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PLEIADENE SYSTEMS—IV

PLEIADENE; THE STEREOCHEMISTRY OF THE DIMERS AND DIELS-ALDER ADDUCTS OF PLEIADENE, ACEPLEIADENE, AND ACEPLEIADYLENE

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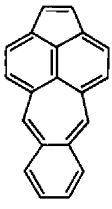
Abstract—Pleiadene, the parent hydrocarbon of the pleiadene series, has been generated both thermally and photolytically from 7,12-dihydropleiadene-7,12-sulphone, as well as by the copper or zinc debromination of 7,12-dibromo-7,12-dihydropleiadene. Like acepleiadene, pleiadene behaves as a very unstable transient intermediate under all conditions of generation investigated. Convenient syntheses of dihydropleiadene and some of its derivatives are described. The stereochemistry of the dimers and N-phenylmaleimide adducts of pleiadene, acepleiadene and acepleiadylene have been determined by a detailed NMR study; all of the dimers have the *anti* configuration, while the adducts all have the *exo* configuration.

THE synthesis of the unstable hydrocarbon acepleiadylene (I) and the generation of the highly reactive species acepleiadene (II) have been described in previous papers of this series.[1] In this paper we report the generation and detection under a variety of conditions of pleiadene (III), the simplest member of the pleiadene series of hydrocarbons; we will discuss also a detailed NMR study which has allowed the complete assignment of stereochemistry to the dimers and N-phenylmaleimide adducts of pleiadene (III), acepleiadene (II), and acepleiadylene (I).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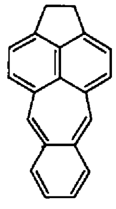
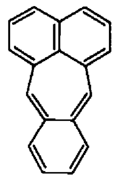

II


III

Synthesis of precursors of pleiadene. The precursors of pleiadene (III) synthesized in this study were 7,12-dihydropleiadene-7,12-sulphone (IV) and 7,12-dibromo-7,12-dihydropleiadene (V). In contrast to the dihydroacepleiadene series, a number of simple 7,12-dihydropleiadenes have been described previously.[2] The most readily available of these compounds is 1-hydroxy-7,12-dihydropleiadene-7,12-dione (VI) which is obtained in one operation by a Friedel-Crafts condensation of β-naphthol with phthalic anhydride in the presence of aluminum chloride.[3] This hydroxydiketone

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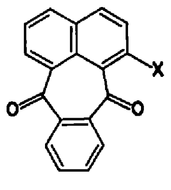
[1a] M. P. Cava and R. H. Schlessinger, *Tetrahedron* **21**, 3051 (1965);
[b] M. P. Cava and R. H. Schlessinger, *Ibid.* **21**, 3065 (1965).

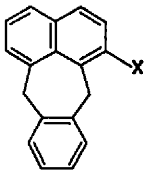
[2] The earlier dihydropleiadene literature has been summarized in, *Elsevier's Encyclopedia of Organic Chemistry* (Edited by E. Josephy and F. Radt) Vol. 14; pp. 396 ff. Elsevier, New York (1940).

[3] L. F. Fieser, *J. Amer. Chem. Soc.* **53**, 3546 (1931).

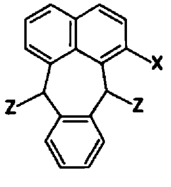
has been reported to react with phosphorus pentachloride to give 1-chloro-7,12-dihydropleiadene-7,12-dione (VII);[3,4] the reduction of 1-chloro-7,12-dihydropleiadene-7,12-dione with hydrazine hydrate and palladium to 7,12-dihydropleiadene-7,12-dione (VIII), and the formation of 7,12-dihydropleiadene (IX) from the latter diketone have also been described briefly.[5] The preparation of the chlorodiketone (VII) in our hands could be carried out smoothly and on a large scale from β-naphthol, using minor modifications of the previously described procedures. The reported dechlorination of the chlorodiketone to diketone VIII with hydrazine was found to be quite unsatisfactory as a preparative method, and afforded a complex mixture of products as determined by thin layer chromatography. The following practical new procedure for the conversion of chlorodiketone VII to diketone VIII in 51% overall yield was developed. The LAH–$AlCl_3$ reduction of chlorodiketone VII afforded 1-chloro-7,12-dihydropleiadene (X); reduction of the latter halide with hydrazine hydrate and Pd gave 7,12-dihydropleiadene (IX) which was oxidized to 7,12-dihydropleiadene-7,12-dione (VIII) by sodium dichromate in acetic acid. Reduction of diketone VIII with $NaBH_4$ gave 7,12-dihydropleiadene-7,12-diol (XI). The latter diol was prepared also from chlorodiketone (VII) in 73% overall yield by $NaBH_4$ reduction to give 1-chloro-7,12-dihydropleiadene-7,12-diol (XII),[6] followed by hydrazine-and-palladium dechlorination to alcohol XI. In analogy with the preparation of 5,10-dihydroacepleiadene-5,10-sulphone[1b] diol XI reacted with phosphorus pentasulphide in carbon disulphide to give 7,12-dihydropleiadene-7,12-sulphide (XIII) which was oxidized readily by peracetic acid to 7,12-dihydropleiadene-7,12-sulphone (IV). In contrast with the corresponding diol of the acepleiadene series, diol XI reacted normally with hydrogen bromide in benzene, giving 7,12-dibromo-7,12-dihydropleiadene (V). The latter dibromide (V) was extremely susceptible to hydrolysis: it fumed in moist air, liberating hydrogen bromide, and it was converted by neutral alumina into 7,12-dihydropleiadene-7,12-oxide (XIV). Attempts to convert dibromide V into sulphide XIII by reaction with alcoholic sodium sulphide gave a practically inseparable mixture of oxide XIV and sulphide XIII, as determined by thin-layer chromatography; dibromide V afforded sulphide XIII directly in fair yield, however, on treatment with phosphorus pentasulphide in carbon disulphide solution.



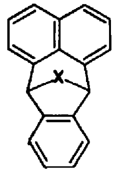
VI, X = OH
VII, X = Cl
VIII, X = H



IX, X = H
X, X = Cl



XI, Z = OH
X = H
XII, Z = OH
X = Cl
V, Z = Br
X = H



XIII, X = S
IV, X = SO_2
XIV, X = O

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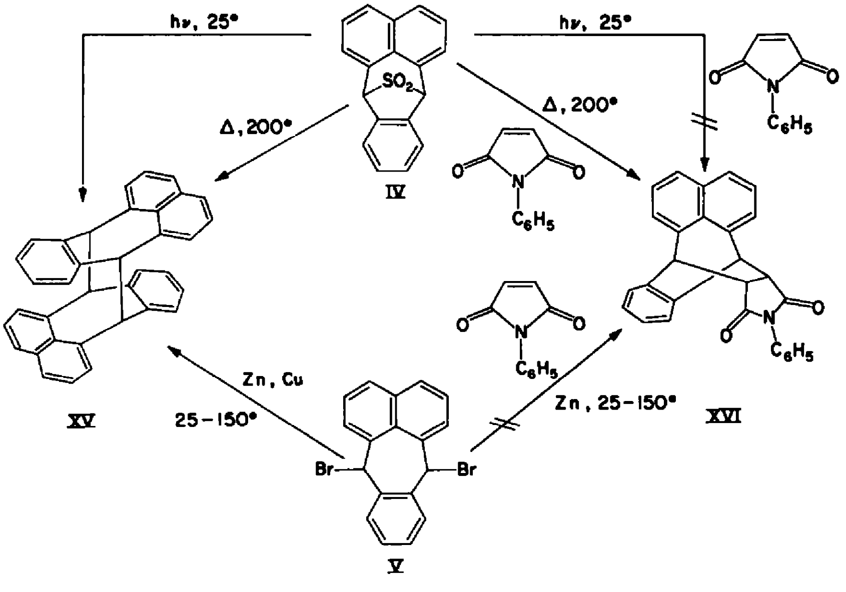
[4] A. Reiche and E. Fruwald, *Ber. Dtsch. Chem. Ges.* **64**, 1603 (1931) and earlier Refs cited therein.

[5] A. Reiche, H. Santhoff and O. Muller, *Ber. Dtsch. Chem. Ges.* **65**, 1371 (1932).

[6] This compound was first prepared by A. R. Sawaya, Master's thesis, The Ohio State University (1955).

Generation and reactions of pleiadene. Pleiadene (III) was generated from 7,12-dihydropleiadene-7,12-sulphone using procedures previously described for the generation of acepleiadene from the corresponding sulphone.[1b] Thus, pyrolysis of 7,12-dihydropleiadene-7,12-sulphone in the molten state at 250° or in diethylphthalate solution at 200° afforded, in 50% yield, a colourless crystalline pleiadene dimer (XV). Thermal decomposition of sulphone IV at 200° in the presence of N-phenylmaleimide gave, in 68% yield, a crystalline pleiadene-N-phenylmaleimide adduct XVI; no pleiadene dimer was formed in this reaction. UV irradiation of a benzene solution of sulphone IV at room temperature gave pleiadene dimer (XV) in a yield comparable with that obtained on pyrolysis of the sulphone. Significantly, pleiadene dimer (XV) was the only crystalline product obtained by the photolytic decomposition of sulphone IV in benzene solution in the presence of N-phenylmaleimide.

Whereas it was possible to generate acepleiadene (II) at moderate temperatures only by photolytic means,[1b] it was possible to generate pleiadene (III) from 7,12-dibromo-7,12-dihydropleiadene (V) by dehalogenation with metals over a fairly wide temperature range. Thus, dehalogenation of dibromide V with zinc or, better, with copper–bronze in an aromatic hydrocarbon solvent at room temperature, 80°, 110°, or 140° afforded pleiadene dimer in high yield. No Diels–Alder adducts of pleiadene were produced when pleiadene was generated in this manner from dibromide V in the presence of N-phenylmaleimide at room temperature, 80°, 110°, or 140°, or in the presence of tetracyanoethylene at room temperature or at 80°: pleiadene dimer (XV) was the sole product obtained from all of these experiments. Thus, it appears that pleiadene undergoes dimerization at a rate considerably greater than that of adduct formation at temperatures as high as 140°. The tendency of pleiadene and of the electronically similar acepleiadene[1b] to undergo dimerization rather than adduct formation when generated photolytically at room temperature in the presence of dienophiles is therefore not a result attributable specifically to their generation under photolytic conditions.



Stereochemistry of the dimers and N*-phenylmaleimide adducts of pleiadene, acepleiadene and acepleiadylene.* It has been shown previously that the dimer of acepleiadene and the acepleiadene-N-phenylmaleimide adduct are identical with the products of catalytic reduction of acepleiadylene dimer and the acepleiadylene-N-phenylmaleimide adduct, respectively.[1b] Since the π-electron system of pleiadene is electronically identical with that of acepleiadene, it may be assumed with virtual certainty that the dimer and the N-phenylmaleimide adduct of pleiadene will belong to the same stereochemical series as those derived from acepleiadene and, indirectly, those derived from acepleiadylene. Consequently, the determination of the stereochemistry of any one of these dimer-adduct pairs would also indicate the stereochemistry of the corresponding pairs in the other two systems. The stereochemistry of these compounds was determined by means of an NMR study; the dimer and N-phenylmaleimide adduct of pleiadene proved to be most suitable for this purpose, since they were the most soluble in deuteriochloroform.

The assignment of stereochemistry to the pleiadene-N-phenylmaleimide adduct involves a choice between the *exo* configuration (XVI) and the *endo* configuration (XVII). The Diels-Alder adduct (XVIII) of anthracene and N-phenylmaleimide was synthesized as a model for an NMR comparison with the pleiadene adduct. It is apparent that the benzhydryl protons (type A) of the anthracene adduct should appear at approximately the same field value as those of the corresponding protons of the pleiadene adduct, regardless of the stereochemistry of the latter. On the other hand those protons (type B) alpha to the carbonyls in the anthracene adduct would be expected to be in an environment magnetically similar to that of the corresponding protons of the *endo* pleiadene adduct (XVII), but magnetically dissimilar to the type B protons of the *exo* pleiadene adduct. Molecular models of the *exo* adduct (XVI) indicate that the type B protons lie near the periphery of the naphthalene ring; hence, they should be deshielded relative to the corresponding type B protons of either the *endo* isomer (XVII) or the anthracene adduct (XVIII), which lie over the corresponding portion of a benzene nucleus.[7] The experimentally determined values for the pleiadene adduct are 5·14 (type A protons) and 6·15 τ (type B protons), while those found for the anthracene adduct XVIII are 5·00 and 6·57 τ, respectively. On the basis of this data the pleiadene-N-phenylmaleimide adduct has been assigned the *exo* configuration (XVI), since its type B protons are clearly deshielded relative to those of the anthracene adduct XVIII. Further evidence in support of this conclusion was obtained by an NMR study of the amines (XIX and XX) obtained by reducing the pleiadene and anthracene adducts with LAD. The deuterioamine (XIX) derived from pleiadene showed type A protons as a singlet at 5·81 τ and type B protons as a singlet at 6·51 τ; the corresponding values for the amine (XX) derived from anthracene were 5·72 and 7·10 τ. Clearly, the type B protons of amine XIX are relatively even more deshielded than those of the adduct from which it was derived.[8]

The NMR spectrum of pleiadene dimer shows a complex multiplet of aromatic protons in the region of 2·3 to 2·7 τ; in addition, the spectrum also shows a sharp

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[7] For an explanation of this phenomena, see L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy* pp. 112–130. Pergamon Press; New York (1959).

[8] The protium analogues of XIX and XX were also prepared by reduction of XVI and XVIII with LAH as described in the experimental section. Type B of these proteo amines formed part of an unresolved complex multiplet with the protons alpha to the N atom.

singlet of four rather highly shielded aromatic protons at 3·22 τ, as well as the expected singlet of four benzhydryl protons at 4·38 τ. For reasons outlined below, the combined presence of the four shielded aromatic protons and of aromatic protons as low downfield as 2·3 τ is compatible only with the assignment of the *anti* configuration (XV) to the pleiadene dimer. It is well known that the aromatic protons of phenyl groups which lie closely over each other experience an appreciable shielding affect[9]; this phenomenon has been employed recently in the assignment of configuration to several isomeric 1,2,3,4-tetraphenylcyclobutanes.[10] An example of this type of shielding involving two naphthalene rings has not heretofore been described. An examination of the NMR spectrum of β-heptacyclene (XXI)[11] has now revealed the expected shielding affect in such a system. Thus, the aromatic protons of β-heptacyclene (XXI) appear in the region of 2·6 to 3·0 τ compared with the normal naphthalene proton range of 2·35 to 2·84 τ observed in the spectrum of acenaphthene. If pleiadene dimer had the *syn* configuration (XXII), the lower field portion of the spectrum would be expected to be similarly shifted to higher fields. The observation of aromatic proton absorption in the spectrum of pleiadene dimer as far downfield as 2.3 τ thus is in much better accord with the assignment of the *anti* configuration (XV) to this substance. The appearance of four aromatic protons as a sharp peak at 3·22 τ is also fully consistent with the *anti* formulation for the dimer. This peak has been assigned to the two sets of *para* hydrogens of the benzene rings (type C, structure XV) which models show to be definitely in the shielding quadrants of the π-electron clouds of the opposing naphthalene rings.[12]

The proximity of the aromatic rings in the upper and lower halves of the pleiadene dimer molecule has an appreciable effect upon its UV spectrum. Thus, the naphthalene system of 7,12-dihydropleiadene has major absorption bands at 288 and 299 mμ, as well as several weaker bands at longer wavelength. In pleiadene dimer, the major bands have been shifted to 304 and 318 mμ, and the fine structure in the spectrum has disappeared.[13]

CONCLUSIONS

Pleiadene (II) has been generated by a variety of methods (thermolysis, photolysis and halogen elimination) from suitable precursors over a temperature range of 25° to 240°. Under all conditions studied, it behaved as a highly reactive transient intermediate which undergoes dimerization readily; at higher temperatures pleiadene is able to act as a diene in the Diels-Alder reaction.

A detailed NMR study has led to assignment of the *anti* configuration to the

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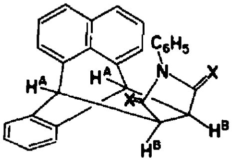
[9] D. Curtin, H. Gruen and B. Shoulders, *Chem. & Ind.* 1205 (1958).

[10] H. Shechter, W. L. Link and G. Tiers, *J. Amer. Chem. Soc.* **85**, 1601 (1963).

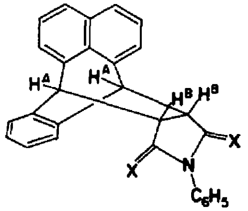
[11] K. Dziewonski and E. Rapalski, *Ber. Dtsch. Chem. Ges.* **45**, 2491 (1912), first reported β-heptacyclene as the minor photodimer resulting from the irradiation of acenaphthylene, the major product being a higher melting isomer α-heptacyclene. J. D. Dunitz and L. Weissman, *Acta Cryst.* **2**, 62 (1949), have shown by X-ray analysis the structure of the α-compound is *trans* while that of the β-compound is *cis*.

[12] An extreme case of this type of shielding by naphthalene rings in *anti*-(2,2)-paracyclonaphthalene has been reported recently: D. J. Cram, C. K. Dalton and G. R. Knox, *J. Amer. Chem. Soc.* **85**, 1088 (1963).

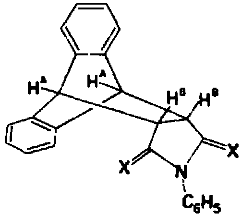
[13] Similar bathochromic shifts compared to model chromophores have been observed in the ultraviolet spectra of acepleiadene dimer and acepleiadylene dimer. See papers I and III of this series.



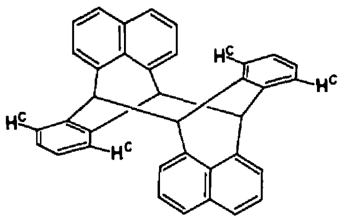
XVII, X = O



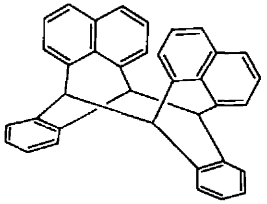
XVI, X = O
XIX, X = D$_2$



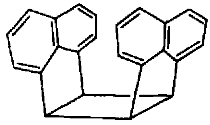
XVIII, X = O
XX, X = D$_2$



XV



XXII



XXI

pleiadene dimer and the *exo* configuration to the adduct of pleiadene and phenylmaleimide. These conclusions lead indirectly to a similar stereochemistry for the dimers and N-phenylmaleimide adducts of acepleiadene (II) and acepleiadylene (I).

EXPERIMENTAL†

1-*Hydroxy*-7,12-*dihydropleiadene*-7,12-*dione* (VI)

β-Naphthol (5·0 g) was added slowly to a molten mass of $AlCl_3$ (32·0 g) and phthalic anhydride (10·0 g) at 180°. The reaction mixture was then heated to 250° and maintained at that temp for 30 min. After cooling to 150°, the melt was poured cautiously into water (1000 ml) containing HCl (40 ml). The resulting precipitate was digested on the steam bath for 1 hr with 6 N HCl (200 ml), then filtered and extracted into hot 20% NaOH aq (100 ml). Acidification of the alkaline extract gave a yellow precipitate which was dried, then treated with activated charcoal in $CHCl_3$ solution, and finally crystallized from benzene to give bright yellow needles of VI (9·3 g, 74%), m.p. 195° (reported[3] 198°).

1-*Chloro*-7,12-*dihydropleiadene*-7,12-*dione* (VII)

A suspension of VI(5·0 g) and PCl_5 (5·5 g) in $POCl_3$ (5·7 g) was heated on the steam bath for 4 min. The reaction mixture was then poured onto ice and the resulting suspension was heated 10 min on the

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† M. ps are uncorrected. Chromatography was carried out using Woelm neutral alumina in the activity grade indicated. The UV spectra were determined in dioxane solution.

steam bath. The solid thus formed was filtered, extracted with hot glacial acetic acid (200 ml), and the extract poured into water (600 ml). The bright yellow precipitate was treated with charcoal in $CHCl_3$ solution, and then crystallized from EtOH to give bright yellow needles of VII (3·6 g, 64%), m.p. 161–162° (reported[3] 165°).

1-*Chloro*-7,12-*dihydropleiadene* (X)

By use of a Soxhlet extractor VII (2·01 g) was introduced into a suspension of LAH (0·762 g) and $AlCl_3$ (5·41 g) in refluxing ether (300 ml). The reaction mixture was then decomposed by the cautious addition of water (30 ml) and worked-up in the usual manner. The yellow solid thus obtained afforded, after chromatography over alumina (grade I, 40 g, CH_2Cl_2 eluent) and subsequent crystallization from hexane, white needles of X (1·30 g, 71%), m.p. 117–119°. (Found: C, 81·81; H, 5·10; Cl, 13·24. Calc. for $C_{18}H_{13}Cl$: C, 81·66; H, 4·95; Cl, 13·39.)

7,12-*Dihydropleiadene* (IX), *from chlorohydrocarbon* (X)

A mixture of X (1·94 g), 10% Pd–C (0.50 g), 75% hydrazine hydrate (25 ml), and alcohol (200 ml) was boiled 6 min. The catalyst was then removed by filtration through Celite and the filtrate was concentrated under red. press. to a volume of 5 ml. Dil. HCl aq (10 ml) was then added and the reaction worked-up in the usual manner. Crystallization of the resulting solid from hexane gave white needles of IX (1·37 g, 82%), m.p. 113–114° (reported[3] 116°); λ_{max} 215 mμ (ε = 105,000), 226 (115,000), 267 (sh, 7,800), 271 (sh, 8,800), 278 (12,000), 288 (14,300), 299 (10,500), 307 (sh, 4,300), 317 (sh, 1,500), 322 (1,800).

On a larger scale, yields of 93% or better of IX were obtained in this reaction.

7,12-*Dihydropleiadene*-7,12-*dione* (VIII)

A solution of IX (1·0 g), sodium dichromate (6·0 g), and glacial acetic acid (50 ml) was refluxed for 4 hr. After cooling, the reaction mixture was poured into water (300 ml). Crystallization of the resulting precipitate from EtOH gave fine white needles of VIII (0·8879 g, 77%), m.p. 168° (reported[4] 178°). Due to the difference in m.p. and colour observed (VIII was previously described as light yellow), an analysis of VIII was carried out. (Found: C, 83·66; H, 3·70. Calc. for $C_{18}H_{10}O_2$: C, 83·71; H, 3·90.)

7,12-*Dihydropleiadene*-7,12-*diol* (XI)

A solution of VIII (0·7144 g) and $NaBH_4$ (0·5 g) in a mixture of benzene (50 ml) and MeOH (30 ml) was stirred at room temp for 1 hr. The reaction mixture was then evaporated to a gummy residue which became granular on treatment with 20% NaOH aq (100 ml) at room temp for 1 hr. Crystallization of resulting solid from cyclohexane gave white prisms of XI (0·650 g, 91%), m.p. 198–200°. (Found: C, 82·20; H, 5·41. Calc. for $C_{18}H_{14}O_2$: C, 82·42; H, 5·38.)

1-*Chloro*-7,12-*dihydropleiadene*-7,12-*diol* (XII)

A solution of VII (2·0 g) and $NaBH_4$ (1·0 g) in a mixture of benzene (80 ml), and MeOH (30 ml) was stirred at room temp for 2 hr. The reaction mixture was then evaporated to a gummy solid which became granular on stirring with 10% NaOH aq (200 ml). Crystallization of this material from benzene afforded white needles of XII (1·90 g, 96%), m.p. 231° (reported[3] 232°).

7,12-*Dihydropleiadene*-7,12-*diol* (XI), *from the chlorodiol* (XII)

A mixture of XII (2·0 g), 5% Pd–C (0·5 g), 75% hydrazine hydrate (25 ml), and EtOH (150 ml) was boiled for 6 min. After separation of the catalyst by filtration, the reaction mixture was diluted with water (150 ml) and then worked-up in the usual manner. The solid thus obtained afforded white prisms of XI (1·25 g, 76%), m.p. 200°, on crystallization from EtOH.

7,12-*Dibromo*-7,12-*dihydropleiadene* (V)

A suspension of XI (0·50 g) and benzene (77 ml) was subjected to a stream of anhydrous HBr for 3 sec. The reaction mixture was then swirled 2 min, treated again with HBr for 3 sec, and again swirled until solution of the diol was complete. The reaction mixture was then rapidly filtered through $MgSO_4$ and evaporated under red. press. to a volume of 3 ml. Cyclohexane (10 ml) was added and the solution allowed to stand overnight under an A atm. Straw coloured needles of V (0·68 g, 90%)

m.p. 134° (dec), were deposited. (Found: C, 56·02; H, 3·28; Br, 41·25. Calc. for $C_{18}H_{12}Br_2$) C, 55·68; H, 3·12; Br, 41·20.)

7,12-*Dihydropleiadene*-7,12-*oxide* (XIV)

A solution of V (0·3 g) in benzene (6 ml) was passed through a column of alumina (grade II, 30 g) Evaporation of the benzene eluate gave a colourless oil which deposited white needles of XIV (0·167 g, 95%), m.p. 128°, on crystallization from cyclohexane. (Found: C, 88·72; H, 5·06. Calc. for $C_{18}H_{12}O$: C, 88·50; H, 4·95.)

7,12-*Dihydropleiadene*-7,12-*sulphide* (XIII)

A. *From dibromide* (V). A suspension of V (0·68 g) and P_2S_5 (0·5 g) in CS_2 (200 ml) was stirred at room temp for 2 days. The reaction mixture was then filtered through Celite and the filtrate evaporated to a yellow solid. Chromatography of this material over alumina (grade I, 40 g, CH_2Cl_2 eluant) followed by crystallization from cyclohexane gave white prisms of XIII (0·20 g,40 %), m.p. 178–179°. A larger scale reaction gave a 65% yield of sulphide XIII. (Found: C, 83·33 H, 4·45; S, 12·18. Calc. for $C_{18}H_{12}S$: C, 83·06; H, 4·65; S, 12·29.)

B. *From diol* (XI). A suspension of XI (0·5 g) and P_2S_5 (0·8 g) in CS_2 (200 ml) was stirred at room temp for 2 days. The reaction mixture was filtered through Celite and the filtrate evaporated to dryness. Chromatography of the residual solid on alumina (grade I, 40 g, CH_2Cl_2 eluant) and subsequent crystallization from cyclohexane afforded white prisms of XIII (0·47 g, 94%), m.p. 177–178°.

7,12-*Dihydropleiadene*-7,12-*sulphone* (IV)

To a warm solution of sulphide XIII (1·90 g) in glacial acetic acid (75 ml) was added 40% peracetic acid (35 ml). The reaction mixture was cooled to room temp and diluted to a volume of 500 ml with water. The resulting precipitate afforded white needles of IV (1·88 g, 88%), m.p. 210–215° (dec), on crystallization from benzene. (Found: C, 73·71; H, 4·21; S, 10·65. Calc. for $C_{18}H_{12}O_2S$: C, 73·96; H, 4·14; S, 10·44.)

Pleiadene dimer (XV)

A. *From dibromide* (V). A suspension of V (0·74 g) and Cu powder (0·4 g) in benzene (100 ml) was refluxed 3 hr. The reaction mixture was then poured while warm onto a column of alumina (grade I, 40 g) and the column was then eluted with benzene. Evaporation of the eluate gave a white solid which crystallized from toluene to give fine white needles of XV (0·37 g, 86%), m.p. 350–370° (dec); λ_{max} 214mμ (90,500), 304 (18,800), 318 (17,000); NMR spectrum ($CDCl_3$): 4·83τ (4H, benzhydryl), 3·22 (4H, shielded aromatic) 2·3–2·7 (16H, aromatic). (Found: C, 94·78; H, 5·38. Calc. for $C_{36}H_{24}$: C, 94·70; H, 5·30. Mol. wt. Calc. for $C_{36}H_{24}$: 456·56. Found (osmometric): 425.)

Dimer XV was obtained in comparable yields when V was treated with either Cu powder or Zn dust in benzene at room temp as well as refluxing toluene or xylene.

B. *By pyrolysis of sulphone* (IV). Finely divided IV (0·5 g) was decomposed in an open test tube at 260° during 4 min. The residue which resulted was dissolved in benzene (50 ml) and purified by chromatography over alumina to give white needles of XV (0·206 g, 51%), m.p. 350–370° (dec), after crystallization from toluene. The decomposition of IV in diethyl phthalate solution at 200° for 10 min also gave dimer XV in 58% yield.

C. *By photolysis of sulphone* (IV). A solution of IV (0·30 g) in benzene (200 ml) was irradiated with a Hg arc at 10° for 75 min.[1b] After work-up and purification as described above, dimer XV was obtained as white needles (0·114 g, 50%) m.p. 350–370° (dec), on crystallization from toluene.

Pleiadene adduct XVI

A finely divided mixture of IV (0·50 g) and N-phenylmaleimide (0·33 g) was heated in an open test tube at 200° for 4 min. The residue which formed was dissolved in benzene (60 ml) and purified by chromatography over alumina (grade II, 50 g). Evaporation of the benzene eluate gave a light yellow solid which afforded white needles of XVI (0·468 g, 68%), m.p. 297° (dec), on crystallization from acetone; NMR spectrum ($CDCl_3$) 6·15τ (2H, α to carbonyl), 5·14 (2H, benzhydryl). (Found: C, 83·98; H, 4·68; N, 3·57. Calc. for $C_{28}H_{19}NO_2$ C, 83·77; H, 4·77; N, 3·49.)

When a benzene solution of IV was photolytically decomposed in the presence of a large excess of N-phenylmaleimide at 25°, the only reaction product was XV; none of adduct XVI could be detected. Similarly, the reaction of V with Zn or Cu powder in the presence of excess N-phenylmaleimide at room temp or refluxing solvents such as benzene, toluene and xylene lead only to the formation of XV. The decomposition of V in the presence of tetracyanoethylene at 80° and 110° also resulted in the exclusive formation of XV.

Anthracene adduct (XVIII)

A finely divided mixture of anthracene (1·0 g) and N-phenylmaleimide (1·0 g) was heated in an open test tube at 200° for 1 min. The resulting glass when crystallized from benzene deposited white needles of XVIII (1·7 g, 84%), m.p. 203° (dec); NMR spectrum ($CDCl_3$) 6·57τ (2H, β to carbonyl), 5·00 (2H, benzhydryl). (Found: C, 81·82; H, 5·03; N, 3·77. Calc. for $C_{24}H_{17}O_2N$: C, 82·03; H, 4·88; N, 3·77.)

Lithium aluminium hydride reduction product of pleiadene adduct XVI

A suspension of LAH (0·05 g) and XVI (0·08 g) in ether (80 ml) was refluxed 6 hr. Water (50 ml) was then added and the resulting two-phase system was filtered through Celite. Evaporation of the dried ethereal phase gave a white residue, which crystallized from cyclohexane as white needles (0·07 g, 93%), m.p. 219–220°; NMR spectrum ($CDCl_3$) 6·0–7·38τ (6H, protons α and β to nitrogen), 5·81τ (2H, benzhydryl). (Found: C, 90·04; H, 6·21; N, 3·75. Calc. for $C_{28}H_{23}N$: C, 90·22; H, 6·14; N, 4·04.)

Lithium aluminium deuteride reduction product (XIX) *of pleiadene adduct* XVI

A suspension of XVI (0·2 g) and LAD (0·3 g) in ether (150 ml) was refluxed 2 days. After work-up as described above, crystallization of the reaction product from cyclohexane afforded white needles of XIX (0·173 g, 92%), m.p. 219°; NMR spectrum ($CDCl_3$) 6·51τ (2H, β to nitrogen), 5·81 (2H, benzhydryl).

Lithium aluminium hydride reduction product of the anthracene adduct (XVIII)

A suspension of XVIII (1·0 g) and LAH (0·5 g) in ether (150 ml) was refluxed 5 hr. After work-up in the manner described above and crystallization of the reaction product from cyclohexane, there were obtained white needles (0·92 g, 98%), m.p. 165–167°; NMR spectrum ($CDCl_3$) 6·3–7·5τ (6H, α and β to nitrogen), 5·72 (2H, benzhydryl). (Found: C, 89·12; H, 6·55; N, 4·33. Calc. for $C_{24}H_{21}N$: C, 89·00; H, 6·55; N, 4·54.)

Lithium aluminium deuteride reduction product (XX) *of anthracene adduct* XVIII

A suspension of XVIII (0·18 g) and LAD (0·2 g) in ether (80 ml) was refluxed 1 day. After work-up in the manner described above, crystallization of the reaction product from cyclohexane gave fine white needles of XX (0·15 g, 90%), m.p. 165°; NMR spectrum ($CDCl_3$) 7·10 τ (2H, β to nitrogen), 5·72 (2H, benzhydryl).

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