solution was cooled to room temperature, diluted with water (100 mL), and extracted with ether (200 mL). The ether layer was washed with water (2 × 50 mL) and dried over sodium sulfate. Vacuum evaporation of solvent gave a solid yellow residue, which was dissolved in methylene chloride (75 mL). Partial removal of solvent to a volume of about 30 mL, followed by addition of methanol and slow crystallization from the warm solution gave 340 mg (63%) of **1d** as yellow crystals, mp 285 °C. The mother liquor was chromatographed on silica gel/methylene chloride to give 102 mg (19%) of **2d** as yellow cubic crystals, mp 208–211 °C. Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.07. Found for **1d**: C, 87.26; H, 5.05. Found for **2d**: C, 87.42; H, 5.05.

(*E*)-1,2-Di-9-anthryl-1-methoxypropene (1e). Methyl iodide (0.5 mL) was added dropwise to an argon-agitated purple-colored solution of dianthrylpropanone **6** (350 mg) and potassium *tert*-butoxide (400 mg). Addition of water (50 mL) to the "decolorized" reaction mixture gave a yellow crystalline precipitate that was removed by filtration and dried. The precipitate (370 mg) was dissolved in hot methylene chloride (25 mL). Hexane (ca. 30 mL) was added to the solution, and methylene chloride was boiled off to give a yellow crystalline precipitate, which was removed from the hot solution by suction filtration. (From the hexane filtrate, 60 mg (16%) of almost colorless **2e** precipitated at room temperature.) The yield of precipitated lemon-yellow **1e** was 240 mg (66%), mp 335–340 °C. Anal. Calcd for $C_{32}H_{24}O$: C, 90.52; H, 5.71. Found: C, 90.59; H, 5.71.

(*Z*)-1,2-Di-9-anthryl-1-methoxypropene (2e). *trans*-Enol **2f** (120 mg) was added to an argon-agitated solution of potassium *tert*-butoxide (120 mg) in DMF (6 mL) to give a deep purple solution. Upon dropwise addition of methyl iodide (ca. 0.5 mL) the color was discharged. Addition of water (3 mL) and methanol (3 mL) gave a colorless crystalline precipitate. It was removed by filtration and chromatographed on silica gel/toluene (column dimensions 2.5 × 30 cm). Recrystallization of **2e** from methylene chloride/hexane gave 100 mg (81%) of almost colorless crystals, mp 300–303 °C. Anal. Calcd for $C_{32}H_{24}O$: C, 90.52; H, 5.71. Found: C, 90.51;, H, 5.72.

(*E*)-1,2-Di-9-anthryl-1-hydroxypropene (1f). The deep purple colored solution of dianthrylpropanone **6** (140 mg) and potassium *tert*-butoxide (140 mg) in DMF (5 mL) was agitated with a stream of nitrogen for 3 min. Dropwise addition of water (6 mL) gave a yellow crystalline precipitate, which was washed with water and dried. The yield was 110 mg (79%). ^{1}H NMR analysis (cf. Table III) revealed the **1f**/**2f** ratio to be 64:36. The mixture was used in the following experiment for the preparation of **2f**.

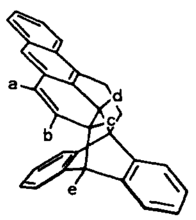
(*Z*)-1,2-Di-9-anthryl-1-hydroxypropene (2f). A. By Acid-Catalyzed Isomerization of 1f. The precipitated **1f**/**2f** mixture obtained in the experiment described above was dissolved in methylene chloride (20 mL) to which some HCl vapor was added (vapor above concentrated aqueous HCl; pipet). Partial evaporation of solvent, followed by dilution of the reaction mixture with toluene (3 mL) gave **2f** (80 mg; 57% yield) as an almost colorless crystalline precipitate, mp 316–318 °C. Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.29; H, 5.41.

B. By Isomerization of Dianthrylpropanone 6 with Sodium Borohydride. A solution of **6** (100 mg) and sodium borohydride (100 mg) in a mixture of methylene chloride (5 mL) and methanol (10 mL) was refluxed for 24 h to give a colorless crystalline precipitate, which was removed by filtration. According to TLC (silica gel/toluene), the precipitate (90 mg) consisted of enol **2f**, which was contaminated with ketone **6**. The precipitate was recrystallized by dissolving it in boiling methylene chloride containing hydrogen chloride gas, adding toluene, and boiling off the methylene chloride. Final purification was accomplished by column chromatography on silica gel/toluene to give 65 mg of **2f** as almost colorless crystals, identical according to ^{1}H NMR with the enol prepared as described above.

1,2-Di-9-anthrylpropanone (6). A solution of 1,2-dianthrylethanone **5** (500 mg) and methyl iodide (10 mL) in methylene chloride (100 mL), placed in a 250-mL separatory funnel, was purged with argon. To this solution were added a solution of potassium hydroxide (10 g) in water (20 mL) and 0.3 mL of phase-transfer catalyst Basacrylsalz AN. (Basacrylsalz AN, obtained from BASF AG Ludwigshafen, Germany, is a mixture of dibenzyldimethylammonium chloride (35%), trimethylbenzylammonium chloride (15%), methanol (5%), ethylene glycol (5%), and water (40%).) The mixture was shaken to give a red-colored methylene chloride layer. After 20 min, additional phase-transfer catalyst (0.4 mL) was added, and the reaction mixture was shaken for 1 h until no more red coloration of the organic layer was detectable. TLC (silica gel/toluene) revealed complete consumption of **5**, as well as the formation of **6** and **2b**. Conventional workup, followed by vacuum evaporation of part of the solvent gave a pale yellow, saturated residual solution. This solution was passed through a column of silica gel/methylene chloride. By this procedure, the "phase-transfer iodide" was retained on the column, while the mixture of alkylation products **2b** and **6** was eluted with methylene chloride. Their separation was accomplished by subsequent flash chromatography on silica gel/toluene. The yield of **2b** was 190 mg (36%), and the yield of ketone **6** was 300 mg (58%), mp 188–190 °C. ^{1}H NMR (at −40 °C) 8.92 (d, *J* = 9 Hz, 1), 8.15–6.61 (m, 17), 6.26 (q, *J* = 6.9 Hz, 1), 2.14 (d, 3). Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.81; H, 5.43.

2,3-Bis-9-anthrylcyclopropenone (7).[9] Tetrachlorocyclopropene[10] (1 g) was added to a suspension of aluminum chloride (750 mg) in dry 1,2-dichloroethane (12 mL). The reaction mixture was stirred at room temperature for 30 min to give a pale brownish suspension. The suspension was then cooled to −30 °C, and anthracene (2 g) was added. Over a period of 1 h, the deep violet colored reaction mixture was allowed to warm up to 0 °C, and stirring was continued at that temperature for 2 h. The reaction mixture was then poured into ice–water. Addition of ether gave an orange-red suspension of **7** in the organic layer. The organic layer was separated, part of the solvent was evaporated in vacuo, and the precipitate was removed by filtration. Recrystallization of crude **7** was accomplished by way of Soxhlet extraction with methylene chloride. The yield was 1.63 g (71%), and the mp was about 284 °C dec (lit.[9] mp >300 °C). ^{1}H NMR 8.73 (s, 2), 8.41–7.35 (m, 16). UV (in methylene chloride) λ_{max} ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1}) 465

Chart I



	H_a	H_b	H_c
δ	6.23 (dd)	5.84 (dd)	3.08 (m)
J, Hz	ab, 9.8; ac, 2.4	ab; bc, 3.7	ac; bc; cd; ce

	H_d	H_e	OMe
δ	3.76 (d)	4.28 (d)	4.21 (s)
J, Hz	cd, 12.2	ce, 1.9	

(17.6), 395 (8.7), 374 (9.0), 355 (5.4), 259 (98), 249 nm (128).

Enolization and Methylation of the [4 + 4] Photocyclomer 9 To Give 8. Sodium methoxide (70 mg) was added to a nitrogen-purged solution of 9 (70 mg) in DMF (7 mL). The light-purple color of the solution was discharged upon dropwise addition of dimethyl sulfate. Addition of water (15 mL) gave a pale yellow crystalline precipitate. It was removed by filtration and recrystallized from methylene chloride solution by precipitation with hexane to give 65 mg (90%) of 8 as colorless needle-shaped crystals, mp 220–240 °C dec ^1H NMR 7.00–6.79 (m, 16), 5.53 (s, 1), 4.54 (s, 2), 4.11 (s, 3). Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.40; H, 5.41.

Photochemical Isomerization of 1b To Give 8. A. Irradiation with Light of Wavelengths >330 nm. A solution of 1b (20 mg) in toluene (120 mL) was irradiated for 4 h at 10 °C under argon with light of wavelengths >330 nm. Vacuum evaporation of solvent from the colorless solution gave a crystalline residue. ^1H NMR analysis revealed complete conversion of 1b into 8. Workup of three identical experiments gave 55 mg (92%) of 8 as colorless, needle-shaped crystals (from methylene chloride/hexane), mp 220–240 °C dec, identical (^1H NMR) with the compound described in the preceding experiment.

B. Irradiation of 1b with Light of Wavelengths >400 nm To Give 8 and 10a. A solution of 1b (10 mg) in toluene (120 mL) was irradiated at 10 °C under argon for 8 h with light of wavelengths >400 nm. Vacuum evaporation of solvent gave a solid pale yellow residue. It was analyzed ^1H NMR and found to consist of 1b (6%), 2b (2%), 8 (72%), and 10a (19%). The structure of 10a is deduced from the following chemical shift data. Proton denotation is as shown in the structure in Chart I.

Photochemical Isomerization of 1e To Give 11. A solution of 1e (70 mg) in methylene chloride (150 mL) under argon was irradiated with light of wavelengths >400 nm at 15 °C for 10 min to give a colorless solution. Vacuum evaporation of solvent gave a colorless crystalline residue. It was recrystallized from methylene chloride by addition of ethanol to give 65 mg (93%) of 11 as colorless crystals, which turn yellow upon heating to 240–250 °C and which melt around 330 °C. ^1H NMR 7.00–6.79 (m, 16), 4.52 (d, J = 11 Hz, 1), 4.47 (d, J = 11 Hz, 1), 4.22 (s, 3), 2.35 (s, 3). Anal. Calcd for $C_{32}H_{24}O$: C, 90.52; H, 5.71. Found: C, 90.51; H, 5.75.

Photochemical Isomerization of 1d To Give 12a. A solution of 1d (50 mg) in toluene (150 mL) was irradiated for 16 h at 10 °C with light of wavelengths >400 nm. UV spectral analysis indicated 95% consumption of 1d. Vacuum evaporation of solvent gave an oily residue, which crystallized upon treatment with ether/pentane. Recrystallization from methylene chloride by precipitation with methanol gave 40 mg (80%) of 12a as colorless crystals, mp around 220 °C dec (final mp 282–284 °C is that of 1d). Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.07. Found: C, 87.19; H, 5.05. ^1H NMR (of 12a) 8.10 (s, 1e, 7.70–6.65 (m, 13), 6.28 (dd, H_a), 5.90 (dd, H_b), 4.26 (d, H_e), 3.67 (d, H_d), 3.12 (m, H_c), 3.94 (s, 3). Coupling constants (Hz) are as follows (proton denotation is as shown above for 10a).

J				
ab	ac	bc	cd	ce
9.8	2.1	4.3	12	1.6

Photochemical Isomerization of Enol 2f To Give 14a. A solution of 2f (30 mg) in methylene chloride (150 mL) was irradiated under argon at 14 °C with wavelengths >400 nm for 40 min. Vacuum evaporation of solvent gave a pale yellow residue which crystallized upon addition of little ether. The residue was chromatographed on silica gel/toluene to give 25 mg (83%) of 14a as yellow crystals, mp 199–200 °C. ^1H NMR 8.41 (s, H-10), 7.93 (d, J = 8 Hz, 2), 8.66 (m, 2), 7.40–7.19 (m, 12), 5.90 (br s, 1, benzylic H), 5.28 (s, 1, 5.25 (d, J = 1.3 Hz, 1), 4.06 (d, J = 18 Hz, 1), 394 (d, J = 18 Hz, 1). Pertinent ^{13}C NMR data: 35.71 (CH_2), 46.22 (CH), 151.03 (C=), 201.30 (CO). Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.56; H, 5.42.

Reduction of 14a with Sodium Borohydride To Give Enol 15a. Sodium borohydride (20 mg) was added to a solution of 14a (60 mg) in a mixture of methylene chloride (10 mL) and methanol (10 mL). After 10 min, the methylene chloride and part of the methanol were removed by vacuum evaporation at about 30 °C, and the remaining solution was diluted with water (10 mL) to give a colorless crystalline precipitate. It was removed by filtration and dried (in methylene chloride/magnesium sulfate). According to ^1H NMR, the crude reduction product consisted of enol 15a (92%) and its ketone 16 (10%). Recrystallization from methylene chloride/*n*-hexane solution gave pure enol 15a (20 mg) as colorless needle-shaped crystals which melt between 195 and 205 °C. (Column chromatography of 15a on silica gel/methylene chloride results in partial isomerization to 16.) ^1H NMR 8.47 (s, H-10), 8.23–7.27 (m, 16), 6.25 (s, 1 benzylic H), 4.26 (d, J = 19 Hz, 1), 4.06 (d, J = 19 Hz, 1), 4.10 (s, OH), 0.87 (s, methyl). Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found, C, 89.9; H, 5.9.

Methylation of Enol 15a To Give 15b. Dimethyl sulfate (4 drops) was added to a stirred mixture of a solution of 15a (10 mg) in methylene chloride (5 mL) and a solution of sodium hydroxide (200 mg) and PT catalyst Basacrylsalz AN (3 drops) in water (1 mL). The reddish organic solution decolorized, and conventional workup after 5 min, followed by column chromatography on silica gel/methylene chloride in order to separate small amounts of ketone 16, gave enol methyl ether 15b as colorless crystals, mp 215–217 °C. ^1H NMR 8.46 (s, H-10), 8.24–7.24 (m, 16), 6.26 (s, 1 benzylic H), 4.23 (d, J = 19 Hz, 1), 4.04 (d, J = 19 Hz, 1), 3.30 (s, methoxy), 0.82 (s, methyl).

Acid-Catalyzed Ketonization of 15a To Give 16. The mother liquor obtained in the experiment leading to 15a was evaporated to dryness, and the residue was dissolved in methylene chloride (10 mL) containing three drops of concentrated hydrochloric acid. After about 2.5 h, TLC analysis revealed almost complete conversion of 15a into 16. Vacuum evaporation of solvent gave a pale yellow oily residue, which gave colorless crystals upon treatment with a little ether. Recrystallization from methylene chloride/*n*-hexane gave 25 mg of 16, mp 178–180 °C. The room temperature ^1H NMR spectrum is characterized by several very broad signals, indicative of hindered rotations. Therefore, the spectrum was recorded at −50 °C: 8.47 (s, H-10), 8.02–7.16 (m, 14), 6.96 ("t", 1), 6.14 (d, 1), 4.89 (d, J = 10.8 Hz, 1 benzylic H), 4.10 (d, J = 18 Hz, 1), 3.96 (d, J = 18 Hz, 1), 3.57 (m, J = 10.8, 7 Hz, 1 methine H), 0.99 (d, J = 7 Hz, methyl). Pertinent ^{13}C data: 211.0 (CO), 52.2, 47.9, 36.1, 17.6 (aliphatic

Chart II

	H_a	H_b	H_c	H_d	H_e	CMe	CH
18a, δ	6.25 (dd)	5.93 (dd)	3.10 (m)	3.65 (d)	4.23 (d)	2.07 (d)	3.93 (q)
J, Hz	ab, 9.8; ac, 2.0	ab; bc, 4.4	ac; bc; cd; ce;	cd, 11.2	ce, 1.2	7.0	7.0
18b, δ	6.26 (dd)	5.88 (dd)	3.30 (m)	4.17 (d)	4.34 (d)	1.74 (d)	4.67 (q)
J, Hz	ab, 9.9; ac, 2.2	ab; bc, 3.8	ac; bc; cd; ce;	cd, 11.7	ce, 1.9	7.8	7.8

C). Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 90.3; H, 6.0.

Photochemical Isomerization of Dianthrylpropanone 6 To Give 17 and 18. A. By Direct Excitation. A solution of **6** (50 mg) in methylene chloride (150 mL) at 14 °C under argon was irradiated with wavelengths >400 nm for 30 min. Vacuum evaporation of solvent gave a colorless crystalline residue, which was analyzed by ^1H NMR and found to consist of the [4 + 4] cyclomer **17** and two isomeric [4 + 2] cyclomers, **18a** and **18b**, in an approximate ratio of 8:1:1. Recrystallization of the crude residue from boiling methylene chloride solution by precipitation with hexane gave the [4 + 4] cyclomer **17** as a colorless crystalline precipitate, which was washed with ether. The crystals turn yellow at about 200 °C, and they melt (dec) around 275–290 °C. ^1H NMR (of **17**) 7.31–6.76 (m, 16), 4.65 (q, J = 7.4 Hz, 1), 4.59 (d, J = 11.3 Hz, 1), 4.54 (d, J = 11.3 Hz, 1), 1.89 (d, J = 7.4 Hz, 3). Anal. Calcd for $C_{31}H_{22}O$: C, 90.39; H, 5.41. Found: C, 90.40; H, 5.41.

B. Biacetyl-Sensitized Isomerization of 6 To Give 18. A solution of **6** (20 mg) and biacetyl (800 mg) in benzene (120 mL) was irradiated under argon at 10 °C with light of wavelengths >420 nm. In order to retain **6** at low concentration, three additional 20-mg portions of **6** were added in 20-min intervals. After a total irradiation time of 80 min, the solvent was removed by vacuum evaporation. The oily residue thus obtained was analyzed by ^1H NMR and found to consist of **17**, **18a**, and **18b** in an approximate ratio of 3:10:7. The residue crystallized upon treatment with ether. Two recrystallizations from a boiling methylene chloride/methanol mixture gave 30 mg of **18a** as colorless crystals (mp 230–233 °C). Anal. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.67; H, 5.35. The combined mother liquors of **18a** were chromatographed on silica gel/toluene. ^1H NMR analysis revealed the eluate to consist of a mixture of **17** (13%), **18a** (8%), and **18b** (79%). Isomers **18a** and **18b** are characterized and distinguishable by the ^1H NMR data in Chart II (proton denotation is as shown above for 10a).

Photolysis of Dianthrylcyclopropenone 7 To Give 1,2-Di-9-anthrylacetylene (19). A solution of **7** (100 mg) in toluene (180 mL) under argon was irradiated at 30 °C for 30 min. Vacuum evaporation of solvent gave an orange-red crystalline residue, which was suspended in a little methylene chloride. Filtration gave 90 mg (97%) of **19** as orange-red, needle-shaped crystals, mp >350 °C. Both the color and the melting point of **19** deserve comment. When **19** was first prepared by a Wittig-type reaction, it was found to form orange-red crystals (from benzene) which decomposed around 310 °C.[22] We have previously prepared **19** by photolysis of **7** in methylene chloride and obtained needle-shaped orange-red crystals (mp >350 °C) by slow recrystallization from methylene chloride at room temperature. Acetylene **19** obtained in this fashion was used in an X-ray diffraction analysis.[28] We now find that recrystallization of **19** from a stirred hot methylene chloride solution gives a "cubic" modification of lemon-yellow crystals which melt around 325 °C. ^1H NMR 8.92 (d, J = 8.6 Hz, 4), 8.52 (s, 2), 8.09 (d, J = 8.8 Hz, 4), 7.68–7.54 (m, 8).

Acknowledgment. We are gratefully indebted to Mr. Gunnar Svensson for technical assistance, to Dr. Kjell Ankner of Hässle AB, Mölndal, for running the ^{13}C spectrum of **14a**, and to Dr. Bernd Ruge of BASF AG, Ludwigshafen, West Germany, for providing the phase-transfer catalyst.

Registry No. **1a**, 3162-57-0; **1b**, 110373-64-3; **1c**, 110373-66-5; **1c** (tetrahydro deriv), 110373-85-8; **1d**, 110373-68-7; **1e**, 110373-70-1; **1f**, 110373-72-3; **2a**, 3849-11-4; **2b**, 110373-65-4; **2c**, 110373-67-6; **2d**, 110373-69-8; **2e**, 110373-71-2; **2f**, 110373-73-4; **5**, 102725-05-3; **6**, 110373-74-5; **7**, 78594-10-2; **8**, 110373-75-6; **9**, 102725-09-7; **10a**, 110373-76-7; **11**, 110373-77-8; **12a**, 110373-78-9; **14a**, 110373-79-0; **15a**, 110373-80-3; **15b**, 110373-82-5; **16**, 110373-81-4; **17**, 110391-23-6; **18a**, 110373-83-6; **18b**, 110391-24-7; **19**, 20199-19-3; tetrachlorocyclopropene, 6262-42-6; anthracene, 120-12-7.

---

(28) Becker, H.-D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1567.

Electrophilic Additions to Alkynyl Tosylates. Formation of Vinyl 1,1-(Bis esters) and Related Compounds. X-ray Structure Determination of (*E*)-1-Chloro-1-(tosyloxy)-3,3-dimethyl-1-butene[†]

Peter J. Stang* and Kenneth A. Roberts[1]

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

Received May 4, 1987

The reaction of alkynyl tosylates, $RC\equiv COTs$, R = *t*-Bu, *sec*-Bu, with a variety of electrophiles, HCl, CF_3COOH, CF_3SO_3H, $ArSO_3H$, and H_3O^+, in CH_2Cl_2 is reported. Only regio- and stereospecific syn-monoaddition products were observed, yielding vinyl 1,1-(bis esters) and related compounds in good yields. The single-crystal X-ray data of the HCl adduct to $t\text{-}BuC\equiv COTs$ is reported. These results and their mechanistic implications are discussed.

Electrophilic addition to alkynes is an important, well-established reaction in synthesis and industrial processes.[2] A variety of alkynes readily add diverse electrophiles under differing reaction conditions. Acid addition and acid-catalyzed hydration of functionalized alkynes, due to the resulting regio- and stereochemistry and the formation of highly functionalized alkynes, are particularly valuable and interesting.[2]

Recently, we reported[3] the preparation of previously unknown alkynyl tosylates and mesylates. As part of our ongoing studies[4] on the reactions of these novel acetylenic

---

[†] Dedicated to Professor George A. Olah on the occasion of his 60th birthday.

(1) Abstracted in part from the Ph.D. Dissertation of K. A. Roberts, The University of Utah, 1988.

(2) Viehe, H. G. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969. De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*; Elsevier: Amsterdam, 1982. Patai, S. *The Chemistry of the Carbon-Carbon Triple Bond*; Wiley: New York, 1978.

(3) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. Stang, P. J.; Surber, B. W. *Ibid.* **1985**, *107*, 1452.

0022-3263/87/1952-5213$01.50/0 © 1987 American Chemical Society