Photocycloaddition of 1-Aminoanthraquinones to Dienes by Visible Light Irradiation

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Summary Photochemical oxetan formation between dienes and 1-aminoanthraquinones were found to be induced by visible light irradiation of the quinones.

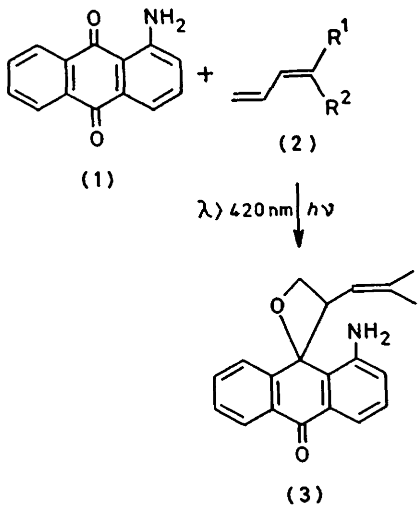
Photochemical cycloaddition of anthraquinone to olefins is known to produce the corresponding oxetan compounds.[1] While it has long been accepted that anthraquinone derivatives having electron donating substituents such as an amino group have no reactivity toward olefins because the lowest excited triplet state is a $\pi\pi^*$ state,[2,3] we have observed photocycloadditions of 1-aminoanthraquinones to dienes using visible light irradiation.

A solution of 1-aminoanthraquinone (**1**) and *trans*- or *cis*-penta-1,3-diene (**2**) in ethanol at 0 °C was irradiated using visible light ($\lambda > 420$ nm). Although the reaction products in each case were very unstable towards acid, light, and heat, they were successfully isolated by alumina t.l.c. in the dark under ammonia below 25 °C. The structure of the product (**3**) was confirmed by i.r., n.m.r., and mass spectroscopy which revealed that the double bond in the 1,2 position of (**2**) had undergone cycloaddition

Table 1. Photocycloaddition of (**1**) to various olefins.[a]

Olefins	Quantum yield ($\times 10^3$) of the disappearance of (**1**)
(**2a**)	7·2
(**2b**)	3·9
Hexa-2,4-dien-1-ol	9·4
Cyclohexa-1,3-diene	25·2
Cyclo-octa-1,3-diene	0·06
Bicyclo[2.2.1]hepta-2,5-diene	0·03
Cyclohexene	0
Cyclo-octene	0
Bicyclo[2.2.1]hept-2-ene	0
Fumaronitrile	0
Diethyl fumarate	0

[a] [(**1**)] *ca.* $1\cdot00 \times 10^{-4}$ mol dm^{-3}; [olefin] *ca.* $5\cdot00 \times 10^{-2}$ mol dm^{-3}; irradiation at λ 470 nm.



a, R^1 = Me, R^2 = H
b, R^1 = H, R^2 = Me

exclusively to the carbonyl group at C-9† of (**1**) the 3,4-double bond having the same conformation as that in (**2**). Compound (**3**) gradually decomposed at 30 °C into several compounds including the starting quinone (**1**). Similar photocycloadditions with (**1**) were also observed with other dienes, while monoenes did not react. (Table 1). The reaction appears to be restricted to 1-aminoanthraquinones as shown in Table 2.

The photocycloaddition of (**1**) to (**2**) was unaffected by the presence of triplet quenchers such as dissolved oxygen and anthracene. The fluorescence of (**1**) was quenched by (**2**) without new emission and the Stern–Volmer constants [(**2a**) *ca.* 0·17 and (**2b**) *ca.* 0·05 $dm^3 mol^{-1}$] agreed well with the values of the ratio between the intercept and slope [(**2a**) *ca.* 0·17 and (**2b**) *ca.* 0·09 $dm^3 mol^{-1}$] in double reciprocal plots of the quantum yield of the reaction and the concentration of (**2**). Moreover, amines such as butylamine, piperidine, triethylamine, and pyridine quenched the reaction, though the fluorescence of (**1**) was hardly affected by those amines. This may be due to exciplex quenching on the reaction pathway. These results suggest that the photoreaction between (**1**) and dienes is not the conventional photocycloaddition *via* the $n\pi^*$ triplet state but is a new type *via* the lowest excited singlet state of (**1**) which has inherently intramolecular charge-transfer nature.[4]

Table 2. Photocycloaddition of various aminoanthraquinones to cyclohexa-1,3-diene[a]

Aminoanthraquinones	Conversion of (**1**)/%
(**1**)	91·8
1-Acetylaminoanthraquinone	63·5
1-Methylaminoanthraquinone	17·9
2-Aminoanthraquinone	0
2-Piperidinoanthraquinone	0

[a] [Aminoanthraquinones] *ca.* 1·00 × 10^{-4} mol dm^{-3}; [cyclohexa-1,3-diene] *ca.* 5·00 × 10^{-2} mol dm^{-3}; 10 min irradiation at λ>420 nm.

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† The i.r. spectrum of (3) (C=O; 1660 cm^{-1}) indicated the disappearance of the carbonyl group at C-9 in (1) (C=O; 1670 and 1630 cm^{-1}).

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[3] H. Inoue and M. Hida, *Yuki Gosei Kagaku Kyokai Shi*, 1974, **32**, 348.
[4] Z. Yoshida and F. Takabayashi, *Tetrahedron* 1968, **24**, 933; H. Inoue, T. Hoshi, J. Yoshino, and Y. Tanizaki, *Bull. Chem. Soc. Japan*, 1972, **45**, 1018; 1973, **46**, 380.