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PLEIADENE SYSTEMS—I
ACEPLEIADYLENE[1]

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Abstract—The synthesis of the unstable hydrocarbon acepleiadylene has been accomplished. The deep blue acepleiadylene, which has been obtained only in solution, has been characterized spectrally. Acepleiadylene undergoes dimerization and behaves as a diene in the Diels-Alder reaction.

MANY recent experimental studies of aromaticity have been directed toward the synthesis of conjugated non-benzenoid systems having potential aromatic character.[2] Among the objects of such investigations have been the hydrocarbons *peri*-cycloheptanaphthylene (I), *peri*-cycloheptacenaphthene (II), and *peri*-cycloheptacenaphthylene (III), all of which have been synthesized and isolated in crystalline form.[3] These compounds were shown to possess a reasonable degree of aromaticity, particularly the red hydrocarbon (III) which failed to react with maleic anhydride at 80° during the time of 8½ days.[3b]

The hitherto unknown hydrocarbons pleiadene (IV), acepleiadene (V), and acepleiadylene (VI), which may be viewed as benzo-analogs of compounds (I–III) are of particular interest because they contain within their framework the elements of an *o*-quinodimethane system fused across the *peri*-positions of naphthalene, acenaphthene and acenaphthylene, respectively.[4] The chemistry of these hydrocarbons might be expected to be quite different from that of their simpler analogs I–III. It was of particular interest in this regard to determine the relative reactivities of these systems and especially to evaluate any tendency of the *o*-quinodimethane moiety of these compounds to undergo reactions such as Diels–Alder additions, polymerization, dimer formation or ring tautomerism leading to fused benzocyclobutenoid systems. In the first paper of this series we will describe the synthesis, characterization, and general chemical properties of the highly reactive hydrocarbon acepleiadylene.

Synthesis and spectral characterization of acepleiadylene. The only compound reported in the literature containing the complete ring system of acepleiadylene is

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[1] For a preliminary report of a portion of this work see M. P. Cava and R. H. Schlessinger, *J. Amer. Chem. Soc.* **85**, 835 (1963).

[2] For a general review see *Non-Benzenoid Aromatic Compounds* (Edited by D. Ginsberg). Interscience, New York (1959).

[3a] V. Boekelheide, W. E. Langland and C. Liu, *J. Amer. Chem. Soc.* **73**, 2432 (1951); [b] V. Boekelheide and G. K. Vick, *Ibid.* **78**, 653 (1956).

[4] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.* **55**, 3031 (1933) first proposed the name pleiadene for the hydrocarbon IV; on this basis the name acepleiadylene for VI follows logically. In 1951[3a] it was suggested that this nomenclature be changed so that the modified name pleiadiene might be reserved for the simpler compound I; in 1956[3b] the name acepleiadylene was used to describe III. After careful consideration we have decided to return to the nomenclature pattern of Fieser and Peters, which is not only officially sanctioned by the IUPAC, *J. Amer. Chem. Soc.* **82**, 5553 (1960), but which has also been used in recent years in publications by other authors (e.g. P. T. Lansbury, *J. Amer. Chem. Soc.* **81**, 4325 (1959); P. T. Lansbury and J. F. Bieron, *Ibid.* **86**, 2524 (1964)).

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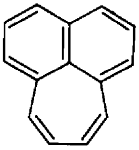
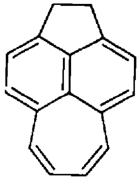


I



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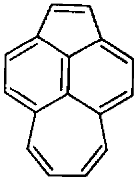
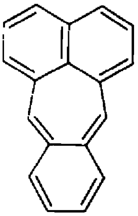
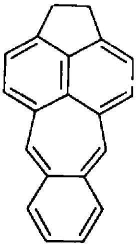


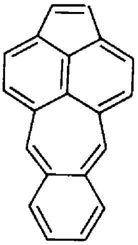
III



IV



V



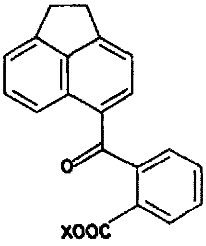
VI

5,10-dihydroacepleiadene-5,10-dione (VII), which was prepared in 37% overall yield from acenaphthene and phthalic anhydride by a two-step Friedel-Crafts condensation consisting of (a) the reaction of acenaphthene with phthalic anhydride and aluminum chloride to give 3′,2-acenaphthoyl benzoic acid (VIII) and (b) intramolecular cyclization of this acid with sodium chloride–aluminum chloride mixture at 150° to give 5,10-dihydroacepleiadene-5,10-dione (VII).[5] Cyclization of keto-acid VIII, in our hands, proved unsatisfactory for preparative purposes and afforded the diketone in less than 1% yield. In view of the fact that the Friedel–Crafts cyclization of the methyl esters of certain γ-keto acids proceeds more smoothly than that of the free acid itself,[6] acid VIII was converted to the corresponding methyl ester (IX) which indeed then afforded diketone VII in good yield (71%) on cyclization with sodium chloride–aluminum chloride mixture at 150°.

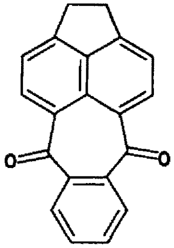
Sodium borohydride reduction of the diketone gave the amorphous 5,10-dihydroacepleiadene-5,10-diol (X) in 77% yield. An attempt to convert the diol to the corresponding dibromide (XI) by reaction with hydrogen bromine in benzene failed, the reaction affording a deep blue, benzene-soluble product which was shown by its reactions to be acepleiadylene (VI), produced unexpectedly by the acid catalysed elimination of two moles of water from the diol. The conversion of diol X to the blue dehydration product could be effected also under a variety of other conditions, including treatment of the diol with tosyl chloride and pyridine, anhydrous hydrogen chloride in dioxane, aqueous hydrogen chloride in dioxane, and aqueous hydrogen chloride with either chloroform or methylene chloride. The most convenient method for generating solutions of acepleiadylene consisted of treating a dioxane suspension of diol X with a few drops of concentrated hydrochloric acid at room temperature.

[5] A. T. Peters and F. M. Rowe, *J. Soc. Dyers Colourists* **59**, 52 (1943).

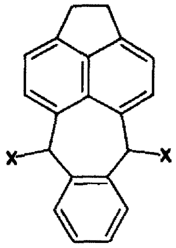
[6] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.* **54**, 3742 (1932).



VIII, X = H
IX, X = CH_3



VII



X, X = OH
XI, X = Br

Under these conditions the diol dissolved and the characteristic deep blue colour of acepleiadylene reached its maximum intensity within a few seconds. A dilute acepleiadylene solution was observed to change colour completely during a forty minute period at room temperature, yellow decomposition products being produced. It was possible, however, using freshly prepared acepleiadylene solutions, to determine the entire ultra-violet and visible spectrum of the hydrocarbon. As shown in Table 1, a total of eight maxima were observed through the region 227 to 674 mμ; all of these maxima had extinction coefficients greater than 1,000.

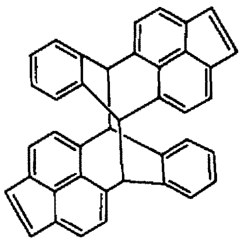
TABLE 1. ABSORPTION MAXIMA OF ACEPLEIADYLENE (VI) IN DIOXANE SOLUTION[a]

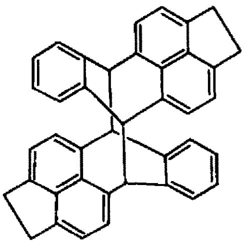
mμ	log ε
227	4·32
240	4·23
283	4·23
293	4·25
361	4·53
377	4·69
617	3·14
649	3·17
674	3·20

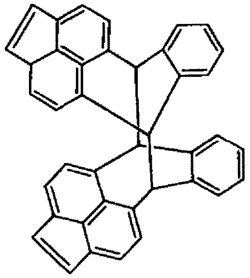
[a] The extinction coefficients recorded should be viewed as minimum values because of the instability of compound VI.

Reactions of acepleiadylene. All attempts to isolate acepleidylene in the solid state failed, evaporation of blue solutions of the hydrocarbon consistently yielding only yellow solid residues. It could be shown that the failure to obtain acepleiadylene in the solid state was not caused by the presence of acid since it was possible to obtain pure acid-free solutions of acepleiadylene in methylene chloride or ether by alumina chromatography at −60°. Purified solutions obtained in this manner likewise afforded only yellow solids on evaporation, and also gave no evidence of complex formation when treated with either 2,4,7-trinitrofluorenone or 1,3,5-trinitrobenzene.

Chromatography of the crude solid decomposition product of acepleiadylene showed it to be a mixture of polymeric material and a sparingly soluble yellow crystalline acepleiadylene dimer. The yield of this dimer varied from 30 to 50% depending upon the conditions of its formation. We have assigned structure XII to this substance on the basis of the evidence outlined below. The presence of an acenaphthylene chromophore in dimer XII was suggested by its yellow colour. Catalytic reduction of the dimer afforded, as expected, a colourless tetrahydro derivative (XIII). Although catalytic reduction of the acepleiadylene dimer to its tetrahydro derivative was accompanied by a hypsochromic shift of about 35 mμ, it was noted that the absorption maxima of XII and XIII appeared at appreciably longer wavelengths than their respective simpler analogs acenaphthylene and acenaphthene. The shift to high wavelengths observed in the dimeric compounds XII and XIII may be attributed to some type of π-interaction between the two close and rigidly held dihydro or tetrahydro acepleiadylene systems. Although the evidence presented up to this point does not allow differentiation between the *syn* and *anti* structures XIV and XII, spectral correlations with related compounds, as discussed in detail in paper IV of this series, support the *anti* configuration XII.


XII


XIII


XIV

Solutions of acepleiadylene failed to react with N-phenylmaleimide at temperatures of 0–10°; acepleiadylene dimer was the only product isolated after disappearance of the blue colour under these conditions. At 25°, however, a yellow N-phenylmaleimide adduct of acepleiadylene was formed in addition to an equimolar amount of acepleiadylene dimer. At 60° or above, the reaction of acepleiadylene with N-phenylmaleimide took place much more rapidly than dimer formation; the Diels–Alder adduct was obtained in good yield (76%) and no dimer was detected. The phenylmaleimide adduct of acepleiadylene was assigned structure XV on spectral grounds. Its ultra-violet spectrum was very similar to that of acenaphthylene; on catalytic reduction it afforded a colourless dihydro derivative XVI, the ultra-violet spectrum of which was clearly consistent with the presence in it of an acenaphthene chromophore. The assignment to this adduct of the *exo* configuration XV rather than the *endo* configuration XVII rests upon spectral correlations with related adducts and model compounds as described fully in paper IV of this series.

Several reactions have been observed in which sulphur dioxide has been added to unstable *o*-quinonoid hydrocarbons to give sulfones.[7] It seemed that acepleiadylene might also undergo this reaction. Indeed, when a solution of the blue hydrocarbon in

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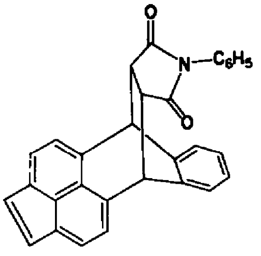
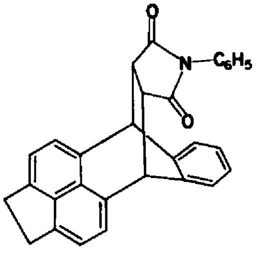
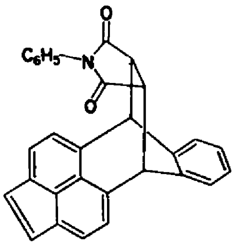
[7a] F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.* **80**, 6149 (1958); [b] F. R. Jensen, W. E. Coleman and A. J. Berlin, *Tetrahedron Letters* No. 1, 15 (1962).



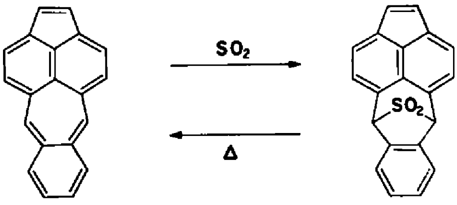
XV



XVI



XVII



VI

XVIII

dioxane was treated with sulphur dioxide the reaction solution became yellow within 15 minutes while the blue colour of a blank reaction solution persisted about 40 minutes. On heating the yellow solution to expel excess sulphur dioxide, the blue colour of acepleiadylene was regenerated briefly before the solution again became yellow. Acepleiadylene dimer was isolated in low yield from this reaction, while the remainder of the reaction product was found to be polymeric.[8] All attempts to isolate the presumed sulfone intermediate (XVIII) failed.[9]

Conclusions. On the basis of the observed chemical behaviour of acepleiadylene (VI), it is clear that this hydrocarbon is considerably less stable than its simple analog *peri*-cycloheptacenaphthylene (III). Indeed, the ease with which acepleiadylene undergoes dimerization and its behaviour as a diene in the Diels-Alder reaction are both indicative of a considerable degree of *o*-quinonoid character in the hydrocarbon. Solutions of acepleiadylene were found to be unaffected by both light and oxygen, suggesting a singlet rather than a triplet ground state for the molecule.

The mechanism of the formation of acepleiadylene from 5,10-dihydroacepleiadene-5,10-diol is discussed in the second paper of this series.

EXPERIMENTAL

M.ps are uncorrected. All UV spectra were determined in dioxan solution.

3′,2-*Acenaphthoyl benzoic acid* (VIII). Aluminum chloride (63·0 g) was added to a suspension of acenaphthene (32·0 g) and phthalic anhydride (33·5 g) in benzene (170 ml) over 30 min at room temp.

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[8] The formation of polymeric materials derived from acepleiadylene or dimer XII is not surprising, for the ready dimerization and polymerization of acenaphthylene itself under a variety of conditions is well documented.

[9] A referee has suggested that the reaction of VI with sulphur dioxide may involve only the formation of a charge-transfer complex. This explanation is certainly possible but we regard it as unlikely, especially in view of the additional evidence concerning the instability of sulphone XVIII described in paper III of this series.

Additional benzene (100 ml) was then added and the reaction mixture poured into conc HCl aq (300 ml), the mixture being subsequently diluted with water to a volume of 2 l. The grey precipitate was filtered and crystallized from chloroform to give white needles of VIII (59·5 g, 95%), m.p. 201–204° (reported,[10] 200°).

Methyl 3′,2-acenaphthoyl benzoate (IX). Acetyl chloride (45 ml) was added dropwise to a suspension of keto acid VIII (10·0 g) in MeOH (150 ml). The reaction mixture was refluxed until it became homogeneous and was then concentrated to one-half its original volume. On standing, ester IX separated as white prisms (9·0 g, 85%), m.p. 125° (reported,[10] 128°).

5,10-*Dihydroacepleiadene*-5,10-*dione* (VII). To a melt of NaCl (10·0 g) and $AlCl_3$ (40·0 g) at 150° was added ester IX (10·0 g) in portions over a 10 min period. The reaction mixture, after heating at 150° for a further 10 min, was poured into crushed ice. The black precipitate was dissolved in hot glacial acetic acid (200 ml), the solution was filtered through Celite, and the filtrate was poured into water (600 ml). The brown solid thus obtained afforded, after chromatography over alumina (Woelm, neutral, grade II, 200 g, benzene eluant) and crystallization from glacial acetic acid, yellow needles of VII (6·0 g, 71%), m.p. 193–194° (reported,[4] 194–195°).

5,10-*Dihydroacepleiadene*-5,10-*diol* (X). A solution of diketone VII (2·45 g) and $NaBH_4$ (1·0 g) in benzene (200 ml) and MeOH (50 ml) was stirred for 6 hr at room temp. Removal of the solvent under red. press. left a tan gum which became granular on treatment with 10% NaOH aq (200 ml). This substance was collected by filtration and washed until white with CH_2Cl_2 (150 ml). The diol (X) thus obtained (1·9 g, 77%), m.p. 212–265° (dec), was amorphous and could not be crystallized. Found: C, 83·56; H, 5·69. Calc. for $C_{20}H_{16}O_2$: C, 83·31; H, 5·59%.)

Generation of acepleiadylene (VI); *isolation of acepleiadylene dimer* (XII). A solution of diol X (0·50 g) in dioxan (50 ml) was treated with 6 drops of conc. HCl aq. The reaction mixture immediately developed an intense blue colour which changed to yellow within 10 min upon warming on the steam bath. Removal of the solvent under red. press. followed by chromatography of the solid residue over alumina (Woelm, neutral, grade I, 40·0 g, benzene eluant) and crystallization from toluene afforded fine yellow needles of dimer XII (0·132 g, 52%), m.p. 418–422° (dec); λ_{max} 221 mμ (ε = 77,000), 248 (35,000), 306 (5,400), 320 (11,600), 335 (18,000) 352 (23,600), 369 (25,600). (Found: C, 95·50; H, 5·06; mol. wt. (osmometric), 445; Calc. for $C_{40}H_{24}$: C, 95·21; H, 4·79%, mol. wt., 504.)

Solutions of acepleiadylene generated as described above remained blue for 40 min when allowed to stand at room temp. Such blue solutions were found to be unchanged by light or O_2; indeed, when solutions of acepleiadylene were irradiated with light from the full spectrum of a Hanovia medium press. Hg-arc (450 watts) either in the presence of air or under an A atm. no change in the rate of disappearance of the blue colour was detected.

Tetrahydro derivative (XIII) *of acepleiadylene dimer*. A suspension of dimer XII (0·132 g) and 5% Pd–C (0·10 g) in benzene (150 ml) was hydrogenated for 17 hr. The reaction mixture was filtered through Celite and the filtrate evaporated under red. press. to give a solid residue which crystallized from toluene to give fine white needles (0·122 g, 94%) of dimer XIII, m.p. 390–400° (dec); λ_{max} 220 mμ (ε = 80,000), 317 (20,800), 334 (20, 500). (Found: C, 94·46; H, 5·45; mol. wt. (osmometric), 450; Calc. for $C_{40}H_{28}$: C, 94·45; H, 5·55%; mol. wt., 509.)

N-*Phenylmaleimide adduct* (XV) *of acepleiadylene*. A solution of diol X (1·0 g) and N-phenylmaleimide (0·596 g) in dioxan (80 ml) was heated to 60°. Dil. HCl aq (3·0 ml) was then added and the solution was heated a further 4 min at 60°. (No blue colour was observed.) Evaporation of the reaction mixture under red. press., followed by chromatography of the residual oil over alumina (Woelm, neutral, grade II, 40·0 g, 10:1 benzene–chloroform eluant) and crystallization from acetone gave yellow needles of adduct XV (1·10 g, 76%), m.p. 300–320° (dec); λ_{max} 218 mμ (ε = 30,000), 242 (29,000), 266 (sh, 4,000), 274 (sh, 3,500), 285 (sh, 2,600), 314 (sh, 6,500), 328 (10,800), 340 (11,000), 350 (7,300), 355 (8,400). (Found: C, 84·58; H, 4·68; N, 3·19. Calc. for $C_{30}H_{19}O_2N$: C, 84·68; H, 4·50; N, 3·29%.)

When the above experiment was carried out at 25°, equimolar quantities of adduct XV and dimer XII were isolated; on the other hand, at 10° only dimer XII was formed. In both of these reactions, a blue colour development upon the addition of HCl aq.

Dihydro derivative (XVI) *of adduct* XV. A suspension of adduct XV (0·176 g), 5% Pd–C (0·02 g), and dioxan (12 ml) was hydrogenated for 2 hr. The reaction mixture was filtered through Celite and

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[10] C. Graebe, *Liebigs Ann.* **327**, 77 (1903).

the filtrate was evaporated to dryness. Crystallization of the residue from acetone afforded white needles of adduct XVI (0·159 g, 79%), m.p. 292–295° (dec); λ_{max} 218 mμ (sh, 50,000), 232 (60,000), 270 (sh, 3,800), 282 (6,200), 293 (10,800), 304 (14,300), 318 (10,000), 328 (4,500). (Found: C, 84·31; H, 5·16; N, 3·29. Calc. for $C_{30}H_{21}O_2N$: C, 84·28; H, 4·95; N, 3·28%.)

Formation of 5,10-*dihydroacepleiadylene*-5,10-*sulphone* (XVIII). A solution of diol X (0·285 g) in dioxan (50 ml) was treated with 3 drops of conc. HCl aq while a gentle stream of SO_2 was passed through it at room temp. The colour of the reaction mixture became greenish blue, turning to yellow within 15 min. In a blank experiment carried out in an identical fashion but without the addition of SO_2, the original blue colour turned to yellow only after 40 min. When the solution which had been treated with SO_2 was heated on the steam bath, its colour changed from yellow to dark blue-green to yellow during a period of 10 min. The solution from the blank experiment exhibited no such colour changes, and remained a constant yellow when warmed. Acepleiadylene dimer (XII) was the only product isolated from both reactions after chromatography.

Acknowledgment—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.