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ON THE PHOTOCYCLOADDITION OF DIMETHYL ACETYLENEDICARBOXYLATE TO BENZO(b)THIOPHENE

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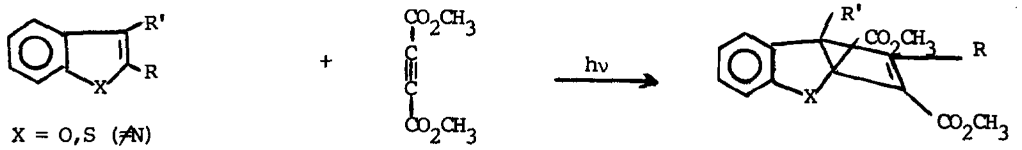
Summary: The products from the photocycloaddition of dimethyl acetylenedicarboxylate to substituted benzo(b)thiophenes are shown to depend on the irradiating wavelength.

Some ten years ago we first reported $(2+2)\pi$ cycloadditions of fused 6-5 heteroaromatic compounds to alkynes.[1] Characteristic is the photorearrangement, observed with benzo(b)thiophene and benzo(b)furan, [2,3] but not observed with alkylated indoles, (1).[4,5,6]



(1)

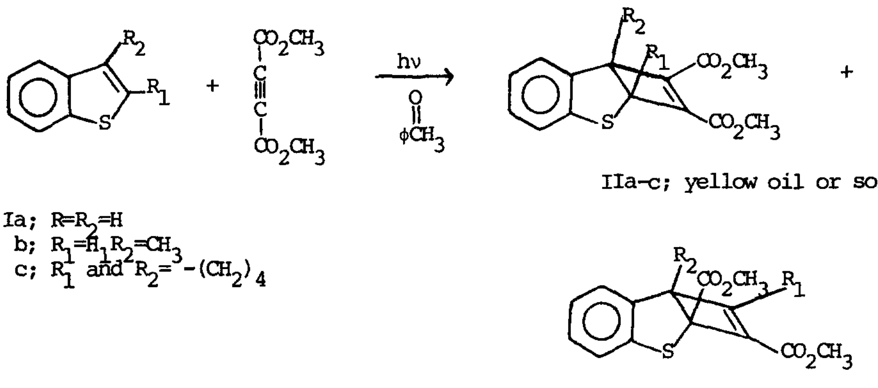
We have reinvestigated the sensitized photocycloaddition of benzo(b)thiophenes to dimethyl acetylenedicarboxylate in order to more fully determine its mechanis Reported herein are the properties of the first observed unrearranged 1:1 cycloadducts from alkyl substituted benzo(b)-thiophenes and the parent benzo(b)thiophene with acetylene dicarboxylate. Crucial to their capture is the discovery of an intramolecular charge transfer complex similar to that previously reported in the elegant work of Davis[4,5,6] but not previously observed with other fused heteroaromatic cyclobutenes. Under the conditions of the original experiments, absorption in this charge transfer complex leads to a facile conversion of the unrearranged adduct to the rearranged product.

In a typical experiment, benzo(b)thiophene (4.0 g, 0.03m) and dimethyl acetylenedicarboxylate (2 g, 0.14m) were irradiated, in benzene (30.0 ml) with acetophenone (0.75 g) as sensitizer, through Pyrex with a 450 watt medium pressure Hanovia mercury arc lamp, to give only the rearranged adduct, IIIa. When the reation was carried to substantial conversion in a Rayonet photochemical reactor using 300 nm lamps, a new yellow 1:1 adduct (IIa) was also obtained. IIa and IIIa were separated on Florisil by column chromatography. IIa is characterized by its N.M.R. spectrum (6H, 2 singlets; 3.85δ: 2H; H_1 and H_5 = AB multiplet, 4.78δ; 4H; multiplet; 7.20δ) and a concentration independent charge transfer absorption (λ_{max}^{CT} 366 nm; $\varepsilon=559$). In contrast, the rearranged adduct shows no such charge transfer absorption, but the typical absorption of a dihydrobenzo(b)thiophene below 280 nm.

Similar observations were made with 3-methylbenzo(b)thiophene Ib and dimethyl acetylenedicarboxylate. The unrearranged adduct IIb, characterized by its nmr spectrum (6H; 2 singlets, 3.83δ 3H; CH_3 = 1.79δ; 1H; 4.4δ)[7], showed the characteristic charge transfer absorption (λ_{max}^{CT} = 369 nm; ε=680). With tetrahydrodibenzo(b)thiophene, Ic, and dimethylacetylene dicarboxylate, the unrearranged adduct, IIc, was separated on fluorosil as a clear yellow solid. Its nmr spectrum showed two ester singlets (6H; 3.83δ; the four methylene groups; broad absorption centered at 2.08δ and the aromatic protons; 7.25δ). The UV (λ_{max}^{CT} = 366, ε=854) is shown in Figure 1.

These three experiments are summarized in Scheme I.

Scheme I



IIa-c; yellow oil or solid

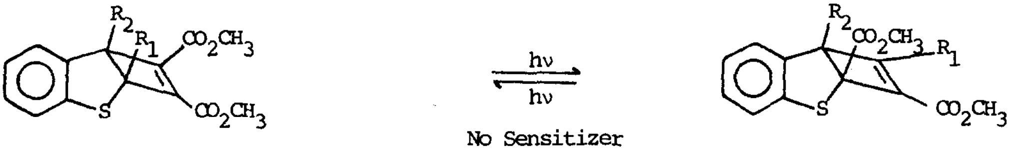
Ia; $R=R_2=H$
b; $R_1=H, R_2=CH_3$
c; R_1 and R_2= $-(CH_2)_4$

IIIa-c

The unrearranged adducts, IIa-c and the rearranged adducts IIIa-c were independently irradiated and converted to a mixture identical in composition of II and III, Table I. This establishes that a photostationary state exists between II and III.

Table I*

Photoequilibration Studies



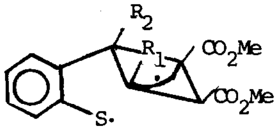
No Sensitizer

% IIa-c	IIIa-c
64	36
70	30
100	0

* Each photoequilibration was carried out at ambient temperatures in a Rayonet photochemical reactor, using 300 nm lamps, and in benzene solvent (N_2 purged) using concentrations between 1.3-1.5 x 10^{-3} M.

Illustrations of the differential absorptions of the unrearranged adducts, II, and the arranged adducts, III, are those obtained from tetrahydrodibenzo(b)thiophene and dimethyl acetylene dicarboxylate (IIc, IIIc), Figure 1. The rearranged adduct absorbs most strongly at the emission maximum of the 300 nm Rayonet lamps. Thus, under these conditions, only IIc is obtained, Table I. With the Hanovia 450 watt lamp, which has substantial emission at 366 nm, only unrearranged adduct IIc absorbs and, under these conditions, mostly rearranged adduct IIIc derives.

As we have established in prior studies$^{1-3}$, rearrangement of IIa-c $\rightleftharpoons$ IIIa-c procedes via an allylic biradical, IV, and product distribution



IV

derives from the typical electronic and steric effects affecting the reactions of these biradicals when competitive light absorption is possible. We have now identified the reason for the observation of only rearranged adducts, however, and indicate it to be the occurrence of non-competitve light absorption by the two stereoisomeric adducts.

Our conclusion is that the charge transfer absorptions of the unrearranged adducts, II control the observed products. Further mechanistic studies of these interesting wavelength dependent systems are in progress.

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7. In contrast, the rearranged adduct IIIb shows a singlet vinyl hydrogen at 6.82δ.

Acknowledgement

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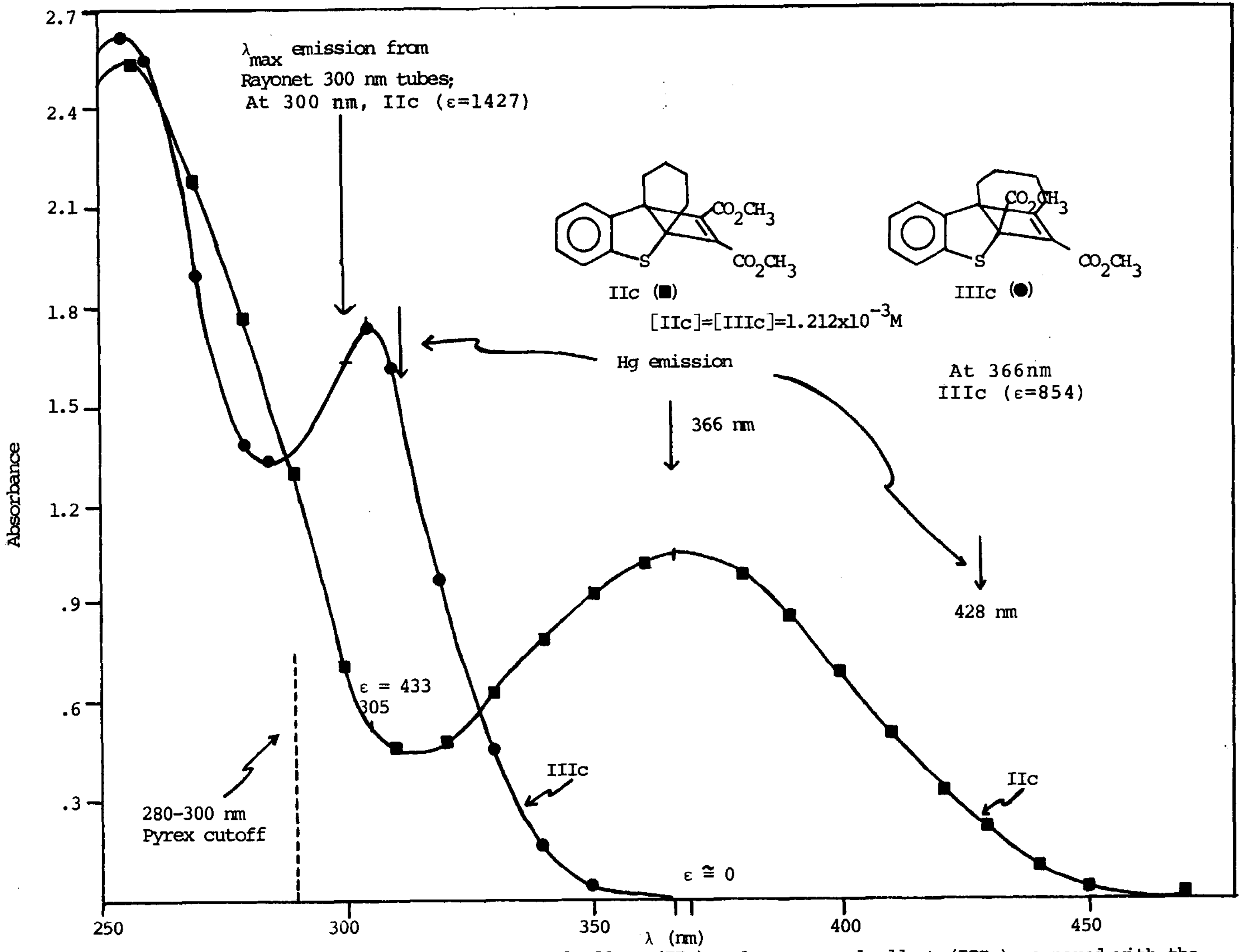

Figure 1. Absorption spectra of unrearranged adduct (IIc) and rearranged adduct (IIIc) compared with the emission characteristics of Rayonet 300 nm lamps and medium pressure mercury arcs.

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