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The Mechanism of the Photoconversion of α-Phenylcinnamic Esters into 9,10-Dihydrophenanthrenes

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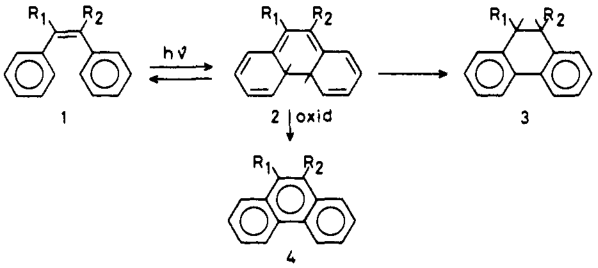
Abstract: The mechanism of the formation of a 9,10-dihydrophenanthrene derivative (**3g**) from methyl α-phenylcinnamate (**1g**) is clarified by demonstrating that the 4a,4b-dihydrophenanthrene derivative (**2g**) is an intermediate. It is formed by photocyclization of the parent compound. Only in a protic solvent this intermediate undergoes a prototropic shift leading to a 4a,9-dihydrophenanthrene derivative (**9g**). This compound is converted into the end product **3g** by a radical process. A necessary condition for the formation of a 9,10-dihydrophenanthrene from a stilbene is the presence of an enolizable group at the double bond of the stilbene.

It has been known for over 25 years that stilbenes undergo photochemical cyclodehydrogenations under oxidative conditions to phenanthrenes.[1] More recently, it has been shown[2,3] that the first step in this reaction is the cyclization from the S_1 state of a *cis*-stilbene (**1**) to a *trans*-4a,4b-dihydrophenanthrene (**2**) (Scheme I). The subsequent dehydrogenation **2** → **4** can occur in several ways.[4]

Scheme I

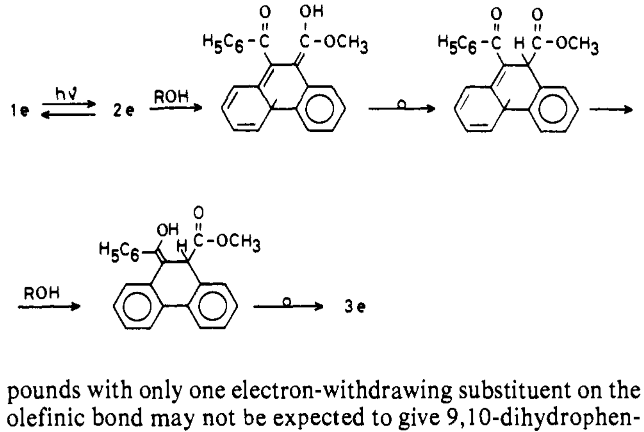


a) $R_1 = R_2 = CN$
b) $R_1R_2 = CO\text{-}O\text{-}CO$
c) $R_1R_2 = CO\text{-}NH\text{-}CO$
d) $R_1 = CO\text{-}C_6H_5$; $R_2 = COOH$
e) $R_1 = CO\text{-}C_6H_5$; $R_2 = COOCH_3$
f) $R_1R_2 = C(C_6H_5)\ OH\text{-}O\text{-}CO$
g) $R_1 = H$; $R_2 = COOCH_3$
h) $R_1 = H$; $R_2 = CN$

In general, the reaction **1** → **2** is completely reversible under nonoxidative conditions; **2** can undergo both thermal and photochemical ring opening[4,5] to *cis*-**1**. In a few cases, however, it was found that irradiation of a stilbene in the absence of an oxidant yielded a 9,10-dihydrophenanthrene (**3**). Thus, Sargent and Timmons[6] reported that the stilbenes **1a–c** which possess two electron-withdrawing substituents on the double bond yield the products **3a–c** on irradiation under nonoxidative conditions. Irradiation of stilbene, triphenylethylene, α-methylstilbene, and α-cyanostilbene under the same conditions gave only cis–trans isomerization. The authors ascribed the formation of the products **3a–c** to photochemically induced H shifts in the primary formed intermediates **2a–c**.

In 1970 Rio and Hardy obtained the 9,10-dihydrophenanthrenes **3d–f** on irradiation of the stilbenes (derivatives) **1d–f** in various alcohols or in a mixture of water–pyridine as the solvent, even when the irradiation was carried out in the presence of oxygen.[7] By performing the reactions in D_2O–pyridine they were able to show that the hydrogen atoms at C_9 and C_{10} in the products **3d–f** were derived from the solvent. On irradiation of the same stilbene derivatives in benzene or chloroform they observed a red coloration of the solution, which was ascribed to the occurrence of the intermediates **2d–f**, but they could not isolate 9,10-dihydrophenanthrenes from the irradiation mixtures. Rio and Hardy suggested a mechanism wherein prototropic shifts are responsible for the isomerization **2** → **3** (see Scheme II). Consequently they state that compounds with only one electron-withdrawing substituent on the olefinic bond may not be expected to give 9,10-dihydrophenanthrenes. Such compounds will only give rise to cis–trans isomerization. Ichimura and Watanabe[8] used a similar mechanism in their study of the pH dependence of the photocyclization **1a** → **3a**.

Scheme II



In 1971 Srinivasan and Hsu[9] reported the first example of a photocyclization wherein a stilbene derivative having only one electron-withdrawing substituent on the olefinic bond gave a 9,10-dihydrophenanthrene as the product. On irradiation of

Table I. Rate Constant of the Thermal Decay of 4a,4b-Dihydro-9-carbomethoxyphenanthrene (**2g**)

			Hexane Solvent		
Temp, °C	6.2	11.0	19.7	28.0	
k,[a] s^{-1}	0.90×10^{-3}	1.04×10^{-3}	1.32×10^{-3}	1.69×10^{-3}	
r[b]	0.997	0.997	0.997	0.996	
			Methanol Solvent		
Temp, °C	23.0	27.5	32.5	39.5	48.0
k,[a] s^{-1}	0.179	0.282	0.362	0.583	0.802
r[b]	0.998	0.995	0.997	0.998	0.995

[a] Computed with the least-squares method from the plots of log I/I_∞ against time. [b] r is the correlation coefficient.

methyl α-phenylcinnamate (**1g**) in methanol they obtained 9,10-dihydro-9-carboxymethylphenanthrene (**3g**). Recently they reported some other examples of this reaction.[10] Relying on the following experiments the authors came to a radical mechanism for this photoreaction: (1) Irradiation of **1g** in CD_3OD yields **3g**, completely deuterated at C_9 and C_{10}. (2) The quantum yield for the formation of **3g** depends on the light intensity; it decreases with increasing light intensity. Their scheme, starting with the photochemical formation of a radical intermediate **5g** (see Scheme III), does not explain, however, why other stilbenes containing only one substituent, appropriate for radical stabilization, do not yield products **3** on irradiation under identical conditions.

Results and Discussion

In order to test the correctness of the mechanism proposed by Srinivasan and Hsu we repeated the irradiation of **1g** in CH_3OD as the solvent. Since the C–H bonds in methanol are better disposed to homolytic cleavage than the O–H bond (bond energies are 92 and 102 kcal/mol, respectively),[11] a radical process in this solvent should not be accompanied by incorporation of deuterium in the product. It appeared, however, that the product (**3g**) from this experiment was completely deuterated at C_9, but did not contain deuterium at C_{10}. To be sure that the isotope had not been introduced by proton exchange between C_9 of **3g** and the solvent (e.g., via an enolization reaction), **3g** was irradiated in CH_3OD. Under these conditions no deuterium incorporation took place. Another explanation for the occurrence of deuterium at C_9 in the product might be that **1g** undergoes a direct photoprotonation.[12] This seems very improbable because no single indication has ever been found for the addition of methanol to the olefinic bond of **1g** under the reaction conditions used. Therefore, the results suggest that the incorporation of hydrogen atoms at C_9 and C_{10} in the photoreaction **1g** → **3g** proceeds via two mechanistically different reactions steps: at C_9 in an ionic process, probably similar to the prototropic shifts proposed by Rio and Hardy; at C_{10}, however, in a homolytic reaction.

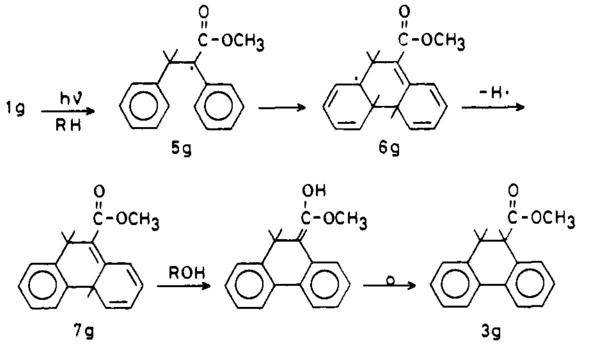
Two pathways based on this conclusion remain possible for the reaction **1g** → **3g**.

A. The primary formation of the radical intermediate **5g**, proposed by Srinivasan and Hsu, followed by an aromatic radical substitution leading to **6g**, which undergoes partial aromatization to **7g** by hydrogen abstraction. The end product arises then by a final prototropic shift in which the enolizable substituent adds a proton from the solvent (see Scheme IIIA).

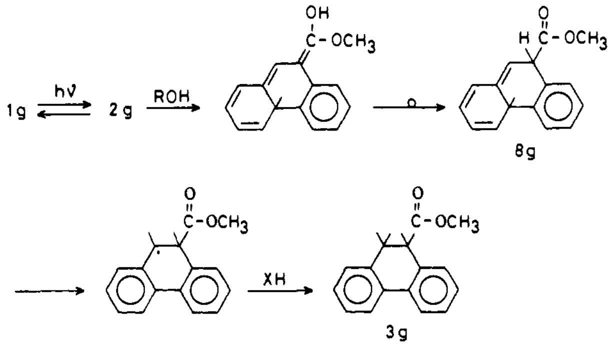
B. The primary step is the concerted, light-induced electrocyclization from **1g** to **2g**, which undergoes proton exchange with the solvent leading to **8g**. The end product **3g** arises then via a homolytic hydrogen abstraction–addition reaction (Scheme IIIB).

Theoretically, a choice between A and B might be possible by measuring the quantum yield for the formation of **3g** from *cis*-**1g** and *trans*-**1g**. According to Scheme IIIA both isomers can be converted into **5g**, but **2g** (Scheme IIIB) can only arise from the cis isomer. This method should only be useful when it is accepted that the primary steps in both schemes are rate limiting. In practice, however, a conclusion from measured quantum yields could not be drawn, because of the larger values for trans–cis (φ = 0.6) and cis–trans isomerization (φ = 0.2) compared to that of the cyclization (φ = 0.03).

Scheme IIIA



Scheme IIIB



Another possible way to decide between Schemes IIIA and IIIB should arise when the occurrence of the intermediate **2g** can be demonstrated. By flash photolysis and rapid scan spectroscopy of **1g** we could show that both in degassed hexane and in methanol a compound is formed to which the structure **2g** can be assigned because of its UV spectrum (λ_{max} 450 nm).[13] The occurrence of **2g** alone does not prove that it is an intermediate in the formation of **3g**; its presence might be due to a reversible side reaction **1g** ⇄ **2g**. Therefore, the thermal decomposition of **2g** was studied both in hexane and methanol. The rate constants are given in Table I.

In hexane, a solvent in which under anaerobic conditions no formation of **3g** takes place, the thermal decomposition of **2g** appeared to be a first-order reaction with a rate constant $k = 1.54 \times 10^{-3}\ s^{-1}$ at 25 °C. The temperature dependency followed the Arrhenius equation, giving $E_a = 4.8$ kcal/mol ($r = 0.99$) and $\Delta S^{\ddagger} = -57.2$ cal mol^{-1} deg^{-1} [14] as the activation energy and activation entropy, respectively. The values fit very well into the isokinetic relation of the thermal ring opening reactions of other 4a,4b-dihydrophenanthrenes in hexane. Muszkat and Fischer[4] and Blackburn, Loader, and Timmons[5] found for these reactions a linear relation between E_a and $\Delta S^{\ddagger}$, represented by $\Delta S^{\ddagger} = 2.85E_a - 70.4$, as was calculated from their data. This isokinetic relation for the decomposition in hexane of **2g** and of other 4a,4b-dihydrophenanthrenes demonstrates that these reactions proceed via similar transition states.[15]

The thermal decomposition of **2g** in methanol is also a first-order reaction, but the rate constant at 25 °C is much higher (k = 0.228 s^{-1}). Moreover, the values of E_a (11.0 kcal/mol, r = 0.98) and $\Delta S^{\neq}$ (−26.5 kcal mol^{-1}) deviate strongly from the given equation. To exclude a trivial solvent effect we measured the rate constant of the thermal decomposition of the 4a,4b-dihydrophenanthrene derivative from β-styrylnaphthalene in methanol. The value appeared to be equal to that measured by Blackburn and Timmons in hexane.[5] So a solvent effect is absent in this case.

From these observations we conclude that **2g** in methanol decomposes via a mechanism different from the ring opening of other 4a,4b-dihydrophenanthrenes. A satisfactory explanation may be that **2g** undergoes a prototropic shift in methanol as formulated in Scheme IIIB. The resulting intermediate **8g** has a calculated[16] absorption maximum at ca. 300 nm coinciding with the region where **1g** shows strong absorption. Thus, on irradiation of **1g** an intermediate **8g** should also be excited, what might result in the further conversion into **3g**.

A priori, this homolytic isomerization might equally be as well a thermal as a photochemical process. We made an attempt to distinguish between both possibilities. By irradiating **1g** in benzene for some time under argon, and then adding, still under argon, methanol to the solution directly after the light had been turned off, we hoped to trap **8g**. However, by GLC–MS analysis no products other than **1g** and a small amount of 9-carbomethoxyphenanthrene (**4g**) were detected. Though the lifetime in hexane of **2g**, as calculated from its decomposition rate, is 7.6 min, its concentration may be too low to react with methanol to a sufficient degree to detect **8g** as a product. The concentration of **2g** in benzene, after the irradiation, was too low to detect a yellow color, as is usual with other stilbenes under anaerobic conditions. The formation of **2g** in benzene, however, was proven by flash photolysis of a 10^{-3} M solution of **1g** in benzene. A broad adsorption (from 400 to 520 nm) with a maximum at 450 nm could be observed. Moreover, it cannot be excluded that **8g** is oxidized during the workup procedure.

In a following paper the photocyclizations of α-(1-cyclohexenyl)cinnamic esters will be described. The product formation from these compounds can be readily explained by the mechanism given above.

The conclusions of our investigations can be summarized as follows.

Stilbene (**1**) is on irradiation generally converted into the corresponding 4a,4b-dihydrophenanthrene **2**, which fate depends on the presence of suitable substituents on the olefinic bond and on the reaction conditions.

When a proper enolizable group is present and the solvent is a suitable proton source, **3** is the normal end product under anaerobic conditions. A proton shift **2** → **8** is decisive for this conversion. The formation of the product can be described by the mechanism given in Scheme IIIB.

Under oxidative conditions **2** is at least partly converted into **4**; **3** can be another product under these circumstances.

When both reactions are excluded **2** reverts to the starting compound **1**. In that case only cis–trans isomerization of **1** is observed.

These conclusions can be illustrated by the photochemical behavior of **1g** under different conditions.

If **1g** is irradiated under argon in benzene only cis–trans isomerization takes place; if the solution is saturated with hydrochloric acid **3g** is formed, as is the case when **1g** is irradiated in methanol. If **1g** is irradiated in the presence of I_2 this results in the formation of **4g**.

As a final test we irradiated α-phenylcinnamonitrile (**1h**) in methanol. At neutral pH no **3h** was formed; at pH 3 (in methanol–water) **3h** could be isolated, even in the presence of oxygen. The result can be ascribed to the lower basicity of the cyano group compared with the carbomethoxy group in **1g**, which prevents formation of **3h** at pH 7. At pH 3 protonation of the cyano group is apparently so strong that the rate constant for the prototropic shift **2h** → **8h** is much larger than the rate constant for the oxidation **2h** → **4h**. A similar explanation was given by Ichimura and Watanabe[8] for the pH dependency of the photoreactions of **1a**. The formation of **3a** on irradiation of **1a** in a benzene solution under anaerobic conditions[6] seems to be an exception to the mechanism pictured above. This might be caused by the strong electron-deficient character of the double bond in this case.

Experimental Section

Spectral data were obtained via the following instrumentation: a Varian MAT SM2B spectrometer, a Finnigen GLC–MS combination, a Perkin-Elmer 254 IR spectrometer, a Bruker WH-90 NMR instrument, and for the UV spectra a Cary 15 UV spectrophotometer. For the rapid scan spectrometry Rapid Spectroscop T-3/13, Howald's Werke (Kiel), was used. The flash photolysis experiments were performed at the Gorlaeus Laboratorium at Leiden.

Irradiations. All preparative irradiations were carried out in a RPR-100 Rayonet photochemical reactor fitted with 300-nm lamps. All solutions were about 2 × 10^{-3} M in benzene, methanol, or monodeuteriomethanol and were flushed with argon for 30 min to prevent formation of oxidation products.

The quantum yields were measured using a similar black box as described by Zimmerman.[17] Ferrioxalate actinometry, in the modification described by Murov,[18] was used to measure the light intensity. For the filter system a three-compartment cell, filled with respectively 2 M $NiSO_4$ in 5% H_2SO_4, 0.8 M $CoSO_4$ in 5% H_2SO_4, and 0.0012 M $Bi(NO_3)_3$ in 2:3 HCl/H_2O, was used. The transmission of this filter system is less than 1% below 265 nm and above 302 nm, and the maximum transmission is 16% at 286 nm.

Conversions were determined by NMR spectroscopy and were always less than 20%. From these conversions the quantum yields were calculated, without making a correction for the back reaction in the cis-trans isomerization. The concentration of the 4a,4b-dihydrophenanthrene **2g** was always very low, so it was not necessary to correct for the absorption of **2g**. The deviation in the given values for Φ trans-cis and Φ cis-trans is less than 10%, and for Φ_{cycl} less than 20%. This latter quantum yield was determined for an equilibrium mixture of *cis*-**1g** and *trans*-**1g**.

For the flash photolysis experiments the solutions were flushed with argon for 30 min. The spectrum of the intermediate was recorded and its decay was measured at the maximum wavelength (450 mm) at several temperatures between 20 and 50 °C.

The decay of **2g** in hexane under argon was measured with the rapid scan spectrometer at 450 nm at temperatures between 5 and 30 °C. The intermediate **2g** was formed in this case by irradiating the cuvette with a Philips HPK-125 lamp.

In the experiment carried out to trap **8g** 500 mL of a 10^{-3} M solution of **1g** in benzene was irradiated under argon during 5 h at 300 nm. The concentration of **2g** was low (the absorption of this solution was <0.01 at 450 nm). After the light was turned off 50 mL of methanol was added under argon and the resulting solution was mixed thoroughly. The solvents were evaporated on a vacuum rotary evaporator, and the resulting oil was dissolved in ether and analyzed on the GLC–MS combination. No other peaks than those of *cis*- and *trans*-**1g** and a small one of **4g** could be detected.

Methyl α-phenylcinnamate (**1g**) was prepared by esterification of the corresponding acid.[19]

9-Carbomethoxy-9,10-dihydrophenanthrene (**3g**) was obtained in 90% yield as a colorless oil from the irradiation of a 2 × 10^{-3} M solution of **1g** in methanol under argon for 16 h.

The NMR spectrum is in accordance with that given by Harvey, Fu, and Rabideau.[20] Mass spectrum m/e (rel intensity) 238 (M^+ 15), 179 ($M^+ - COOCH_3$, 95), 178 ($C_{14}H_{10}$, 100), 165 (40).

On chromatography over Al_2O_3 the compound hydrolyzed to 9,10-dihydro-9-phenanthrenecarboxylic acid (mp 123-124 °C).[21]

Irradiation of **1g** in benzene saturated with HCl gas under argon gives rise to **3g** (50%) together with some **4g**, phenanthrene, and unidentified products.

α-Phenylcinnamonitrile (1h) was prepared according to the prescription in "Organic Syntheses".[22]

9-Cyano-9,10-dihydrophenanthrene (3h) was obtained by irradiating a 2×10^{-3} M solution in a mixture of methanol and water (1:1), buffered at pH 3 for 16 h. The yield, after purification by column chromatography over Al_2O_3 with hexane–toluene (3:1) as the eluent, was 80%: mp 84-85 °C (lit.[20] 83–84 °C); UV λ_{max} (CH_3OH) 297 nm (log ϵ 3.53), 280 (4.16), 267 (4.34), and 259 (4.29). The NMR spectrum matched that reported.[22] Mass spectrum *m/e* (rel intensity) 205 (M^+, 100), 204 (60), 203 (45), 190 (M − 15, 40), 178 ($C_{14}H_{10}$, 45), and 165 (65).

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Effect of Sulfuric Acid Concentration on the Rates of Hydrolysis of Ethyl Benzoate, Ethyl Thiolbenzoate, and Ethyl Thionbenzoate

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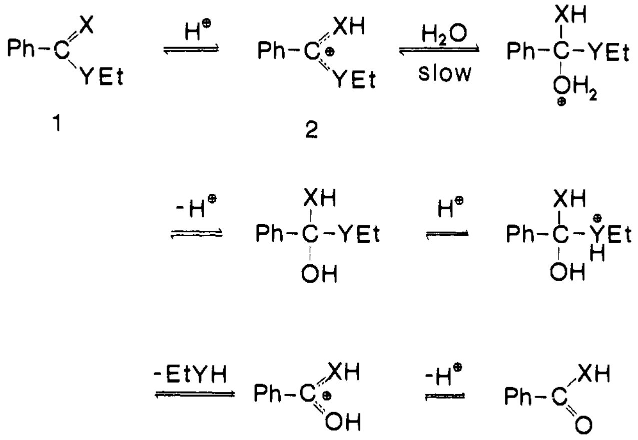
Abstract: The kinetics of the hydrolysis of ethyl benzoate, ethyl thiolbenzoate, and ethyl thionbenzoate has been studied in 30-99% sulfuric acid. Application of Yates-McClelland r and $f_{S^{\ddagger}}{}^{*}$ treatments to the data shows that ethyl thionbenzoate hydrolyzes by an $A_{Ac}2$ mechanism in all concentrations of acid, while ethyl thiolbenzoate hydrolyzes by an $A_{Ac}2$ mechanism in acid concentrations up to 60%, but by an $A_{Ac}1$ mechanism in more concentrated acid. The results show the greatly superior stability of the acylium ion as compared with the thioacylium ion.

The role of coenzyme A as a natural acylating agent[1] and the use of thiol esters for peptide synthesis[2] depend on the "energy-rich" nature of the *S*-acyl linkage.[3] In water, a reaction competitive of these acylations is acyl transfer to the solvent (hydrolysis). This reaction has received considerable attention recently, and persuasive evidence for a tetrahedral intermediate has been advanced.[4] However, there has been no study of the rate-acidity profile for these hydrolyses in varying concentrations of sulfuric acid. The power of this mechanistic probe has been amply demonstrated by Yates and his colleagues.[5-8] The rate-acidity profile of a typical ester hydrolyzing in a large excess of acid has the following features: the pseudo-first-order rate constant k_ψ reaches a maximum in 50–60% sulfuric acid, and then decreases to a minimum in 80% acid; over this range of concentrations the ester is hydrolyzing by an $A_{Ac}2$ mechanism (Scheme I, X = Y = O). In higher concentrations of acid k_ψ increases again, the ester now hydrolyzing by an $A_{Ac}1$ (Scheme II, X = Y = O) or an $A_{Al}1$ mechanism.

Scheme I



Recently, Yates and his colleagues[7,8] have shown how to obtain information about the transition state of the A-2 and A-1 reactions by combining a study of the change in the activity coefficient of the substrate along with the change in k_ψ with changing acid concentration. In the present paper we