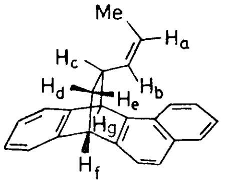
A Triplet State Path for Adduct Formation between Benz[*a*]anthracene and the Penta-1,3-dienes[1]

By JACK SALTIEL,* DAVID E. TOWNSEND, LEWIS L. METTS, MARK WRIGHTON, WARREN MUELLER, and RICHARD C. ROSANSKE

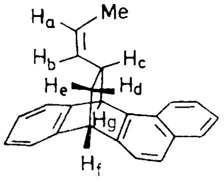
(*Department of Chemistry, Florida State University, Tallahassee, Florida* 32306)

Summary Irradiation of benzene solutions of benz[*a*]-anthracene in the presence of either *cis*- or *trans*-penta-1,3-diene gives distinct sets of four products involving addition of C(7) and C(12) of benz[*a*]anthracene triplets to the C(1)–C(2) bond of the dienes.

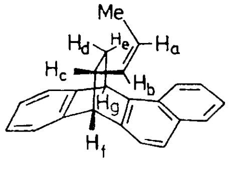
SINGLET exciplexes arise generally from the interaction of excited aromatic hydrocarbons with 1,3-dienes,[1,2] giving rise to fluorescence,[3,4] and adducts,[5,6] and providing additional pathways for reaction of one of the partners with other molecules.[4] The striking influence of substitution in anthracene on the orientation of addition has been attributed to changes in the polarity of the arene–diene singlet exciplex.[6] For example, 2,5-dimethylhexa-2,4-diene undergoes 1,4 addition ($4\pi_s + 4\pi_s$) exclusively only with the parent anthracene. 9,10-Difluoroanthracene gives both 1,4 and 1,2 addition ($4\pi_s + 2\pi_s$), while 9,10-dichloro- and 9,10-dicyanoanthracenes undergo only 1,2 addition on the diene system. The latter reaction has been attributed to stepwise collapse of the more polar singlet exciplexes.[6] Our observations with the benz[*a*]anthracene–penta-1,3-diene (*cis* and *trans*) (BA–*c*P and BA–*t*P) systems suggest the alternative explanation that 1,2 addition is a nonconcerted reaction involving the arene triplet state and/or a triplet arene–1,3-diene exciplex.



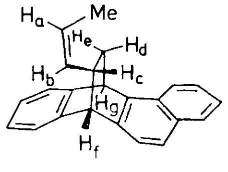
(1)



(2)



(3)



(4)

Irradiation (366 nm) of degassed benzene solutions of BA in the presence of either *c*P or *t*P gives distinct sets of similar amounts of four adducts (g.l.c.; n.m.r.). G.l.c. analysis at 185 °C on a $\frac{1}{8} \times 6$ in column packed with 5% Apiezon M on Chromosorb W gives two adduct peaks for *c*P in *ca.* 1 : 3 ratio and three adduct peaks for *t*P in *ca.* 1 : 2 : 1 ratio. Above 200 °C the adducts dissociate giving BA on g.l.c. analysis. Preliminary attempts to separate the adducts by liquid chromatography were unsuccessful. Structures (**1**)—(**4**) are assigned to the *c*P adducts based primarily on the n.m.r. spectrum of the mixture. Proton resonances were assigned by comparison with n.m.r. spectra of adducts obtained from BA–1,1,4-trideuterio-*cis*-penta-1,3-diene and from 7-deuteriobenz[*a*]anthracene–*c*P and by standard spin-decoupling techniques (*cf.* Figure).

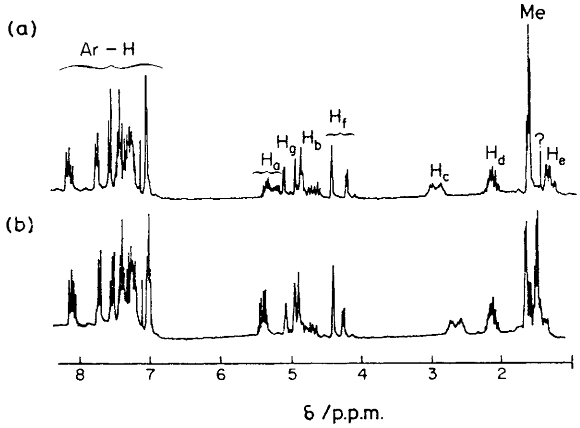


FIGURE. The 270 MHz ^1H n.m.r. spectra ($CDCl_3$) of the adduct mixtures obtained with benz[*a*]anthracene and (a) *cis*-penta-1,3-diene; (b) *trans*-penta-1,3-diene.

The n.m.r. spectrum of the adducts obtained with *t*P is very similar to that obtained with *c*P (Figure). The only difference in the structures is that the *trans* stereochemistry at the C(3)–C(4) diene double bond is retained. This excludes adduct formation by addition of 1,3-diene triplets to BA. Furthermore, formation of 1,3-diene triplets by excitation transfer from BA is not a significant process since no *cis* ⇌ *trans* photoisomerization occurs during these reactions ($\phi_{c\rightarrow t}$, $\phi_{t\rightarrow c} \leqslant 0.01$).

BA fluorescence intensity and lifetime measurements in the presence of *cis*-penta-1,3-diene reveal a reversibly formed singlet exciplex.[7] If all decay from this exciplex gave adducts, the adduct quantum yield from the singlet pathway can be calculated from the rate parameters in ref. 7 using equation (1); at [D] = 0·10 M, $\phi_s^{max} < 0.01$.[7] Since the measured quantum yield at this concentration is 0·15 a singlet pathway for adduct formation is not significant.[7]

$$\phi_s^{max} = k_y k_e[D]/\lambda_1\lambda_2 \qquad (1)$$

Quantum yields for benz[*a*]anthracene disappearance were determined at 30 °C using a merry-go-round apparatus with a 366 nm filter system.[8] The benzophenone-sensitized isomerization of *cis*-penta-1,3-diene was used as the actinometer.[9] The quantum yields vary between 0·14 and 0·16 for $0.050\,M \leqslant [cP] \leqslant 1.50\,M$ and $[BA] = 8.3 \times 10^{-4}\,M$.

Fluorenone and Michler's ketone photosensitize the addition of BA to *c*P and *t*P yielding adduct mixtures identical (g.l.c.; n.m.r.) to those obtained upon direct excitation of BA. The quantum yield for the fluorenone-sensitized (405 nm) adduct formation is independent of light intensity (3 fold change), excluding BA singlet involvement through triplet–triplet annihilation. The fluorenone-sensitized isomerization of *cis*-penta-1,3-diene was used for actinometry.[10] For a benzene solution containing BA ($1\cdot3 \times 10^{-3}$ M), *c*P (0·20 M), and fluorenone ($1\cdot0 \times 10^{-3}$ M), the quantum yield of adduct formation is $0\cdot11_6$ and that of diene *cis*→*trans* isomerization is 0·29. Owing to the high pentadiene concentration *cis*→*trans* isomerization gives insufficient amounts (0·39% *t*P in this experiment) of the other diene isomer to alter adduct compositions. Excitation transfer from fluorenone (E_T 53·3 kcal mol^{-1} [11]) to *c*P (E_T 57·3 kcal mol^{-1} [12]), being endothermic, is expected to be much less efficient than exothermic excitation transfer to BA (E_T 47 kcal mol^{-1} [11]). Correcting for the intersystem crossing efficiency of fluorenone (0·93),[9] and for the fraction of fluorenone triplets which transfer excitation to *c*P instead of to BA gives $f_{ad} = 0\cdot29$ as the fraction of ^{3}BA–*c*P interactions giving adducts. Assuming that the direct excitation mechanism also involves BA triplet addition to *c*P, correction of the observed quantum yield for the intersystem crossing efficiency of BA (0·54†) gives $f_{ad} = 0\cdot31$, in excellent agreement with the value obtained from the fluorenone experiment. Rate constants for the quenching of BA and 7-deuterio-BA triplets by *c*P in benzene, determined by flash kinetic spectroscopy, are $2\cdot24 \times 10^4$ and $2\cdot03 \times 10^4$ l mol^{-1} s^{-1}, respectively.

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† The intersystem crossing quantum yield of BA is concentration dependent (H. Labhart, *Helv. Chim. Acta.*, 1964, **47**, 2279; J. Saltiel and M. Wrighton, unpublished results). A value of 0·54 for the concentration used in benzene was employed.

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