Tetrahedron Letters,Vol.30,No.16,pp 2137-2140,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

FORMATION AND PHOTOCHEMICAL REARRANGEMENT OF CARBON-OXYGEN-LINKED ANTHRACENES

Hans-Dieter Becker*,[a] Eva Hammarberg,[a] Brian W. Skelton,[b] and Allan H. White[b]

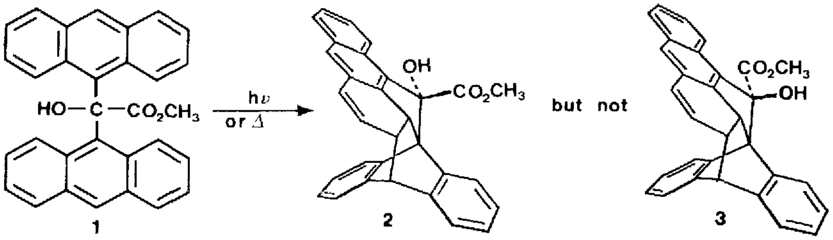
a: Department of Organic Chemistry, Chalmers University of Technology
and University of Gothenburg, S-412 96 Gothenburg, Sweden

b: Department of Physical and Inorganic Chemistry, The University of Western Australia,
Nedlands, Western Australia 6009

Abstract: Alkyl esters of 9-anthrilic acid isomerize both thermally and photochemically by stereoselective Diels-Alder reaction, while treatment with base induces the shift of 9-anthryl from carbon to oxygen. Photoexcitation of carbon-oxygen-linked bichromophoric anthracenes results in a migratory 9-anthryloxy - 9-anthronyl rearrangement.

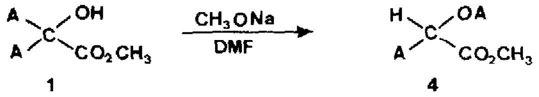
Photoexcited anthracene derivatives typically dimerize in their excited singlet state by 4π+4π cycloadditions which involve the diene moiety of the central ring, though other modes of cyclomerization have been found in recent years.[1-3] As for methano- and ethano-linked bichromophoric anthracenes, their isomerizations involving the excited triplet state tend to proceed as Diels-Alder reactions, in which a lateral ring of the anthracene π-system participates as dienophile, and quantum yields usually are << 0.01.[4,5]

We have now found that photoexcited alkyl esters of 9-anthrilic acid[6] isomerize in solution by stereoselective 4π+2π cycloadditions for which quantum yields are as high as 0.45. When a solution of 1 (200 mg) in toluene (125 mL) was irradiated for 10 min with light of wavelengths > 400 nm,[7] the Diels-Alder product 2 (colorless crystals, mp 290-294 °C) was formed, virtually quantitatively, and we have found no evidence for the formation of stereoisomer 3. Numerous other alkyl anthrilates (e.g. ethyl, propyl, butyl) were found to react in the same fashion. Molecular oxygen does not affect the quantum yields, so we presume that the cycloadditions proceed in the excited singlet state.



Alkyl 9-anthrilate 1 also isomerizes smoothly upon melting (~200 °C) to give cycloadduct 2. It is possible that the high efficiency of the Diels-Alder reactions is attributable to steric overcrowding.[8] The electronic absorption spectrum of 1 is broad (ε_{max} 12,000 $M^{-1}cm^{-1}$), and is bathochromically shifted by 8 nm relative to that of dianthrylmethanol, suggestive of intramolecular π-orbital interaction of the two anthracene moieties.

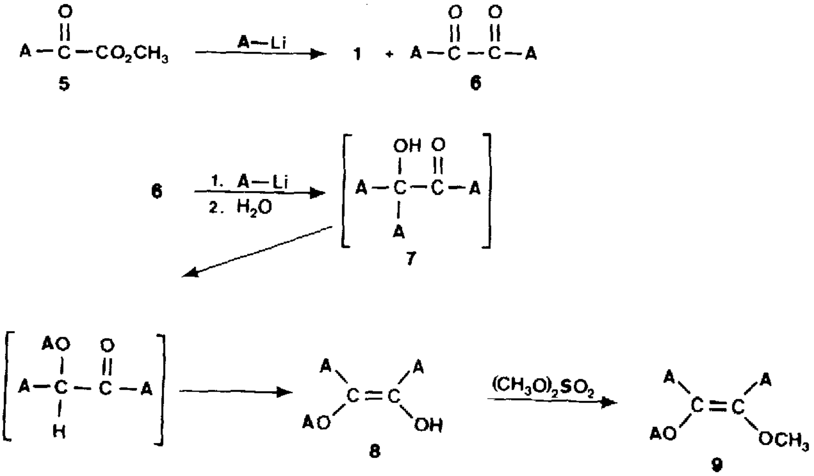
Steric strain, we believe, makes alkyl 9-anthrilates uniquely reactive: When sodium methoxide (100 mg) is added to a solution of 1 (600 mg) in dimethylformamide (10 mL) under nitrogen, the reaction mixture turns dark brown. Addition of methanol (10 mL) after 10 min, and acetic acid (3 drops) gives a light orange colored solution from which isomer 4 (yellow crystals, mp 147-150 °C; from dichloromethane/methanol; 80% yield) precipitates upon slow addition of water (15 mL). It is worth noting that the electronic aborption spectrum of 4, in spite of its auxochromic 9-anthryloxy group, is hypsochromically shifted by 8 nm relative to that of its precursor 1.



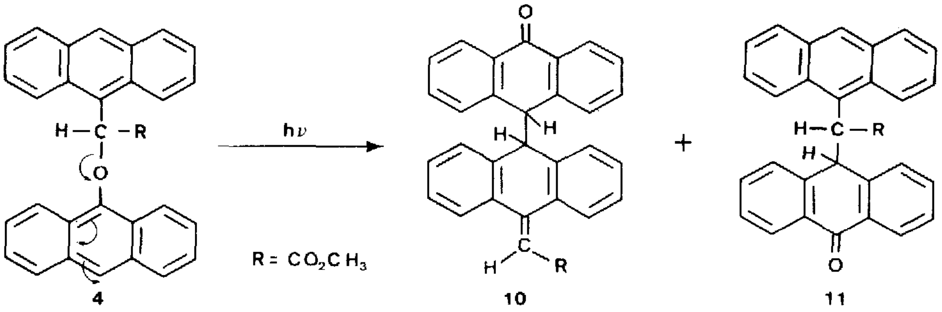
A = 9-anthryl

The migration of 9-anthryl from carbon to oxygen associated with the base-induced rearrangement of 1 into 4 appears to be typical of 1,1-di-9-anthryl substituted tertiary carbinols. Thus, the reaction of 9-anthryllithium (6 mmol) with 9-anthrylglyoxalate 5 (3 mmol) not only gives 1 (50% yield), but affords the 9-anthryloxy substituted dianthrylethenol 8 in 18% yield (yellow crystals, mp 212-214 °C; dec). We explain the formation of 8 by base-catalyzed rearrangement of carbinol 7, and we have ascertained that 8 indeed is formed by reaction of 9-anthryllithium with 9,9'-anthril (6). As for the geometry of substitution of ethenol 8, its structure has been confirmed by X-ray diffraction analysis of its methyl ether 9 (yellow crystals, mp 242-244 °C).

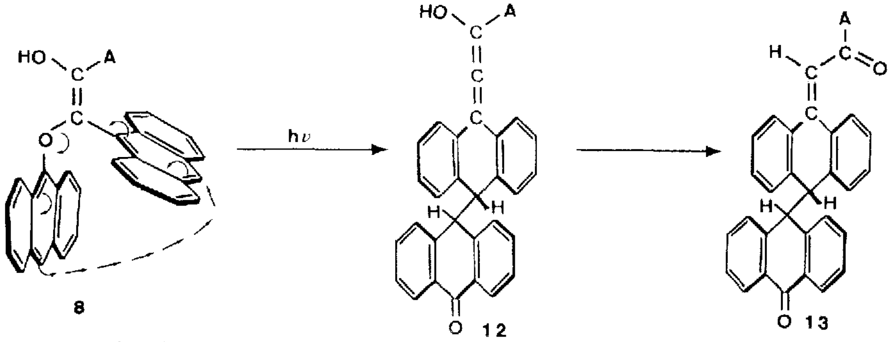
A = 9-anthryl



Bichromophoric anthracenes 4, 8, and 9 are characterized by the previously unexplored 9-anthryl 9-anthrylmethyl ether moiety, which we found to be rather light-sensitive. In toluene solution, photoexcited 4 disappears with a quantum yield of 0.57. On a preparative scale, irradiation[7] of 4 (220 mg) in ethyl acetate (125 mL), using light of wavelengths > 400 nm, results in complete consumption of starting material within 12 min. Surprisingly, however, the reaction leads neither to a 4π+4π nor a 4π+2π cyclomer, but gives substituted anthrones 10 (colorless crystals, mp 168-172 °C; 68% yield) and 11 (greenish-yellow crystals, mp 178-183 °C; 15% yield), which were separated by flash chromatography on silica gel/dichloromethane. We rationalize the isomerization of 4 leading to 10 and 11 by a heterolytic 9-anthryloxy - 9-anthronyl rearrangement.[9]

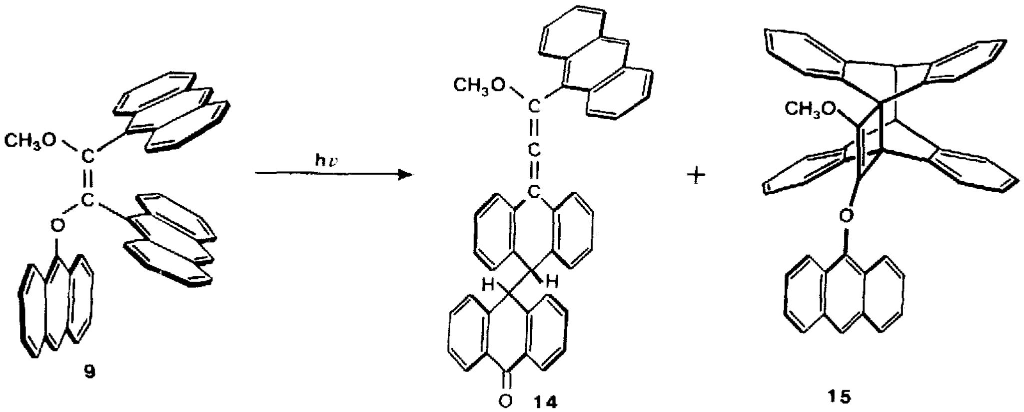


Migration of the 9-anthryloxy group also turned out to be the predominant chemical deactivation mode of photoexcited substituted ethenol 8 and its methyl ether 9, which isomerize in toluene solution with quantum yields of 0.09 and 0.16, respectively. Irradiation (λ > 400 nm) of enol 8 (30 mg) in toluene (125 mL) for 90 sec gave an isomer (yellow crystals; mp 210-214 °C) which was isolated in 54% yield by column chromatography (silica gel/dichloromethane), and for which elemental analysis, IR (C=O at 1680 cm^{-1}), ^1H and ^{13}C NMR (C=O at 196.79 and 184.76 ppm), and electronic absorption spectra suggest structure 13. We believe the formation of 13 is explicable by a "1,5 shift" of the anthryloxy⟶anthronyl group, followed by ketonization of the allenol 12.[10]



A = 9-anthryl

In accord with the formation of allenol 12, irradiation of 9 (200 mg) in ethyl acetate for 2 min gives as major product (67% yield) the 9-anthryl substituted allenol ether 14 (pale yellow crystals, mp 179-181 °C). Its structure is supported by elemental analysis, IR (C=C=C at 1910 cm^{-1}), ^{13}C NMR (=C= at 192.41 ppm; C=O at 184.48 ppm), and UV spectra. Moreover, structure 14 was established by X-ray diffraction.[11]



A second photoisomer of 9, (yellow crystals, mp 242-244 °C), was separated from allene 14 by column chromatography (silica gel/dichloromethane) and isolated in 13% yield. Its ^1H and ^{13}C NMR spectra, as well as its electronic absorption spectrum are in agreement with the cyclobutene 15. We conclude, therefore, that 4π+4π cycloaddition of the cis-1,2-di-9-anthrylethylene moiety in photoexcited 9, and isomerization by way of migratory rearrangement of the 9-anthryloxy group are competing deactivation processes.[12]

References and Notes

1. J.-P. Desvergne, N. Bitit, A. Castellan, M. Webb, and H. Bouas-Laurent, J. Chem. Soc., Perkin Trans. 2, 1885 (1988); and references cited there.
2. F. Fages, J.-P. Desvergne, I. Frisch, and H. Bouas-Laurent, Chem. Comm., 1413 (1988).
3. H.-D. Becker, K. Sandros, and K. Andersson, Angew. Chem. Inter. Ed. Engl., 22, 495 (1983).
4. H.-D. Becker and K. Andersson, Tetrahedron Lett., 26, 6129 (1985);
5. H.-D. Becker, L. Hansen, and K. Andersson, J. Org. Chem., 51, 2956 (1986).
6. Alkyl 9-anthrilates such as 1 were synthesized by reaction of 9-anthryllithium with either dialkyl oxalates or alkyl 9-anthrylglyoxalates.
7. Irradiations were carried out under argon at 10 °C with a 125 W high-pressure mercury lamp in an immersion well apparatus equipped with a liquid-filter set-up. The 400 nm cut-off filter was chosen in order to protect the photoproducts from light exposure.
8. X-Ray diffraction analysis of crystalline 1 reveals that the anthracene π-systems deviate from planarity. The dihedral angle between the lateral rings in 1 is about 10 deg.
9. In agreement with an ionic mechanism, anthrones 10 and 11 are also formed from 4 in an acid-catalyzed ground state reaction.
10. The UV spectral changes associated with the photochemical isomerization of enol 8 are such as to suggest that the enol - ketone tautomerization 12 ⟶ 13 is a ground state process which is acid-catalyzed, and which occurs during work-up.
11. The X-ray diffraction analyses of 1, 2, 4, 9, 10, and 14 will be discussed in a comprehensive structural paper.
12. Experimental and spectroscopic details will be presented in a forthcoming full paper.

(Received in UK 3 January 1989)