RETRO-DIELS–ALDER REACTION INDUCED BY π,π* EXCITATION AND BY ELECTRON IMPACT

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Abstract—The title photoreaction is observed upon irradiation of styrene- and indene-anthracene adducts giving anthracene photodimers, while other Diels–Alder adducts of anthracene are photostable. The dissociation is rationalized by assuming a stepwise mechanism involving a diradical intermediate. This behaviour shows that a close correlation exists between cation radicals produced on electron impact and π,π* excited species.

WHILE thermal dissociation of Diels–Alder adducts is well known,[1] there is only one example of such retrogression induced photochemically: viz the photolysis of bicyclo[2.2.1]heptadiene yielding cyclopentadiene and acetylene.[2] We now record a photochemical retro-Diels–Alder reaction observed with certain dihydroethano-anthracene derivatives.

When a 1% solution of styrene–anthracene adduct (I) in ethanol was irradiated with a high-pressure mercury arc for 20 hr (65% conversion), a photodimer of anthracene (II) was obtained in a 60% yield. Monitoring the reaction by UV absorption indicated the formation of anthracene (340, 357 and 376 nm) and styrene (280 and 292 nm) both in low yields (<1%). Another adduct of indene and anthracene (III) photolysed rather sluggishly (20% conversion after 30 hr) to give dianthracene II in a 70% yield together with a trace amount of anthracene. Indene was not detected among the photolysates. This would be due to facile secondary photochemical reactions.†
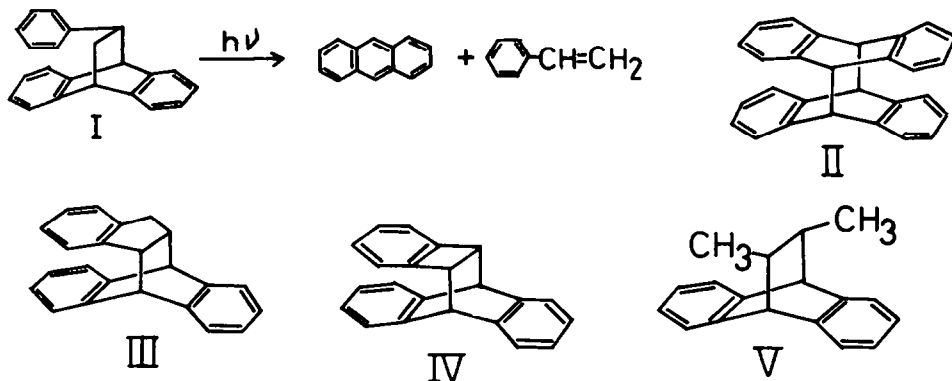

† Polystyrene and polyindene was isolated in an amount corresponding II in each case. See Experimental.

Certain diene adducts are known to equilibrate in solution with the diene and the corresponding olefin component,[3] but careful examination revealed that such thermal dissociation of I and III was completely absent under the reaction conditions. Thus the foregoing observations should be ascribed to *photochemical* cleavage of the adducts affording anthracene and olefins, the former being further dimerized photochemically.

On the other hand, benzocyclobutadiene-anthracene adduct (IV) was found to be remarkably stable under similar photolytic conditions. Although a trace amount of anthracene was detected by UV absorption, dianthracene (II) was not isolated even after 72 hr irradiation. This was also the case with *trans*-2-butene adduct (V) and exposure for 120 hr resulted in over 85% recovery of V.

Conservation rule of orbital symmetries suggests that this type of dissociation is forbidden *photochemically*,[4]† and the observed reactivities would be explained by either a stepwise mechanism involving a diradical intermediate produced *via* the electronically excited states (S_1 or T_1) or, alternatively, by a concerted mechanism through the vibrationally excited ground states.‡ To elucidate this point, an optically active ester VIb§ was prepared and subjected to similar reaction conditions. Irradiation of VIb ($[\alpha]_D^{20}$ +4·93°) derived from the carboxylic acid VIa ($[\alpha]_D^{20}$ −30·5°) for 10 hr followed by workup gave 16% of II and 38% of VIb. The unchanged ester VIb showed feeble dextrorotation ($[\alpha]_D^{20} \ll$ +1·5°). Careful hydrolysis of this sample was conducted at room temperature to give VIa ($[\alpha]_D^{20}$ −1·84°). The definite reduction of the rotatory value would be accounted for by assuming the intermediacy of a fairly stable diradical VII. Rotation around the C_{11}—C_{12} bond (as shown by an arrow) would bring about racemization of the starting material. The diradicals similar to VII would probably be the intermediate in the present photocleavage.

VIa, R = H

VIb, R = CH$_3$

VII
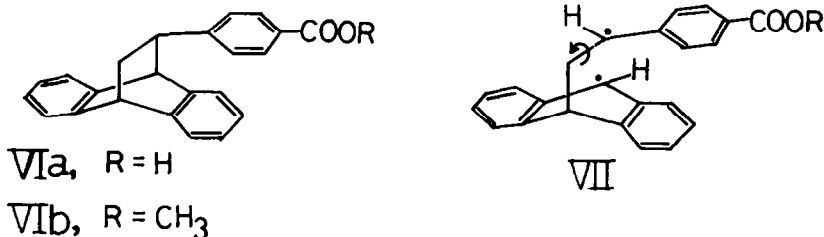
Interest has recently been focused on the similarity in behaviour of excited species produced by irradiation and by electron impact.[7] However, most of photochemical studies have dealt with the molecules having an n,π* state and little attention has been given to the correspondence between π,π* states.‖ Table 1 summarizes the mass spectra of I, III, IV and V at ionization voltage of 20 and 80 eV. As expected, retro-Diels–Alder fragmentation[8] appeared to be the only prominent pathway particularly

† For photochemical Diels–Alder type reaction (direct irradiation), see Ref. 5.

‡ Because collisional deactivation of such a state is normally very rapid in solution, it seems unlikely. Possible participation of hot ground state to chemical reaction, however, has been recorded (Ref. 6).

§ The absolute configuration is unknown.

‖ Correlation between photochemical and mass spectrometric decomposition of benzylcyclopropane was discussed (Ref. 7a).

at the low ionization voltage. It should be noted that there are marked differences between the behaviour of I or III and that of IV or V. Mass spectra of photochemically stable adducts (IV and V) showed the parent peaks (M^+) and the metastable peaks arising from the retro-Diels–Alder transition ($M^+ \rightarrow 178^+$ (anthracene)). In contrast,

TABLE 1. MASS SPECTROMETRIC RETRO-DIELS–ALDER FRAGMENTATION[a]

Compound[b, c]	m/e	% of Base peak	
		20 eV[d]	80 eV
I	282 (M^+)	0	0
	178 ($C_{14}H_{10}^+$)	100	100
	104 ($C_8H_8^+$)	0·95	2·7
III	294 (M^+)	0	0
	178 ($C_{14}H_{10}^+$)	100	100
	116 ($C_9H_8^+$)	13	9·3
IV	280 (M^+)	26	13
	178 ($C_{14}H_{10}^+$)	100	100
	113 (metastable[e])	0·26	0
	102 ($C_8H_6^+$)	2·6	10
V	234 (M^+)	1·9	0·74
	178 ($C_{14}H_{10}^+$)	100	100
	135 (metastable[e])	0·20	tr
	56 ($C_4H_8^+$)	0	0·50

[a] Spectra were taken on Hitachi RMU 6D mass spectrometer at probe temp of 200° using heated inlet systems.

[b] All the compounds were stable under these conditions, and no appreciable dissociations were observed at 200° in a sealed tube.

[c] Adduct VIb also gave neither the parent peak nor the metastable one (both at 20 and 80 eV).

[d] At lower voltage retro-Diels–Alder reaction was practically an exclusive fragmentation process.

[e] Transition due to $M^+ \rightarrow C_{14}H_{10}^+$.

photo-labile adducts I and III gave neither the molecular peaks nor the respective metastable ones even at 20 eV. This would imply that the molecular ions produced on electron bombardment are likely to decompose instantaneously by elimination of olefins. Thus it should be concluded that these results demonstrate qualitatively an intimate correlation between the stability of the π,π^* states of Diels–Alder adducts and that of mass spectrometric molecular ions.

EXPERIMENTAL

All m.ps are corrected. NMR spectra were obtained in $CDCl_3$ soln (TMS as an internal standard) using JEOL C-60-H spectrometer. Anthracene adducts I,[9] III[10] and IV[10] were prepared by the known procedures. UV maxima of I (EtOH): λ 253, 259, 265 and 272 nm (log ε 2·94, 3·04, 3·19 and 3·24, resp.). III: λ 244, 249, 255, 261, 269 and 276 nm (log ε 3·36, 3·49, 3·65, 3·71, 3·74 and 3·75). IV: λ 262s, 268 and 274 nm (log ε 3·40, 3·57 and 3·62). Other anthracene adducts were prepared as shown below.

9,10-*Dihydro*-9,10-*bis(hydroxymethyl)ethano]anthracene* (VIII). To a soln of 9,10-dihydro-9,10-[*trans*-11,12-bis(carbomethoxy)ethano] anthracene[11] (16·5 g, 51 mmoles) in anhyd ether (70 ml) was added dropwise with stirring an ethereal soln (30 ml) containing LAH (3·0 g, 79 mmoles) in the course of 30 min. After the exothermic reaction had ceased, the mixture was heated under reflux for an additional

1 hr. Excess of LAH was destroyed with dil HCl aq and the ethereal layer was separated, washed and dried (Na$_2$SO$_4$). Concentration *in vacuo* gave a crystalline mass, which was recrystallized from MeOH to afford pure 9,10-*dihydro*-9,10-[trans-11,12-*bis(hydroxymethyl)ethano*]*anthracene* (VIII; 9·0 g, 67% yield). m.p. 198·5–199·5°; IR (KBr): 3400 cm^{-1} (OH); NMR: δ 7·2–6·9 (m, 8, aromatics), 4·20 (narrow d, 2, C$_{9, 10}$—H), 3·5–3·0 (m, 4, —CH$_2$O—), 1·65 (s, 2, OH) and 1·8–1·2 ppm (broad m, 2, C$_{11, 12}$—H). (Found: C, 81·0; H, 6·8. C$_{18}$H$_{18}$O$_2$ requires: C, 81·2; H, 6·8%).

9,10-*Dihydro*-9,10-[trans-11,12-*bis(tosyloxymethyl)ethano*]*anthracene* (IX). A soln of p-toluenesulphonyl chloride (9·5 g, 46 mmoles) in pyridine (20 ml) was carefully added to an ice-cooled soln of VIII (6·5 g, 24 mmoles) in pyridine (10 ml) during 3 hr, the reaction temp being kept below 10°. After being treated with water, the mixture was extracted with benzene. The combined extracts were washed, dried (Na$_2$SO$_4$) and concentrated *in vacuo* to yield a solid mass. Recrystallization from EtOH afforded an analytical sample of 9,10-*dihydro*-9,10-[trans-11,12-*bis(tosyloxymethyl)ethano*]*anthracene* (IX; 6·2 g, 46%), m.p. 125·5–126·5°; IR (KBr): 1370, 1180 cm^{-1} (—OSO$_2$—); NMR: δ 7·8–6·9 (m, 16, aromatics), 4·20 (narrow d, 2, C$_{9, 10}$—H), 3·8–3·1 (m, 4, CH$_2$OTs), 2·45 (s, 6, Me) and 1·8–1·4 ppm (m, 2, C$_{11, 12}$—H). (Found: C, 66·8; H, 5·6. C$_{32}$H$_{30}$O$_6$S$_2$ requires: C, 66·9; H, 5·3%).

9,10-*Dihydro*-9,10-(trans-11,12-*dimethylethano*)*anthracene* (V). A soln of LAH (4·0 g, 105 mmoles) in dry THF (30 ml) was added dropwise to a well-stirred soln of IX (6·2 g, 11 mmoles) in THF (40 ml) at room temp during 2 hr, and the mixture was heated under reflux for 24 hr and cooled. Treatment with NH$_4$Cl aq followed by workup in a usual manner gave a crude solid mass, which was dissolved in a small amount of benzene and passed through an alumina column. Recrystallization of the resulting hydrocarbon from n-hexane yielded 9,10-*dihydro*-9,10-(trans-11,12-*dimethylethano*)*anthracene* (V) as colourless crystals (2·2 g, 86% yield), m.p. 89·0–89·5°; NMR δ 7·3–6·8 (A$_2$B$_2$ pattern, 8, aromatics), 3·80 (narrow d, 2, C$_{9, 10}$—H), 1·5–1·0 (m, 2, C$_{11-12}$—H) and 0·75 ppm (d, 6, $J = 6$ Hz, Me); UV (EtOH): λ 266 and 273 nm (log ε 3·24 and 3·31, resp.). (Found: C, 92·2; H, 8·0. C$_{18}$H$_{18}$ requires: C, 92·3; H, 7·7%).

Photolysis of Diels–Alder adducts. A 1% soln of each adduct in EtOH was placed in a quartz tube (1 × 8 cm) under N$_2$ atm and irradiated externally by means of a 200W high-pressure Hg lamp (no filter) at a distance of 2 cm at room temp. Crystalline dianthracene II pptd was collected by filtration and identified by comparison of the IR spectrum with the one of authentic specimen.[12] Yields as well as conversions were calculated on the basis of the weight of the starting materials which was not recovered upon alumina column chromatography of the photolysates. Photolysis of I or III followed by chromatographic separation (alumina) yielded considerable amounts of polymeric fractions, the IR spectra of which showed close resemblance to ones of polystyrene[13] and polyindene,[14] respectively. Ether bands around 1100 cm^{-1} indicated that solvent EtOH was partly incorporated into the polymer chains.

9,10-*Dihydro*-9,10-(11-p-bromophenyl)*ethanoanthracene* (X). A mixture of freshly distilled p-bromostyrene (9·5 g, 52 mmoles), anthracene (8·0 g, 45 mmoles), p-t-butylcatechol (50 mg) in xylene (80 ml) was heated at 250° in an autoclave for 12 hr. After cooling, pptd anthracene was removed by filtration and the filtrate was treated with maleic anhydride to remove anthracene completely.[15] The resulting viscous oil was distilled *in vacuo* to recover unchanged p-bromostyrene (4·5 g). The residue was dissolved in minimum amount of benzene and chromatographed on alumina column. Benzene elution gave 9,10-*dihydro*-9,10-(11-p-bromophenyl)*ethano anthracene* (X) as colourless crystals, which was recrystallized from EtOH to afford the pure sample (4·1 g, 41%), m.p. 138·0–139·5°. NMR: δ 7·3–6·2 (m, 12, aromatics), 4·3 (t, 1, C$_9$—H), 4·0 (d, 1, C$_{10}$—H), 3·2–2·9 (m, 1, C$_{11}$—H) and 2·4–1·4 ppm (m, 2, C$_{12}$-H$_2$). (Found: C, 73·0; H, 4·9. C$_{22}$H$_{17}$Br requires: C, 73·1; H, 4·8%).

9,10-*Dihydro*-9,10-(11-phenyl)*ethanoanthracene*-4′-*carboxylic acid* (VIa). A soln of X (4·0 g, 11 mmoles) in dry THF (10 ml) was added dropwise to Mg (1·0 g, 41 mg-atoms) covered with a small amount of THF at room temp, and the mixture was heated under reflux for 2 hr under N$_2$ atm. After cooling, dry CO$_2$ gas was bubbled into the mixture in the course of 3 hr at room temp. Resulting carbonate salt was treated with a small amount of dil HCl aq and then extracted with 2N NaOH aq. The extracts were acidified again with dil HCl aq and extracted with benzene repeatedly. The benzene soln was dried (Na$_2$SO$_4$) and concentrated *in vacuo* to afford crude carboxylic acid. Recrystallization from EtOH gave 2·1 g (58%) of 9,10-*dihydro*-9,10-(11-phenyl)*ethanoanthracene*-4′-*carboxylic acid* (VIa), m.p. 242·5–244·0°; IR (KBr): 1685 cm^{-1} (C=O). NMR: δ 8·7 (s, 1, COOH), 7·9–6·6 (m, 12, aromatics), 4·4 (narrow 5, 1, C$_9$—H), 4·2 (narrow d, 1, C$_{10}$—H), 3·3–3·1 (m, 1, C$_{11}$—H) and 2·5–1·5 ppm (m, 2, C$_{12}$-H$_2$). (Found: C, 84·8; H, 5·5. C$_{23}$H$_{18}$O$_2$ requires: C, 84·6; H, 5·6%).

Optical resolution of carboxylic acid (VIa). A soln of VIa (9·0 g, 28 mmoles) and (R)- (—)-α-phenethylamine (4·0 g, 30 mmoles, [α]$_D^{20}$ —39·9° in CHCl$_3$) in 400 ml of MeOH was allowed to stand for 20 hr to

afford crystalline salt (4·7 g), m.p. 207–216° and $[\alpha]_D^{20}$ +87·5° (c 0·72, CHCl₃). Treatment with dil HCl, extraction with CHCl₃ and following recrystallizations from EtOH gave a sample showing $[\alpha]_D^{20}$ −30·5° (c 1·83, CHCl₃), m.p. 243·5–245° (yield 1·4 g). (Found: C, 84·4; H, 5·5. $C_{23}H_{18}O_2$ requires: C, 84·6; H, 5·6%).

Treatment of VIa with diazomethane in ethereal soln in a usual manner gave 9,10-*dihydro*-9,10-(11-*phenyl)ethanoanthracene-4'-carboxylic acid methyl ester* (VIb) in an optically active form, $[\alpha]_D^{20}$ +4·93° (c 1·20, CHCl₃) and m.p. 166–167° (from EtOH); IR (KBr): 1720 cm⁻¹ (C=O); UV (EtOH): λ 250, 273 and 284 nm (log ε 4·25, 3·65 and 3·05). NMR: δ 7·8–6·5 (m, 12, aromatics), 4·4 (narrow t, 1, C₉—H), 4·1 (narrow d, 1, C₁₀—H), 3·8 (s, 3, Me), 3·3–3·1 (m, 1, C₁₁—H) and 2·3–1·6 ppm (m, 2, C₁₂—H₂). (Found: C, 84·5; H, 6·0. $C_{24}H_{20}O_2$ requires: C, 84·7; H, 5·9%).

Photolysis of optically active ester (VIb). A 1% EtOH soln containing 177 mg (0·52 mmole) of optically active VIb was irradiated as described above for 10 hr. After removal of pptd II (15 mg, 16% yield) by filtration, the filtrate was concentrated *in vacuo*. Alumina column chromatography of the residue using benzene as an eluant gave unchanged ester (67 mg, 38% recovery), m.p. 160–165° and $[\alpha]_D^{20}$ ≪ +1·5° (c 1·34, CHCl₃); IR and NMR as well as elemental analyses supported the structure. Stirring with 2N KOHaq at room temp for 20 hr followed by careful workup yielded free acid VIa (44 mg, 68%), m.p. 239–244° and $[\alpha]_D^{20}$ −1·84° (c 0·88, CHCl₃), which gave correct elemental analyses; IR (CHCl₃) and NMR were superimposable on those of the starting acid. The workup conditions did not cause recemization of VIa, which was confirmed by a control experiment.

REFERENCES

[1] H. Kwart and K. King, *Chem. Rev.* **68**, 415 (1968).
[2] B. B. Roquitte, *J. Am. Chem. Soc.* **85**, 3700 (1963).
[3] M. C. Kloetzel, *Org. Reactions* **4**, 1 (1948).
[4] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 2045 (1965).
[5] [a] W. R. Roth and B. Peltzer, *Angew. Chem.* **76**, 378 (1964);
    [b] J. Zirner and S. Winstein, *Proc. Chem. Soc.* 235 (1964);
    [c] O. L. Chapman, G. W. Borden, R. W. King and B. Winkler, *J. Am. Chem. Soc.* **86**, 2660 (1964);
    [d] J. A. Elix, M. V. Sargent and F. Sondheimer, *Ibid.* **89**, 5081 (1967).
[6] [a] W. G. Dauben, R. L. Cargill, R. M. Coates and J. Saltiel, *Ibid.* **88**, 2742 (1966);
    [b] J. M. Holovka and P. F. Gardner, *Ibid.* **89**, 6390 (1967).
[7] For example, [a] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner and P. D'Angelo, *Ibid.* **87**, 4097 (1965);
    [b] A. L. Burlingame, C. Fenselau, W. J. Richter, W. G. Dauben, G. W. Shaffer and N. D. Vietmeyer, *Ibid.* **89**, 3346 (1967);
    [c] N. J. Turro, D. S. Weiss, W. F. Haddon and F. W. McLafferty, *Ibid.* **89**, 3370 (1967);
    [d] M. M. Bursey, L. R. Dusold and A. Padwa, *Tetrahedron Letters* 2649 (1967).
[8] H. Budzikiewicz, J. I. Brauman and C. Djerrassi, *Tetrahedron* **21**, 1855 (1965).
[9] W. E. Noland, M. S. Baker and H. I. Freeman, *J. Am. Chem. Soc.* **78**, 2233 (1956).
[10] K. Sisido, R. Noyori, N. Kôzaki and H. Nozaki, *Tetrahedron* **19**, 1185 (1963).
[11] W. E. Bachman and L. B. Scott, *J. Am. Chem. Soc.* **70**, 1460 (1948).
[12] C. A. Coulson, L. E. Orgel, W. Taylor and J. Weiss, *J. Chem. Soc.* 2961 (1955).
[13] R. G. W. Norrish and J. P. Simons, *Proc. Roy. Soc.* (London) A**251**, 4 (1959).
[14] J. Bowyer and Q. N. Porter, *Austr. J. Chem.* **19**, 1455 (1966).
[15] E. Clar, *Ber. Dtsch. Chem. Ges.* **64**, 2194 (1931).