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THE PHOTO-ADDITION OF DIPHENYLACETYLENE TO BENZO[b]THIOPHEN

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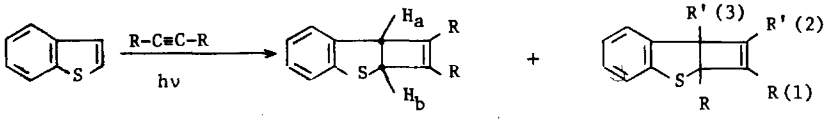
During studies of photo-additions of diphenylacetylene (DPA) to aromatic hydrocarbons we examined the effects of pyrex-filtered u.v. light on mixtures of DPA and benzo[b]thiophen (1). We now report the formation of two 1:1 photo-adducts (I) and (II) in these reactions, and the photo-isomerisation of adduct (I) to adduct (II). We also record differences in the thermal stabilities of adducts (I) and (II). Our findings have a bearing on the recent report by Neckers, Dopper and Wynberg (2) concerning the formation of adduct (III) from dimethyl acetylenedicarboxylate and benzo[b]thiophen. These authors did not adduce any evidence for the formation of the isomeric adduct (IV) in this reaction but the present results support their suggestion that (III) could be derived from a primary adduct (IV) by photo-isomerisation.



(I): R = Ph
(IV): R = $COOCH_3$

(II): R = Ph; R' = H
(III): R = $COOCH_3$; R' = H
(V): R = H; R' = Ph

A degassed solution of benzo[b]thiophen (10g) and DPA (1.78g) in benzene (80 ml) was irradiated in a pyrex reactor (3) with a Hanovia 250 W mercury medium pressure lamp in an atmosphere of "oxygen-free" nitrogen at 35-40° for 50 hours. Chromatography on activated silicic acid gave on elution with petrol (b.p. 60-80°) - benzene (95:5) adduct (II) (1.04g; 30%) followed by adduct (I) (0.11g; 3%). Adduct (I) separated from petrol (4) as colourless needles, m.p. 123-124° (5); adduct (II) crystallised from methanol as colourless needles, m.p. 152-154° (5). The structures assigned to these compounds rest on their spectral properties and on chemical degradations described below.

The mass spectrum (6) of (I)[m/e (% relative abundance): 313(7), 312(30; molecular ion), 311(5), 280(2), 279(3), 278(3), 235(4), 211(3), 210(10), 179(8), 178(100), 176(4), 152(3), 151(2), 135(2), 134(34); other peaks less than 2%] and the p.m.r. spectrum (9) [δ^{CDCl_3} : AB quartet with H_a at 5.02 (sl. broadened) H_b at 4.97, and J=4.5 Hz; multiplet at 6.9-7.7 (14H,Ar-H)] closely resemble those of other annellated 1,2-diphenylcyclobutenes formed in photo-additions with DPA (7,8). The stilbene group in (I) is reflected in the u.v. spectrum [$\lambda_{max}^{95\%\ EtOH}$ (ε) at 253 (18,200) and at 298 nm (15,000)(extending towards longer wavelengths, i.e., ε = 7,500 at 3250 nm) and a point of inflection (at 260 nm (16,400)].

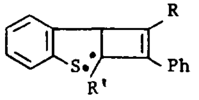
The most prominent peak in the mass spectrum of (II) corresponds to the loss of phenylacetylene (M-102)[m/e: 313(6), 312(33; molecular ion), 311(6), 280(8), 279(7), 278(6), 235(2), 234(3), 211(4), 210(100), 178(10), 165(4), 134(7); other peaks less than 3%], suggesting the presence of a 1-phenylcyclobutene ring. This is supported by the u.v. spectrum [$\lambda_{max}^{95\%\ EtOH}$ (ε) at 250(22,000), and at 305 nm (2,000). The chemical shift position of the upfield signal in the p.m.r. spectrum of (II) and its splitting pattern eliminate structure (V) [δ^{CDCl_3}: broadened doublet at 4.31(1H, 3-H);J=0.9Hz), doublet at 6.45 (1H, 2-H; J=0.95 Hz), and a multiplet at 7.0-7.7 (14H, Ar-H)].

Treatment of each adduct with W-5 Raney nickel (8.5-fold excess) at room temperature in benzene-ethanol (9.5:1) for 2 hours gave the same mixture (1.0:6.0:0.8 by g.l.c.). The major product crystallised from petrol (4) at -50° as colourless plates, m.p. 65°(5). Its spectra suggest that it is one of the stereoisomeric 1,2,3-triphenylcyclobutanes [δ^{CDCl_3} : multiplets at 2.6-3.2 (2H), 3.9-4.6(3H), and at 6.6-7.2(15H). m/e: 284 (1.5; molecular ion), 202(1), 193(2), 191(2), 181(40), 180(100), 179(60), 178(32), 166(8), 143(2), 142(6), 141(4), 115(6), 104(4), 103(3), 102(3); other peaks less than 1%]. The two minor products were not separated but their spectra suggest that they are stereoisomers of the major product. The conditions for these desulphurisations are critical, probably because they involve the hydrogenation and equilibration of several stereoisomeric 1,2,3-triphenylcyclobutenes and -cyclobutanes. At higher temperatures more complex mixtures are formed, apparently because of carbon-carbon bond hydrogenolysis.

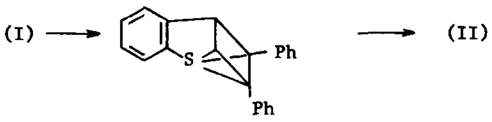
On treatment with copper bronze in boiling dimethyl formamide for two hours adduct (II) was converted to a mixture of 1,2-diphenylnaphthalene (*ca.* 75%), m.p. 114°, picrate m.p. 146-147°(10) [$\delta_{max}^{95\%\ EtOH}$ (ε) at 230 (29,500), 241(40,000), and at 287 nm (8,000)(*cf.* (10)); δ^{CDCl_3} : multiplet at 7.1-8.0, doublet at 7.57 (J=8.5 Hz), broadened doublet at 7.92 (J=8.5 Hz)], and 2-phenylbenzo[b]thiophen (*ca.* 5%), identified by direct comparison (11). Under these conditions adduct (I) was recovered quantitatively.

Subsequently it was found that (II) extrudes sulphur at 150° even in the absence of copper. Thus, when (II) was heated neat at 150° for 20 minutes analysis by g.l.c. showed the formation of 1,2-diphenylnaphthalene and 2-phenylbenzo[b]thiophen (ratio 25:1); at least three other products were detected by t.l.c. It is noteworthy that adduct (I) is thermally far more stable than adduct (II). For instance (I) was recovered almost quantitatively after being heated at 250° for 10 minutes and 65% was unchanged after (I) had been kept at 300° for 10 minutes when the formation of at least five other compounds, including 2,3-diphenylnaphthalene was indicated by g.l.c. This work will be described elsewhere but it is now concluded that the thermolysis of adducts (I) and (II) does not induce concerted rearrangements. This is consistent with orbital symmetry rules which forbid concerted mechanisms for the thermal rearrangements of adducts (I) - (IV) to the corresponding benzo[b]thiepins as suggested by Neckers and his collaborators(2).

The differences in the thermal stabilities of adducts (I) and (II) are consistent with stepwise homolytic carbon-sulphur bond fission leading to radicals such as (VI) and (VII) since the formation of the latter should be favoured by benzylic stabilisation.



(VI): R = Ph, R' = H
(VII): R = H, R' = Ph



(VIII)

In contrast to the thermal reactions of (I) the irradiation of (I) (degassed benzene solution, pyrex filter) produced adduct (II) rapidly and quantitatively. In view of the dramatic difference in the rates and selectivities of the thermal and photochemical reactions of (I) we prefer to formulate the latter reaction as involving the bridged species (VIII) [cf. (12)] rather than the radical (VI) as did Neckers, Dopper and Wynberg(2). On this basis the direction of the photochemical conversion of (I) to (II) is primarily caused by the difference in the ultraviolet absorption spectra of (I) and (II) above 300 nm. A full account of this work will be given elsewhere.

References

1. An outline of this work was presented during a symposium of the Heterocyclic Division of the Royal Australian Chemical Institute at Sydney in August 1968.
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5. Satisfactory microanalytical data have been obtained for this compound.
6. We thank Dr. C.S. Barnes, C.S.R. Research Laboratories Roseville, N.S.W. for several mass spectra.
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