

Photocycloaddition of 1-Aminoanthraquinones to Dienes by Visible Light Irradiation¹

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1-Aminoanthraquinones have been found to undergo cycloaddition reactions with dienes in ethanol to produce the corresponding oxetans when subjected to visible light irradiation. Monoene and acetylenic compounds do not react and the reaction in ethanol is restricted to 1-aminoanthraquinones, 2-aminoanthraquinones showing no reactivity. The reaction does not appear to be a conventional photocycloaddition *via* the $n\pi^*$ triplet state of the quinone, but a new type occurring *via* the intramolecular charge-transfer ($\pi\pi^*$) excited state.

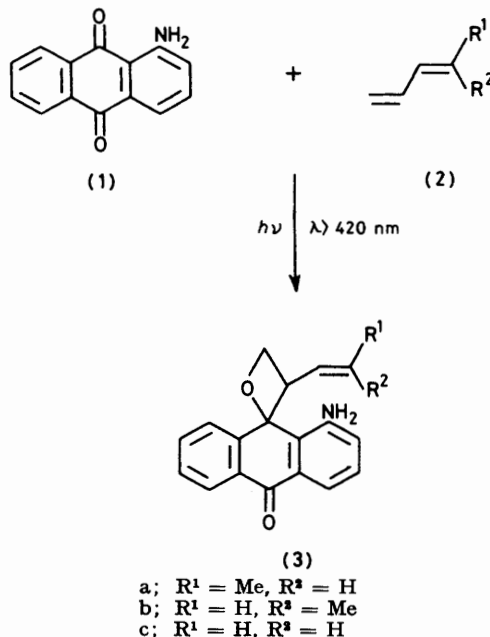
THE photochemical cycloaddition of anthraquinones to olefins is known to produce the corresponding oxetans.² Since the reaction is a result of the anthraquinone's excited $n\pi^*$ triplet state it is restricted to olefins with a higher triplet energy than this; in fact, most dienes show low reactivity.^{2,3} On the other hand, anthraquinones with electron-donating substituents such as an amino-group have long been accepted as not having any reactivity toward olefins because their lowest excited triplet state is an intramolecular charge-transfer ($\pi\pi^*$) state.^{3,4} However, we have found that photocycloadditions of 1-aminoanthraquinones to dienes are effectively induced by visible light irradiation. The contrasting characteristics of these two types of reaction suggest that the latter is not a conventional photocycloaddition *via* the $n\pi^*$ triplet state of the quinone, but a new type occurring *via* the intramolecular charge-transfer ($\pi\pi^*$) excited state.

RESULTS AND DISCUSSION

A solution of 1-aminoanthraquinone (1) (1.00×10^{-4} mol dm⁻³) and *trans*- or *cis*-penta-1,3-diene (2a or b) (5.00×10^{-2} mol dm⁻³) in ethanol was irradiated at 0 °C by visible light of $\lambda > 420$ nm. The absorption intensity of the intramolecular charge-transfer band of (1) (λ_{max} , 477 nm) decreased on irradiation, and had isosbestic points at λ 410 and 350 nm. T.l.c. (silica gel or alumina) of the reaction mixture afforded very complex chromatograms in normal light, but exhibited only two spots, of the product and compound (1), when taken on alumina in the dark. The sole reaction product in each case was very unstable towards acid, light, and heat. Since aerial carbon dioxide caused the products to decompose they were successfully isolated by preparative t.l.c. (on alumina) in the dark under ammonia below 25 °C. The isolated products were stored under nitrogen below 5 °C and their structures (3a and b) were confirmed by i.r., n.m.r., and mass spectroscopy. Their mass spectra [m/e 291(M^+), 223, and 68] clearly indicated that compounds (3a and b) are 1:1 adducts of compounds (1) and (2a or b). The i.r. spectra showed the appearance of the oxetan group (990 cm⁻¹) and the disappearance of the carbonyl group at C-9 (CO, 1 630 cm⁻¹) in the aminoanthraquinone (1). The n.m.r. spectra revealed that the

1,2-double bond of the diene (2) had undergone cycloaddition exclusively to the carbonyl group at C-9 of compound (1), the 3,4-double bond having the same conformation as in the precursor (2). The chemical shifts and coupling patterns of the aromatic protons clearly indicated that the addition occurs at the 9-carbonyl group of the aminoanthraquinone (1). The spectral data are summarized in Table 1.

In the cases of buta-1,3-diene and styrene the oxetans could also be isolated and the similarity of their structures (3c) and (4) to those of compounds (3a and b) was confirmed. Although the photo-products in the cases of cyclohexa-1,3-diene and cyclopentadiene could not be isolated because of their instability, the mass spectra of the reaction mixtures indicated the presence of 1:1 adducts with compound (1).



Compound (4) was shown to have the following stereochemistry. The coupling constant of a typical AMX coupling pattern among the oxetan ring protons showed H^a and H^t to be in a *cis*- (J_{at} 8 Hz) and H^e, H^t in a *trans*-orientation (J_{et} 4 Hz) to each other. Moreover, the fact

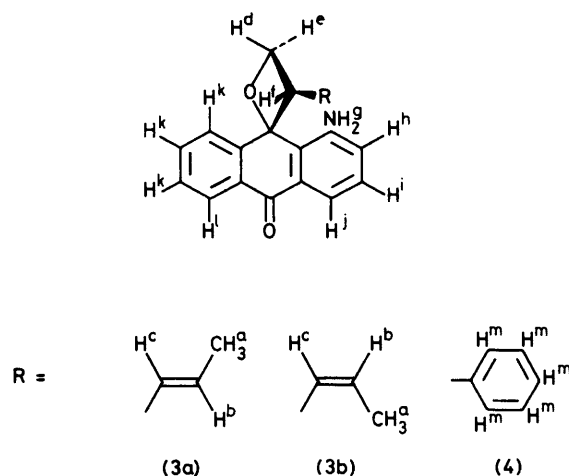
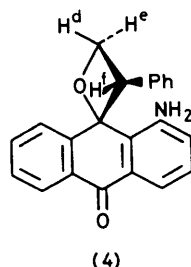


TABLE 1

¹H N.m.r. spectral data for compounds (3a), (3b), and (4)
Chemical shifts/p.p.m. (in CDCl₃)
(multiplicities)

Compd.	H ^a	H ^b	H ^c	H ^d	H ^e	H ^f	H ^g	H ^h	H ⁱ	H ^j	H ^k	H ^l	H ^m	Coupling constant/Hz
(3a)	1.2 (dd)	5.4 (qd)	4.8 (qdd)	4.0 (dd)	3.0—3.6 (m)			6.6 (dd)	6.9—7.6 (m)			8.0 (m)		<i>J</i> _{ab} 6.0, <i>J</i> _{ac} 0.9, <i>J</i> _{bc} 15.0, <i>J</i> _{cf} 8, <i>J</i> _{de} 11.0, <i>J</i> _{df} 4.3, <i>J</i> _{hi} 8.0, <i>J</i> _{hj} 1
(3b)	1.7 (dd)	5.1 (qd)	4.8 (qdd)	4.1 (dd)	2.9—3.7 (m)			6.6 (dd)	7.1—7.7 (m)			8.0 (m)		<i>J</i> _{ab} 6.0, <i>J</i> _{ac} 1.5, <i>J</i> _{bc} 10.0, <i>J</i> _{cf} 8, <i>J</i> _{de} 12.0, <i>J</i> _{df} 4.0, <i>J</i> _{hi} 8.0, <i>J</i> _{hj} 1
(4)				4.4 (dd)	3.6 (dd)	4.0 (dd)	1.6br	6.7 (dd)	7.1—7.7 (m)			8.1 (m)	6.9 (m)	<i>J</i> _{ef} 4.0, <i>J</i> _{de} 20.0, <i>J</i> _{df} 8.0

that the amino-protons are at higher field (1.6 p.p.m.) compared with those of compound (3) (3.0—3.6 p.p.m.) strongly suggests that they are deshielded by the phenyl group. This indicates that the phenyl group lies over the amino-group as shown in structure (4).



The reactivities of various olefins in these photocycloadditions are compared in Table 2. Dienes and conjugated olefins such as styrene and indene were reactive, while monoenes and diphenylacetylene did not react. This contrasts with the photocycloaddition of anthraquinone, in which monoenes and diphenylacetylene were reactive while most of the dienes showed little reactivity.^{2,3,5}

These photocycloadditions in ethanol appear to be restricted to 1-aminoanthraquinones, as shown in Table 3.

The photocycloaddition of 1-aminoanthraquinone (1) to the diene (2) was not affected by the presence of triplet quenchers such as dissolved oxygen and anthracene (5.0×10^{-2} mol dm⁻³). Since the visible light irradiation

($\lambda > 420$ nm) cannot excite aminoanthraquinones to their $n\pi^*$ levels, but only to their intramolecular charge-transfer ones,^{4,6} the results favour the suggestion that

TABLE 2

Photocycloaddition of 1-aminoanthraquinone (1) to various olefins ^{a, b}

Olefins	Quantum yield ($\times 10^3$) for the disappearance of compound (1)
(2a)	5.4
(2b)	3.3
Hexa-2,4-dien-1-ol	6.5
Cyclohexa-1,3-diene	18.0
Cyclopentadiene	10.0
2,5-Dimethylhexa-2,4-diene	5.9
Styrene	4.6 ^c
Indene	4.3 ^c
Methyl sorbate	0.16 ^c
Cyclo-octa-1,3-diene	0.045
Bicyclo[2.2.1]hepta-2,5-diene	0.03
Cyclohexene	0
Cyclo-octene	0
Bicyclo[2.2.1]hept-2-ene	0
Fumarodinitrile	0
Diethyl fumarate	0
1,2-Diphenylacetylene	0

^a [1-Aminoanthraquinone (1)] 1.0×10^{-4} mol dm⁻³; [Olefin] 5.00×10^{-1} mol dm⁻³. ^b Irradiation at λ 470 nm. ^c [Olefin] 5.00×10^{-2} mol dm⁻³.

the reaction is of a new type. The lesser reactivities of 2-aminoanthraquinones may be due to their extremely short-lived, singlet charge-transfer levels in ethanol.⁷ Detailed mechanistic studies are now in progress.

TABLE 3

Photocycloaddition of various aminoanthraquinones to cyclohexa-1,3-diene ^a

Aminoanthraquinones	Conversion (%)
(1)	91.8
1-Acetylaminoanthraquinone	63.5
1-Methylaminoanthraquinone	17.9
2-Aminoanthraquinone	0
2-Piperidinoanthraquinone	0

^a [Aminoanthraquinones] 1.00×10^{-4} mol dm⁻³; [cyclohexa-1,3-diene] 5.00×10^{-2} mol dm⁻³; irradiation for 10 min at $\lambda > 420$ nm.

EXPERIMENTAL

U.v. and visible absorption spectra were recorded with a Shimadzu UV-200 spectrophotometer. I.r. spectra were recorded with a JASCO IR-1A instrument. N.m.r. measurements were made with Hitachi R-24 (60 MHz) and JEOL JNM FX-100 spectrometers. Mass spectra were measured with a JEOL JMS D-100 instrument. Quantum yields were determined using potassium tris(oxalato)ferrate(III) as a chemical actinometer.

1-Aminoanthraquinone,⁸ 1-acetylaminoanthraquinone,⁸ 1-methylaminoanthraquinone,⁷ 2-aminoanthraquinone,⁸ and 2-piperidinoanthraquinone⁸ were prepared and purified as reported elsewhere. The olefins, except for fumaronitrile, diethyl fumarate, and 1,2-diphenylacetylene, were purified by vacuum distillation and were stored under nitrogen below 5 °C. 1,2-Diphenylacetylene (Tokyo Kasei, G.R.) was purified by elution with hexane through a silica gel column. Fumaronitrile and diethyl fumarate (Tokyo Kasei, G.R.) were used without further purification. Ethanol was dried [Mg(EtO)₂] and distilled under nitrogen.

Procedure for Photocyclisation.—The aminoanthraquinones (1.00×10^{-4} mol dm⁻³) and olefins (5.0×10^{-1} — 5.0×10^{-2} mol dm⁻³) in ethanol (800 ml) were irradiated at 0 °C using a 300-W high-pressure mercury lamp (Eikosha); a solution filter (saturated aqueous NaNO₂) was used to give radiation of $\lambda > 420$ nm. The irradiated reaction mixture was evaporated and the product isolated by means of preparative t.l.c. (on alumina). Several drops of 28% aqueous ammonia were added to the eluant (benzene-ethanol, 97 : 3) to prevent decomposition of the oxetans. The product was extracted from the alumina with chloroform and stored under nitrogen below 5 °C. The preparative t.l.c. was repeated, to remove the decomposition products, until the chromatogram exhibited only one spot. All these steps were carried out in the dark below 25 °C.

trans-1-Amino-9,10-dihydro-10-oxo-3'-prop-1-enylanthracene-9-spiro-2'-oxetan (3a).—The oxetan compound (3a) was obtained from the photocycloaddition of 1-aminoanthraquinone (1) to *trans*-penta-1,3-diene; ν_{\max} (KBr) 3 400, 2 950, 1 660, 1 300, and 990 cm⁻¹; m/e 291 (M^+), 223, and 68; ¹H n.m.r. data are in Table 1; λ_{\max} (CHCl₃) 407 nm (ϵ 2 070²).

cis-1-Amino-9,10-dihydro-10-oxo-3'-prop-1-enylanthracene-9-spiro-2'-oxetan (3b).—The oxetan compound (3b) was obtained from the photocycloaddition of 1-aminoanthraquinone (1) to *cis*-penta-1,3-diene; ν_{\max} (KBr) 3 400, 2 950, 1 660, 1 300, and 990 cm⁻¹; m/e 291 (M^+), 223, and 68; ¹H n.m.r. data are in Table 1.

1-Amino-9,10-dihydro-10-oxo-3'-vinylanthracene-9-spiro-2'-oxetan (3c).—The oxetan (3c) was obtained from the photocycloaddition of 1-aminoanthraquinone (1) to buta-1,3-diene; ν_{\max} (KBr) 3 400, 2 950, 1 655, 1 420, and 990 cm⁻¹; m/e 277 (M^+), 223, and 54; δ (CDCl₃) 8.3—6.6 (7 H, m, ArH), 5.2 (2 H, m, =CH₂), 4.75 (1 H, m, CH=), 4.07 (1 H, AMX dd, J 4.3 and 12.0 Hz), 3.2—4.5 (2 H, br, NH₂), and 3.2—3.5 (2 H, m); λ_{\max} (CHCl₃) 403 nm (ϵ 1 780).

1-Amino-9,10-dihydro-10-oxo-3'-phenylanthracene-9-spiro-2'-oxetan (4).—The oxetan (4) was obtained from the photocycloaddition of 1-aminoanthraquinone (1) to styrene; ν_{\max} (KBr) 3 420, 2 950, 1 655, and 970 cm⁻¹; m/e 327 (M^+) 223 and 104; ¹H n.m.r. data are in Table 1; λ_{\max} (CHCl₃) 405 nm (ϵ 1 700).

The products of the photoreactions of 1-acetylaminoanthraquinone and 1-methylaminoanthraquinone with cyclohexa-1,3-diene could not be isolated because of their instability.

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