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PHOTOCHEMISTRY OF THE ANTHRACENE CHROMOPHORE: NOVEL ISOMERIZATION OF 1-(9-ANTHRYL)-2-BENZOYLETHYLENES

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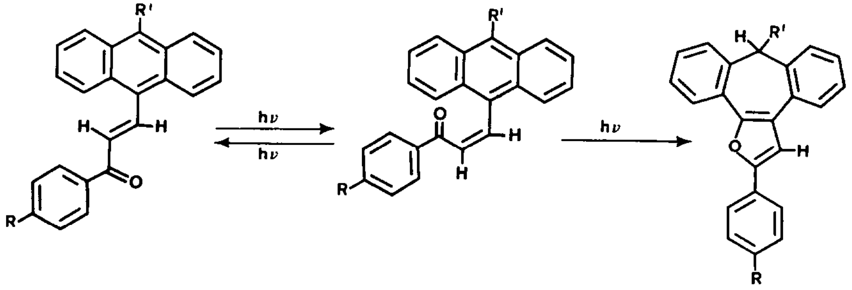
Abstract: Photoexcited cis-1-(9-anthryl)2-benzoylethylenes undergo a novel type of isomerization by skeletal rearrangement to give furano-annelated 5H-dibenzo[a,d]cycloheptenes.

The photochemistry of the anthracene chromophore is characterized by cycloadditions in which the central ring represents a 4π electron system or, more rarely, one of the lateral rings reacts as a diene or dienophile.[1] 9-Anthrylalkenes upon photoexcitation may undergo geometrical isomerization of the alkene moiety, but quantum yields of the cis-trans-isomerization vary greatly. Neither cis-9-(β-styryl)anthracene nor cis-1,2-di(9-anthryl)ethylene are accessible by photochemical isomerization of their trans-isomers, but trans-1-(9-anthryl)-2-benzoylethylene (1a) isomerizes upon irradiation to give the cis-isomer 2a.[2] We have now found that photoexcited cis-1-(9-anthryl)-2-benzoylethylenes 2, in a reaction competing with cis-trans isomerization, undergo a skeletal transformation into furano-annelated 5H-dibenzo[a,d]cycloheptenes 3.



1 2 3

1-3	R	R'
a	H	H
b	CH_3O	H
c	CH_3CO	H
d	C_6H_5	H
e	H	C_6H_5

Irradiation of 1a (50 mg) in ethyl acetate (175 mL) under argon for 3 h (125 W high-pressure Hg lamp, immersion well apparatus equipped with a 330 nm cut-off filter, 18 °C) results in the formation and subsequent disappearance of 2a. Work-up of the virtually colorless solution by vacuum evaporation of solvent, followed by column chromatography on silica gel/methylene chloride gives 3a in 80% yield as colorless crystals. Substituted 1-(9-anthryl)-2-benzoylethylenes 1b-1e isomerize upon irradiation in solution in the same way as described for 1a, and they give the substituted photoproducts 3b - 3e which are easily detected by virtue of their blue fluorescence (see Table 1).

Table 1. Photochemical Conversion of 1 into 3 [a)]

	R	R'	mg	cut-off filter	irr. time	product (yield)	mp °C	Fluorescence quantum yield [d)]
1a,	H	H	50	330 nm [b)]	3 h	3a (80%)	136-139	0.47
1b,	CH_3O	H	50	330 nm [b)]	3 h	3b (67%)	124-128	0.47
1c,	CH_3CO	H	100	400 nm [c)]	7 h	3c (60%)	139-144	0.0025
1d,	C_6H_5	H	100	Pyrex	6 h	3d (76%)	190-194	0.56
1e,	H	C_6H_5	100	Pyrex	7 h	3e (92%)	175-178	0.45

a) in 175 mL of ethyl acetate. b) 1 M aqueous solution of potassium nitrate. c) potassium nitrite (150 g) in water (200 mL). d) in cyclohexane.

The assignment of structure 3 rests on the spectroscopic properties of the photoproducts. Their high-resolution mass spectra confirm them to be isomers of 1. In their ^{13}C-NMR spectra, two singlets at δ 150 and 153 ppm are typical of C-2 and C-5 in furans (cf. Table 2). ^{1}H-NMR data are summarized in Table 3. The sharp singlet at δ 3.8 ppm due to the methylene protons in 3a - 3d is transformed at -65 °C into an AB spectrum (J_{AB}=14Hz), as is in agreement with the conformational mobility of 7-membered carbocycles.[3] The axial position of the phenyl group at the sp^3 carbon in 3e is associated with shielding by the benzo moieties, as is deduced from the upfield shift of two multiplets (3H:2H).

Table 2. Selected ^{13}C-NMR Data of 3a-3c

3	C-O-C	=CH	CH_2	R
a	153.3; 149.7	105.7	41.7	-
b	153.7; 149.0	104.3	41.9	55.4
c	152.1; 151.0	108.1	41.8	197.0;26.5

Table 3. ^{1}H-NMR Data of 3a-3e

3	arom H	=CH	CH_2	R
a	7.88-7.29	7.15	3.84	
b	7.82-6.97	7.02	3.83	3.87
c	8.06-7.25	7.29	3.84	2.64
d	7.94-7.29	7.18	3.85	arom
e	7.94-6.62	6.94	(CHR': 5.45)	

all spectra in deuterated chloroform;
chemical shifts in δ ppm downfield from TMS

The electronic absorption spectra of photoproducts 3a, 3b, and 3e (Fig. 1) closely resemble that of tetraphenylfuran. The enhanced absorption of 3d may reflect the extended conjugation, and the large bathochromic shift of the spectrum of 3c is explicable by resonance contributions of structure 3c'. The exceptionally low fluorescence yield (0.0025; cf.Table 1) of "acetophenone" 3c probably reflects enhanced intersystem crossing to the triplet state.

Mechanism studies were carried out with 1a in degassed benzene by measuring the absorption spectral changes during the irradiation, and by monitoring the appearance of 3a by emission spectroscopy, to reveal the following.

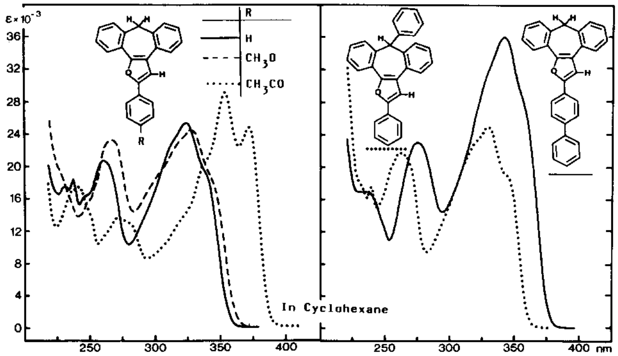
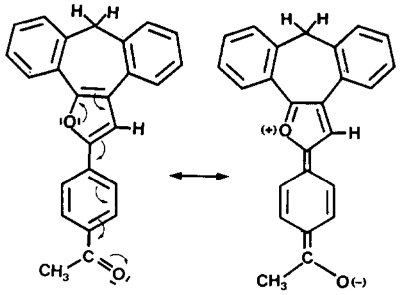


Fig.1. Electron Spectra of 3a - 3e



3c

3c'

The rate of formation of 3a is found to be negligibly low at the beginning of the irradiation when virtually all light is absorbed by the trans-isomer. As the concentration of the cis-isomer 2a increases, the rate of formation of 3a increases. After the photostationary state of the cis-trans isomerization has been established, the rate of formation of 3a becomes constant, and the set of reaction spectra exhibits an isosbestic point (see Fig.2). Therefore, we conclude, 3a is formed predominantly, or exclusively, by photoexcitation of the cis-isomer. The quantum yield of formation of 2a from its trans-isomer 1a is 0.28. Photoexcited 2a isomerizes to reform 1a with a quantum yield of 0.10, and it isomerizes to give 3a with a quantum yield of 8×10^{-4}.[4] Neither the rate of formation of 2a from photoexcited 1a, nor the rate of formation of 3a from photoexcited 2a are noticeably affected by molecular oxygen.[5] Apparently, both isomerizations proceed from the excited singlet state.

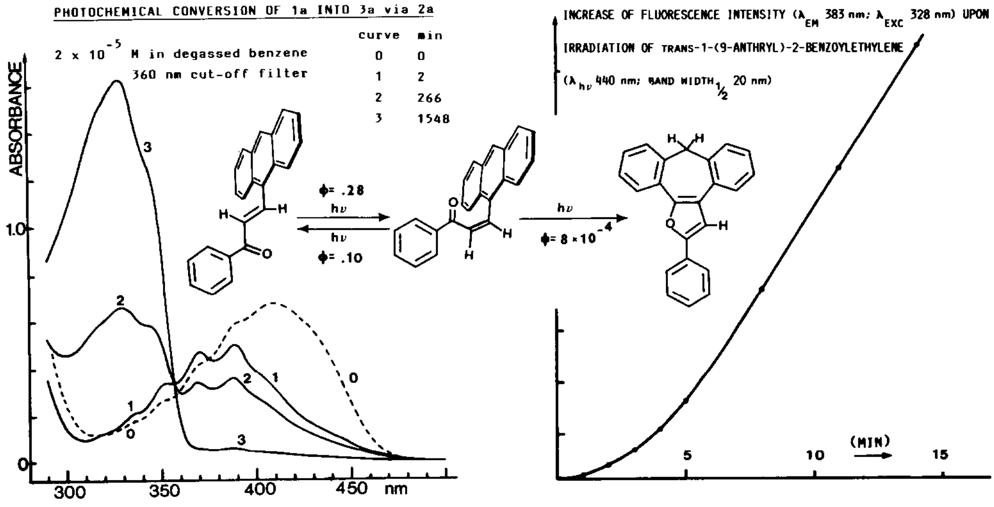
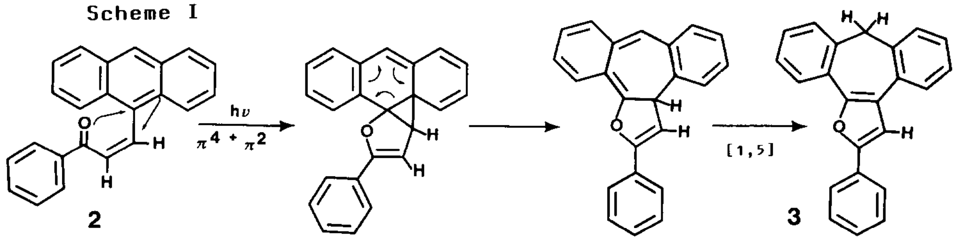


Fig.2. Absorption and Emission Spectroscopic Detection of 3a.

The conversion of cis-1-(9-anthryl)-2-benzoylethylenes into furano-annelated 5H-dibenzo[a,d]cycloheptenes is a transformation without precedence in both anthracene and enone photochemistry. We rationalize the formation of 3 by a reaction sequence which begins with a 4 + 2 cycloaddition involving the photoexcited conjugated "dienone" 2 (Scheme I).[6] The subsequent steps leading to 3 are straightforward. There are examples in ground state carbene chemistry for the formation of 5H-dibenzo[a,d]cycloheptenes from anthracene.[7]

Scheme I



The molecular geometry of 2 probably plays an important role in the photochemical conversion into 3. Inspection of molecular models suggests that the plane of the anthracene and that of the ene form an angle of about 80 degrees[8] and, significantly, the cis-enone undergoing the photoreaction exists in the s-cis conformation. This means that the distance between the carbonyl oxygen and the reacting 9-position of the anthracene presumably is not larger than 3 Å, and the conversion of photoexcited 2 into 3 is geometrically facilitated.

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(3) From the coalescence temperature of 238 K, the activation energy associated with the folding process was calculated to be 11 kcal/mol, (cf. Kost, D.; Carlson, E. H.; Raban, M. Chem. Comm. **1971**, 656). For the parent 5H-dibenzo[a,d]cycloheptene, an activation energy of 9.2 kcal/mol has been found: Hales, N .J.; Smith, D. J. H.; Swindles, M. E. Chem. Comm. **1976**, 981. Cf. also Tochtermann, W. Fortschr. Chem. Forsch. **1970**, 15, 378.

(4) Quantum yield measurements are based on the K-ferrioxalate actinometer.

(5) Molecular oxygen does react with photoexcited 3.

(6) The formation of the 4 + 2 cycloaddition product may be described to involve biradical intermediates. Cf. the photochemical isomerizations of 2,4-dienones and α,β,δ,ε-unsaturated carbonyl compounds which give α-pyrans and dihydropyrans, respectively: a) Büchi, G.; Yang, N. C. J. Am. Chem. Soc. **1957**, 79, 2318. b) Schneider, R. A.; Meinwald, J. J. Am. Chem. Soc. **1967**, 89, 2023.

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(8) The corresponding angle in cis-9-(β-styryl)anthracene is 78.4 degrees: Becker, H.-D.; Patrick, V. A.; White, A. H. Aust. J. Chem. **1984**, 37, 2215.

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