Tetrahedron, 1963, Vol. 19, pp. 1185 to 1188. Pergamon Press Ltd. Printed in Northern Ireland

9,10-BRIDGED 9,10-DIHYDROANTHRACENES

K. Sisido, R. Noyori, N. Kôzaki and H. Nozaki
Department of Industrial Chemistry, Kyôto University, Japan

(*Received* 25 *February* 1963)

Abstract—Anthracene reacts with benzocyclobutene at 300° to give 9,10-dihydro-9,10-*o*-xylyleneanthracene (I). With benzocyclobutadiene *in situ* in boiling ethanol a Diels-Alder adduct (II) is obtained. The reaction of anthracene with indene at 280° affords the known 1,2-adduct (IV), to which convincing evidences of the structure have been given.

9,10-DIHYDRO-9,10-*o*-XYLYLENEANTHRACENE (I) has previously[1,2] been prepared by the reaction of anthracene with *o*-xylylene produced by pyrolyzing 1,3-dihydroisothiaaphthene-2,2-dioxide.[3] As known already, *o*-xylylene can conveniently be obtained by thermal isomerization of benzocyclobutene.[4] We have now succeeded in preparing I by heating an equimolar mixture of anthracene and benzocyclobutene at 300° in the presence or absence of diethyl phthalate as a solvent with 30% and 11% yields, respectively.

A 1 : 1 adduct (II) of anthracene and benzocyclobutadiene was isolated in 15% yield, when debromination of 1,2-dibromobenzocyclobutene[5,6] was carried out in the presence of a large excess of anthracene by means of zinc dust suspended in ethanol. Spectral data of II including N.M.R. spectrum gave conclusive evidence regarding the structure given.[7,8]

The *o*-xylylene group of the hydrocarbon I has been considered to be rapidly flipping over two "A" conformations having no Baeyer strain.[2] In the case of the hydrocarbon II, a new cross linking inhibits completely this conformational exchange. Since the U.V. spectra of both hydrocarbons (I and II) are fairly similar,[9] the Frank-Condon principle may be cited as warranting our previous supposition that the "B"

---

[1] K. Sisido, Y. Udô and H. Nozaki, *J. Org. Chem.* **26**, 584 (1961).

[2] K. Sisido, R. Noyori and H. Nozaki, *J. Amer. Chem. Soc.* **84**, 3562 (1962).

[3] M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.* **81**, 4266 (1959).

[4] F. R. Jensen, W. E. Coleman and A. J. Berlin, *Tetrahedron Letters* No. 1, 15 (1962).

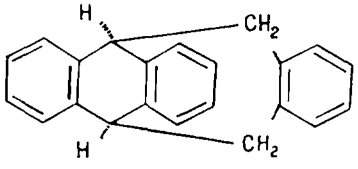
[5] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **78**, 500 (1956); [b] M. P. Cava and D. R. Napier, *Ibid.* **79**, 1701 (1957); [c] M. Avram, D. Dinu and C. D. Nenitzescu, *Chem. & Ind.* 257 (1959); [d] M. Avram, G. D. Mateescu, D. Dinu, I. G. Dinulescu and C. D. Nenitzescu, *Acad. Rep. Populare Romine, Studii Cercetari Chim.* **9**, 435 (1961); *Chem. Abstr.* **57**, 4605 (1962); [e] M. Avram, I. G. Dinulescu, D. Dinu and C. D. Nenitzescu, *Chem. & Ind.* 555 (1962).

[6] For Diels-Alder reactions of benzocyclobutadiene, see [a] M. P. Cava and M. J. Mitchell, *J. Amer. Chem. Soc.* **81**, 5409 (1959); [b] C. D. Nenitzescu, M. Avram and D. Dinu, *Chem. Ber.* **90**, 2541 (1957); [c] M. P. Cava and R. Pohlke, *J. Org. Chem.* **27**, 1564 (1962).

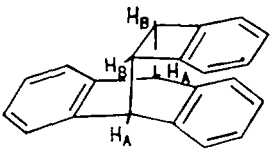
[7] All N.M.R. spectra in this paper were obtained on a 60 mc Varian instrument with tetramethylsilane as an internal reference and are given in the order of peak position in p.p.m. from the reference signal, area in parentheses, splitting and assignment.

[8] N.M.R. data of II measured in carbon tetrachloride are about 7·0 (6). multiplet, aromatic hydrogens; 4·43 (1), narrow multiplet, H_A protons; 3·61 (1), narrow quartet, H_B protons.

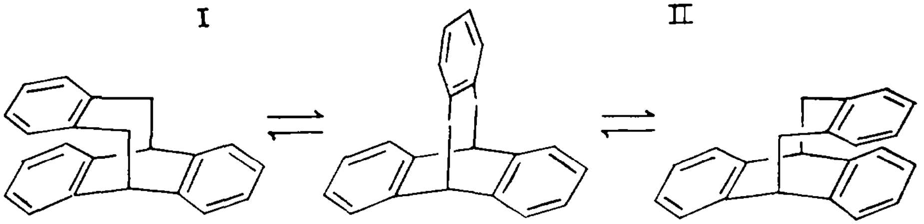
[9] In 99% ethanol λ_{max} (log ε) of I are 252 (3·33), 260sh. (3·01), 266·5 (3·16) and 274 mμ (3·21). Maxima of II in the same solvent are 262 sh. (3·40), 267·5 (3·57) and 274 mμ (3·62).



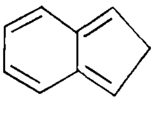
I



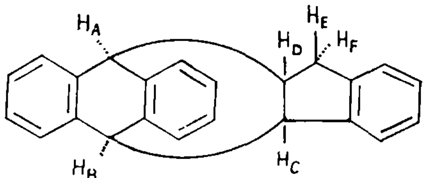
II



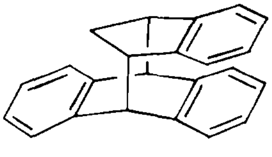
IA IB IA'



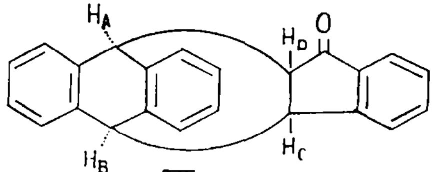
III



IV



V



VI

conformation of I would constitute an energy barrier rather than an energy minimum.[10]

The Diels-Alder addition of maleic anhydride to indene has been explained by Alder[11] as involving the initial isomerization of indene to isoindene (III), which is an *o*-xylylene derivative. Indene-anthracene adduct[12] is already known and formula IV has been assigned to it. Published data are, however, not enough to exclude the possibility of the structure V, which should be formed by the addition of isoindene to anthracene and would provide us another example of the rigid "A" conformation.

The N.M.R. spectra[13] of the indene-anthracene adduct and of a novel ketone (VI)

---

[10] Roberts and Westheimer have estimated the strain energy of the transition state for conversion of the boat and chair conformations of 1,6-dichlorocyclooctadiene-1,5 (see F. H. Westheimer, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) John Wiley, New York (1956). If analogous arguments are applicable to the hydrocarbon I, the "A" conformation should be roughly 10 kcal/mole more stable than the "B" conformation.

[11a] K. Alder, F. Pascher and H. Vagt, *Ber. Dtsch. Chem. Ges.* **75**, 1501 (1942); [b] K. Alder and M. Fremery, *Tetrahedron* **14**, 190 (1961).

[12] E. Mameli, A. Pancotto and V. Crestani, *Gazz. Chim. Ital.* **67**, 669 (1937).

[13] N.M.R. data of IV in carbon tetrachloride are about 7·10 (8), multiplet, aromatic hydrogens; 6·75 (4), multiplet, aromatic hydrogens; 4·40 (1), doublet, H_A or H_B proton; 4·12 (1), doublet, H_B or H_A proton; 3·67 (1), multiplet, H_C proton; 3·05 (1), multiplet, H_E or H_F proton; 2·88 (1), multiplet, H_E or H_F proton; 2·51 (1), multiplet, H_D proton. NMR data of VI in deuterochloroform are 7·30 (8), multiplet, aromatic hydrogens; 6·81 (4), multiplet, aromatic hydrogens; 4·80 (1), doublet, H_B or H_A proton; 4·63 (1), doublet, H_A or H_B proton; 3·82 (1), poorly resolved quartet, H_D proton; 3·12 (1), quartet, H_C proton. $J_{AD} = J_{BC} = 3·5$ c.p.s. and $J_{CD} = 7·5$ c.p.s.

produced by oxidizing IV gave unquestionable supports in favour of formulas IV and VI, respectively, leaving the formula V meaningless. The abnormal Diels-Alder reaction of indene with maleic anhydride has recently been re-interpreted by Berson and Patton.[14] A cyclo-addition and following skeletal rearrangement are assumed instead of the initial formation of isoindene. The present work may be taken as a token warranting the latter authors' view.

EXPERIMENTAL

All temps are uncorrected. Microanalyses were performed by Miss Kenko Ogawa.

Reaction of benzocyclobutene with anthracene. A solution of 1·0 g (9·6 mmoles) benzocyclobutene[11b] and 2·0 g (10·6 mmoles) anthracene in 20 ml diethyl phthalate was placed in a sealed tube filled with nitrogen and heated at 300° for 24 hr. The solvent was removed by hydrolyzing with 80 ml of 15% sodium hydroxide solution (15 hr at 100°) and the product purified by column chromatography on alumina. Two recrystallizations from ethanol afforded 810 mg (30%) of 9,10-dihydro-9,10-*o*-xylyleneanthracene (I), m.p. and mixed m.p. 179°.

In the absence of diethyl phthalate similar reaction at 300° for 48 hr gave 11% yield of I.

Diels-Alder reaction of benzocyclobutadiene with anthracene. A solution of 5 g (19 mmoles) 1,2-dibromobenzocyclobutene in 350 ml of 99% ethanol was added slowly in the course of 7 hr to a mixture of 10 g (56 mmoles) anthracene, 20 g zinc powder activated by washing with ammonium chloride solution, 0·3 g hydroquinone and 200 ml 99% ethanol. During the addition and the following 30 hr the mixture was kept refluxing and was vigorously stirred in nitrogen atmosphere. The reaction mixture was then concentrated to 150 ml, treated with water and extracted with benzene. After washing and drying the benzene solution was concentrated and the residue dissolved in 70 ml dry dioxane. To this solution 16 g maleic anhydride was added and the mixture heated at 100° for 20 hr. After evaporation of dioxane, the residue was treated with 100 ml 40% potassium hydroxide solution on a water-bath for a few min in order to remove anthracene-maleic anhydride adduct. The insoluble parts were taken up in benzene and the benzene solution was washed, dried and concentrated *in vacuo*. In this way unchanged anthracene was removed almost completely. The crude product was purified by passing its n-hexane–benzene (1:1) solution through a short column of alumina. Two recrystallizations from ethanol gave 0·8 g (15% yield based on 1,2-dibromobenzocyclobutene) of the adduct, 9,10-*dihydro-benzocyclobuteno*-(1′,2′:9,10)-*anthracene* (II), m.p. 164–165°. (Found: C, 94·36; H, 5·79. $C_{22}H_{16}$ requires: C, 94·25; H, 5·75%). I.R. absorptions (Nujol) at 745 and 733 cm^{-1} indicate the presence of *o*-disubstituted benzene ring.

From the mother liquor of II, 1·2 g (65%) benzocyclobutadiene dimer was obtained after recrystallizations from ethanol, m.p. 74° (lit.[11] 74·7–74·9°).

When a solution of the hydrocarbon II in cyclohexane was passed through a hot tube electrically heated up to 600° and packed with small pieces of porous tile, anthracene was isolated from the pyrolyzates. Treatment of II with chromic anhydride in acetic acid at 100° resulted in 90% recovery of the unchanged material.

Diels-Alder reaction of indene and anthracene. A mixture of 9·6 g (83 mmoles) indene and 40 ml diethyl phthalate was added dropwise to a solution of 14·2 g (80 mmoles) anthracene in 100 ml diethyl phthalate heated at 280°. The addition required 45 min and the resulting mixture was kept at 260–280° for 1 hr. These procedures were carried out in nitrogen atmosphere. After cooling to room temp, the reaction mixture was stirred with 500 ml 15% sodium hydroxide solution to hydrolyze the solvent. The precipitating solids were collected by filtration, washed with water, dried and recrystallized from benzene to remove unchanged anthracene. Concentrating the mother liquor gave a black tar, which was taken up in a small amount of a 1:1 mixture of n-hexane and benzene and was chromatographed on an alumina column. From fractions eluted with the same solvent, 2·2 g (9% yield based on indene) of the adduct (IV) was obtained, m.p. 115–116° (lit.[12] 118°) after three recrystallizations from ligroin (b.p. 80–100°). (Found: C, 93·95; H, 6·37. Calc. for $C_{23}H_{18}$: C, 93·84; H, 6·16%). $\lambda_{\max}^{\text{isooctane}}$ in mμ (log ε): 266·5 (3·48), 268·5 (3·49), 272sh. (3·43) and 275·5 (3·54).

Oxidation of IV *to* VI. To a solution of 700 mg (2·4 mmoles) hydrocarbon IV in 15 ml glacial acetic acid, a solution of 950 mg (9·5 mmoles) chromic anhydride in 1·9 ml acetic acid was added

---

[14] J. A. Berson and J. W. Patton, *J. Amer. Chem. Soc.* **84**, 3406 (1962).

dropwise with stirring. The addition was completed within 30 min at room temp and then the mixture was heated at 95–100° for 1 hr, whereupon a considerable amount of anthraquinone, m.p. and mixed m.p. 280°, separated out. The filtrate was diluted with water, extracted with ether and the ethereal solution was washed, dried and evaporated. The residue was freed of anthraquinone by recrystallizations from benzene. The mother liquor was concentrated and chromatographed on an alumina column. Elution with benzene gave 300 mg pale yellow solid. Upon two recrystallizations from ethanol 200 mg (27%) ketone VI, 9,10-*dihydro*-1′-*indanono*-(2′,3′:9,10)-*anthracene*, was obtained, m.p. 202–203°. (Found: C, 89·49: H, 5·48. $C_{22}H_{16}O$ requires: C, 89·58; H, 5·23%). $\lambda_{\max}^{\text{isooctane}}$ in mμ (log ε): 239·5 (4·13), 247sh. (3·03), 266 (3·30), 273 (3·36), 286 (3·29) and 295 (3·36). $\lambda_{\max}^{\text{EtOH}}$ in mμ (log ε): 247 (4·13), 272·5 (3·45), 291sh. (3·34) and 297 (3·36). I.R. absorption (carbon tetrachloride) at 1726 cm^{-1} suggests the presence of α,β-unsaturated carbonyl group in a five-membered ring.

A small amount of phthalic acid was isolated from the aqueous layer and was identified by comparison with authentic sample.

Acknowledgements—The authors are grateful to the Ministry of Education, Japanese Government, for a Scientific Research Grant in support of this work. They are also grateful to Dr. Ken-ichi Takeda and his associates at Shionogi Pharmaceuticals Research Institute for NMR spectra herein recorded.

Note added to proof—While this paper was in press, compound II was reported by Cava and Pohlke (M. P. Cava and Pohlke, *J. Org. Chem.* **28**, 1012 (1963)).