[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

# A Synthesis of Pleiadiene and Acepleiadylene[1]

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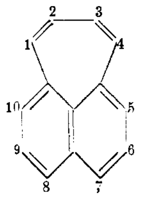
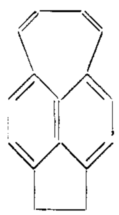
The preparation of pleiadiene (cyclohepta[de]naphthalene, I) by a ten-step synthesis from 1,8-naphthalic anhydride is reported. Also, the dehydrogenation of acepleiadiene to give acepleiadylene (III), a naphtholog of azulene, is described. A preliminary report of the properties of these unusual hydrocarbons is given.

In a previous communication,[3] the synthesis of pleiadiene (cyclohepta[de]naphthalene, I) was posed as a problem of theoretical interest. On the basis of the Hückel theory of aromaticity,[4] it might be expected that this peri isomer of phenanthrene and anthracene would show similar aromatic properties. In the previous study, the synthesis of acepleiadiene (II), a molecule containing the desired conjugated system but substituted at the 7,8-positions was accomplished and it was found that a preliminary study of its chemical behavior indicated qualitative agreement with prediction.

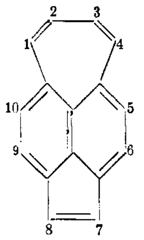
Following our previous report, Pullman, Pullman, Berthier and Pontis[5] made a theoretical study of pleiadiene, acepleiadiene and acepleiadylene using the molecular orbital method. From their calculations they were able to make predictions regarding the bond orders, electron distribution, dipole moments and ultraviolet absorption spectra of the three hydrocarbons. The availability of these theoretical data made it highly desirable to complete the syntheses of these hydrocarbons so that a direct correlation between experimentally-derived and theoretically-predicted values could be made. It is the purpose of the present communication to report syntheses of the remaining two hydrocarbons, pleiadiene (I) and acepleiadylene (III).



I

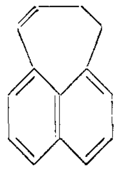


II



III

From the beginning it appeared unlikely that the formation of the peri ring of pleiadiene by a Friedel–Crafts type cyclization would be satisfactory. In the case of acepleiadiene this route could be utilized because of the orientation influence exerted by the five-membered ace ring. However with molecules lacking this directive influence peri cyclization fails.[6] Although Gardner and Horton[7] have by-passed this difficulty by carrying out such cyclizations with tetralin derivatives, their attempts to prepare pleiadiene were also unsuccessful. In this instance they were unable to find satisfactory conditions for effecting the dehydrogenation of 1-pleiadene (IV) to pleiadiene (I). In view of this it appeared desirable that a route be chosen which would lead directly to pleiadiene without involving dehydrogenation as a final step. The successful scheme which evolved is illustrated below.



IV

The conversion of 1,8-naphthalic anhydride (V) to 1,8-naphthalenedimethanol (VI) was accomplished in 74% yield using lithium aluminum hydride. When this diol was treated in the usual fashion with thionyl chloride to effect replacement of the hydroxyl groups by chlorine, concomitant formation of the corresponding cyclic ether occurred. By the use of concentrated hydrochloric acid at 0° this side reaction was avoided and the desired 1,8-bis-(chloromethyl)-naphthalene (VII) resulted in 93% yield.

The next step was the formation of a seven-membered peri ring with suitable substituents attached so that the desired unsaturation could be introduced at a later stage. For this purpose the alkylation of 1,1,2,2-tetracarbethoxyethane was chosen. Despite the intensive effort which has been devoted to the synthesis of unsaturated seven-membered rings, this approach apparently has not been realized previously. When excess 1,1,2,2-tetracarbethoxyethane was employed as solvent, the alkylation proceeded smoothly in 53% yield to give VIII. Alkaline hydrolysis of VIII was accompanied by decarboxylation and gave *trans*-2,3-pleiadanedicarboxylic acid (IX) in quantitative yield. The assignment of the *trans* configuration to this dicarboxylic acid is based on the fact that it shows no tendency toward anhydride formation and is recovered unchanged after melting.

Removal of the carboxylic acid groups and introduction of the desired unsaturation followed in a straight-forward fashion. The dimethyl ester (X) was produced by esterification and this, on treatment with hydrazine hydrate, gave the dihydrazide XI. It was shown that the dihydrazide underwent the normal Curtius degradation to give 2,3-diaminopleiadane. However, the report by Finholt, Anderson and Agre that the isocyanate grouping can be converted to a methylamino

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[1] Supported in part by the Office of Ordnance Research, Army Ordnance Contract No. DA-30-115-O.R.D.-421.

[2] Union Carbide and Carbon Corporation Predoctoral Fellow, 1954–1955.

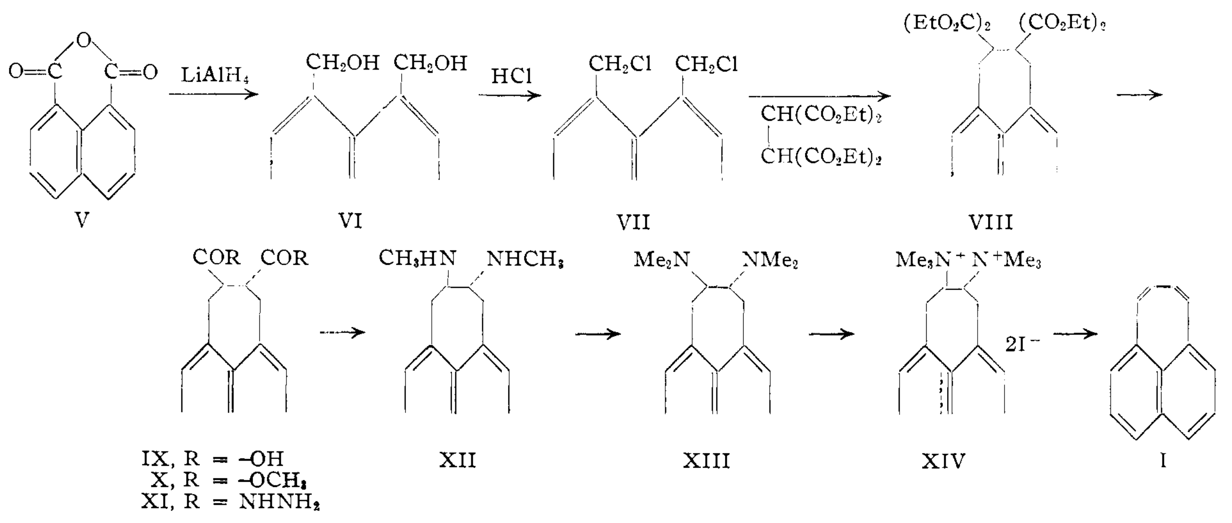
[3] V. Boekelheide, W. E. Langeland and Chu-Tsin Liu, THIS JOURNAL, **73**, 2432 (1951).

[4] E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).

[5] B. Pullman, A. Pullman, G. Berthier and J. Pontis, *J. chim. phys.*, **49**, 20 (1952).

[6] L. F. Fieser and M. A. Peters, THIS JOURNAL, **54**, 4347 (1932).

[7] P. D. Gardner and W. J. Horton, *ibid.*, **74**, 657 (1952).



group by lithium aluminum hydride[8] suggested a means of shortening the procedure. When the dihydrazide XI was treated with nitrous acid to give the diazide, the crude diazide was dried, heated in benzene to effect rearrangement to the corresponding diisocyanate and then reduced directly with lithium aluminum hydride. In this way 2,3-bis-(N-methylamino)-pleiadane (XII) was produced in one operation. In actual practice the crude diamine XII was treated directly with formaldehyde and formic acid to give XIII in an over-all yield from XI of 57%.

Treatment of XIII with an excess of methyl iodide readily gave the quaternary salt XIV and this on being subjected to the conditions of the Hofmann elimination gave the desired pleiadiene. After some experimentation it was found that the best conditions for effecting the Hofmann elimination were sodium ethoxide in boiling absolute ethanol. By this procedure pleiadiene (I) formed in 74% yield.

Pleiadiene occurs as bright red crystals, m.p. 87–90°. That the structure assigned to pleiadiene is correct was shown by hydrogenation studies. Catalytic reduction of pleiadiene over platinum as catalyst resulted in the uptake of two moles of hydrogen and gave pleiadane, m.p. 57–58°, in excellent yield. Gilmore and Horton[9] have reported the melting point of pleiadane (7,8,9,10-tetrahydrocyclohepta[de]naphthalene) as 55–57°. A comparison of the picrate of our sample with that of an authentic sample of pleiadane picrate kindly provided by Professor Horton showed the two to be identical.

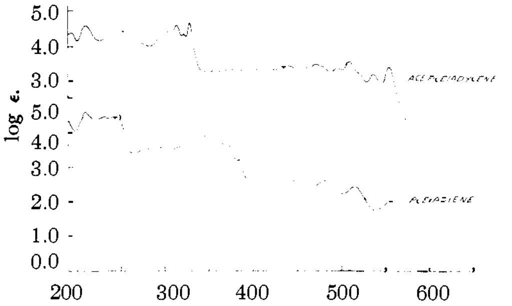


Fig. 1.—Ultraviolet absorption spectra of pleiadiene (I) and acepleiadylene (III) in 95% ethanol.

With pleiadiene thus available by synthesis, it seemed desirable to reinvestigate possible routes to acepleiadylene (III) so that simultaneous comparison of these three hydrocarbons, I, II and III, might be made. Reinvestigation of the palladium dehydrogenation of acepleiadiene eventually led to the successful isolation of acepleiadylene as deep red crystals in 20% yield. Actually, the reaction is better described as a diproportionation since less than 10% of the expected quantity of hydrogen was evolved. From chromatography of the products there was isolated, in addition to acepleiadylene and acepleiadiene, a white solid, m.p. 85–86°, having the correct composition for acepleiadene (XV). Support for this assignment was readily available from hydrogenation studies. All three hydrocarbons II, III and XV, were converted by catalytic reduction over platinum to acepleiadane (XVI) the hydrogen uptake being two, three and one moles of hydrogen, respectively. Although the ultraviolet absorption spectrum of XV showed that the aliphatic double bond was in conjugation with the naphthalene nucleus, the question of whether this conjugate unsaturation is present in the five- or seven-membered ring cannot be decided readily from spectral data alone. Such reference compounds as perinaphthene[10a] and acenaphthylene[10b] have very similar spectra in the ultraviolet.

The ultraviolet absorption spectra of pleiadiene, acepleiadiene and acepleiadylene are very similar, in agreement with the expectations of Pullman, Pullman, Berthier and Pontis.[5] The outstanding differences lie in the values of the extinction coefficients which are about tenfold greater for acepleiadylene than for the other two hydrocarbons.

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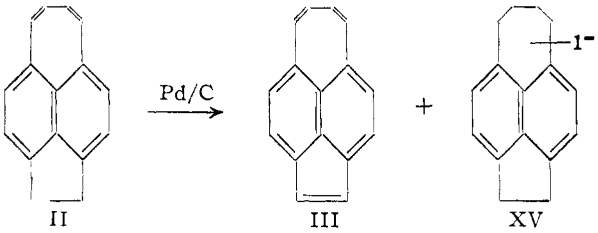
(8) A. E. Finholt, C. D. Anderson and C. L. Agre, *J. Org. Chem.*, **18**, 1338 (1953).

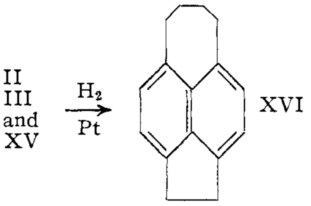
(9) R. C. Gilmore, Jr., and W. J. Horton, This Journal, **73**, 1411 (1951).

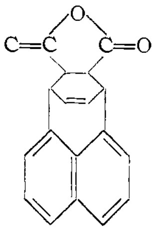
(10) (a) V. Boekelheide and C. E. Larrabee, *ibid.*, **72**, 1245 (1950); (b) L. C. Craig, W. A. Jacobs and G. I. Lavin, *J. Biol. Chem.*, **139**, 277 (1941).

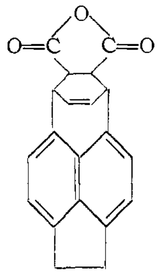
Also, acepleiadylene is strongly fluorescent in contrast to the other two hydrocarbons.

The first chemical test applied to compare the reactivity of the three hydrocarbons was reaction with maleic anhydride. This was chosen to try to determine to what extent the diene system in the seven-membered ring would behave as an ordinary aliphatic diene. In boiling benzene, the reaction of pleiadiene and maleic anhydride was complete in ten hours; with acepleiadiene two and one-half days were required for completion of the reaction, whereas with acepleiadylene there was no evidence of reaction after eight and one-half days of heating. The ultraviolet absorption of the maleic anhydride adducts were essentially the same as those of pleiadane and acepleiadane and thus support the assignment of structures XVII and XVIII to these adducts.






XVII


XVIII

In investigating the behavior of these hydrocarbons toward electrophilic substitution, the studies of Anderson, Nelson and Tazuma on the electrophilic substitution of azulene[11] were taken as a model. Of the reactions which they described—diazonium coupling, Friedel–Crafts acylation and nitration—the only reaction which led to well-defined products in our series was nitration. Nitration of pleiadiene using cupric nitrate and acetic anhydride gave a brick-red mononitro derivative in 8% yield. Similarly, acepleiadylene gave a red mononitro derivative in 30% yield. Although acepleiadiene also gave a product having the correct composition for a mononitro derivative, it was a high-melting yellow solid whose molecular weight indicated that it was a dimer, possibly through self-addition in a Diels–Alder type condensation. Evidence that the products were nitro derivatives was obtained not only from elementary analysis, which showed the derivatives had the correct composition and contained nitrogen, but also from a study of their infrared spectra. As Bellamy has demonstrated,[12] the nitro group shows absorption in the 6.41–6.67 and 7.35–7.69 $\mu$ regions. All three of our derivatives showed the expected absorption in these regions.

Unfortunately the amount of material available from the nitration experiments was insufficient to permit determination of the position occupied by the nitro group. From the calculations of Pullman, *et al.*, it would be expected that pleiadiene would undergo electrophilic substitution first at the 5-position whereas acepleiadylene would substitute first at the 7-position. It is hoped that eventually this point can be established experimentally.

As yet dipole moment and heats of combustion data are not available, although it is hoped that these can be reported in the future. It is expected that the dipole moments of these hydrocarbons are relatively large and that the directions of the dipoles for pleiadiene and acenaphthylene are opposite. Whether these molecules are planar or not poses yet another question requiring X-ray studies.

From the preliminary evidence at hand it would appear that acepleiadylene shows the greatest stability, or aromatic character, of the three hydrocarbons. This is borne out by its greater ease of nitration, its lack of reactivity toward maleic anhydride and its formation from acepleiadiene by disproportionation. This conclusion is somewhat unexpected since acepleiadylene has 16 $\pi$-electrons and does not fit the simple $4n + 2$ requirement of Hückel, whereas pleiadiene and acepleiadiene with 14 $\pi$-electrons do. In this respect acepleiadylene is similar to its isomer, pyrene, which is an aromatic hydrocarbon having 16 $\pi$-electrons. The apparent conclusion to be drawn from these experiments is that the extension of the Hückel rule to polycyclic molecules containing peri ring fusion is not justified.

## Experimental[13]

**1,8-Naphthalenedimethanol (VI).**—The naphthalic anhydride used in this study was prepared from acenaphthene following the directions of Graebe and Gfeller.[14] Although Beyler and Sarett[15] have previously reported the preparation of 1,8-naphthalenedimethanol by the lithium aluminum hydride reduction of naphthalic anhydride in tetrahydrofuran, the preparation given below was more suitable for large scale preparation and avoided the concomitant formation of 2-oxaperinaphthane.

To a stirred slurry of 60.0 g. of lithium aluminum hydride in a mixture of 1.4 l. of absolute ether and 1.15 l. of dry benzene there was added 150.0 g. of naphthalic anhydride at a rate sufficient to maintain gentle boiling. After the addition was complete the mixture was boiled under reflux for an additional 12 hours. The excess lithium aluminum hydride was decomposed by addition of water and the precipitated solid was collected. The inorganic salts were removed by washing with dilute acid and the remaining solid was recrystallized from a 50% solution of methanol in benzene. This gave 102.0 g. (74%) of needles, m.p. 157–158°

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[11] A. G. Anderson, J. A. Nelson and J. J. Tazuma, THIS JOURNAL, **75**, 4980 (1953).

[12] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 250.

[13] All melting points are corrected. Analyses by Miss A. E. Smith. Infrared and ultraviolet spectra by Carl A. Whiteman.

[14] C. Graebe and E. Gfeller, *Ber.*, **25**, 652 (1892).

[15] R. E. Beyler and L. H. Sarett, THIS JOURNAL, **74**, 1406 (1952)

(Beyler and Sarett[15] report 158°; Beeby, Cookson and Mann[16] give 152–154°).

**1,8-Bis-(chloromethyl)-naphthalene (VII).**—To 1.4 l. of concentrated hydrochloric held at 0° there was added slowly with stirring 104.5 g. of finely divided 1,8-naphthalenedimethanol. After the addition was complete, the mixture was stirred for two hours at 0° and then an additional three hours at room temperature. The insoluble precipitate was collected, washed well with water and dried. After recrystallization from hexane it gave 118.2 g. (93%) of crystals, m.p. 87–90°. The analytical sample was obtained, after several additional recrystallizations from hexane, as colorless plates, m.p. 90.5–91.0°.

*Anal.* Calcd. for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.48. Found: C, 64.11; H, 4.51.

**Tetraethyl 2,2,3,3-Pleiadanetetracarboxylate (VIII).**—The 1,1,2,2-tetracarbethoxyethane used in this study was prepared according to the procedure of Bischoff and Rath[17] except that for large-scale runs it was more convenient to substitute bromine for the solution of iodine in ether which they employed. A mixture of 61.0 g. of the disodioenolate of tetracarbethoxyethane[18] in 146 g. of tetracarbethoxyethane as solvent was heated at 115° and then 31.9 g. of finely-divided 1,8-bis-(chloromethyl)-naphthalene was slowly added with stirring. After an additional six hours stirring at 115°, the mixture was allowed to cool. Ether was added to take up the 1,1,2,2-tetracarbethoxyethane and the insoluble residue was collected. After washing with water and drying, this residue gave 40.3 g. (53%) of colorless crystals, m.p. 150–158°. The analytical sample was obtained, after recrystallization from an ethanol–benzene mixture, as diamond-shaped crystals, m.p. 161.5–162.0°. By concentration of the ether solution there was recovered 132 g. of 1,1,2,2-tetracarbethoxyethane in sufficiently pure state for use in another run.

*Anal.* Calcd. for $C_{22}H_{30}O_8$: C, 66.37; H, 6.45. Found: C, 66.53; H, 6.52.

***trans*-2,3-Pleiadanedicarboxylic Acid (IX).**—A solution of 51.7 g. of tetraethyl 2,2,3,3-pleiadanetetracarboxylate and 59.2 g. of potassium hydroxide in 335 ml. of diethylene glycol was heated at 110° for 4 hours. Then the solution was cooled, diluted by the addition of 1 l. of water, and brought to a *p*H of 5 by addition of hydrochloric acid. After two days, the separation of crystals was complete and these were collected and dried. There was obtained 25.6 g. (98%) of slightly tan crystals, m.p. 203–206°. The analytical sample was obtained after recrystallization from ethyl acetate as white cubes, m.p. 208–210°. On cooling the melt recrystallized and was unchanged in melting point.

*Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135. Found: C, 70.98; H, 5.22; neut. equiv., 139.

**Dimethyl 2,3-Pleiadanedicarboxylate (X).**—A solution of 25.6 g. of 2,3-pleiadanedicarboxylic acid in 750 ml. of methanol containing anhydrous hydrogen chloride was boiled under reflux for 26 hours. After the solution had been neutralized with aqueous sodium bicarbonate, it was diluted with 1.5 l. of water and extracted with ether. The ethereal solution was dried and concentrated and the residual oil distilled under reduced pressure to give 28.1 g. (99%) of an oil that solidified to a yellow solid, m.p. 59–62°. Recrystallization of this material from pentane gave colorless needles, m.p. 63–64°. Depending on the conditions used in the crystallization either one of two crystalline modifications—needles, m.p. 63–64°, or bars, m.p. 61–63°—could be obtained. That this was the result of polymorphism was shown by the interconvertibility of the two forms by seeding appropriate supersaturated solutions.

*Anal.* Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.63; H, 6.20.

**2,3-Pleiadanedicarbohydrazide (XI).**—A solution of 6.56 g. of dimethyl 2,3-pleiadanedicarboxylate and 5 g. of 85% hydrazine hydrate in 500 ml. of methanol was boiled under reflux for 6 days. During this period 2-g. portions of 85% hydrazine hydrate were added twice to the mixture. The crystalline solid, which had formed, was then collected and dried to give 5.74 g. (88%) of white crystals, m.p. 261° dec. The analytical sample was obtained after recrystallization from dimethylformamide as white needles, m.p. 261° dec.

*Anal.* Calcd. for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.18. Found: C, 64.45; H, 6.23.

**Diethyl 2,3-Pleiadanedicarbamate.**—To a solution of 1.30 g. of 2,3-pleiadanedicarbohydrazide (XI) in 15 ml. of 1.2 *N* hydrochloric acid and 25 ml. of water held at 0° there was added 0.80 g. of sodium nitrite in 39 ml. of water over a period of 20 min. The mixture was stirred in the cold for 25 min. and then filtered. The caramel-colored solid, which was collected, was pressed dry and dissolved in 70 ml. of absolute ethanol. After the ethanolic solution had boiled under reflux for 4 hours, it was concentrated and allowed to cool. There separated 1.00 g. (65%) of white crystals, m.p. 211–215°. Recrystallization of a sample from a pyridine–water mixture gave colorless needles, m.p. 221–222°.

*Anal.* Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.39; H, 6.79. Found: C, 67.37; H, 6.98.

**2,3-Diaminopleiadane Dipicrate.**—A mixture of 300 mg. of diethyl 2,3-pleiadanedicarbamate, 20 ml. of concentrated hydrochloric acid and 10 ml. of glacial acetic acid was boiled under reflux for 13 hours and then concentrated under reduced pressure to dryness. The residue was dissolved in water, made basic with aqueous sodium hydroxide solution and extracted with ether. Concentration of the ether gave 77 mg. of a brown oil which was dissolved in ethanol and treated with ethanolic picric acid. The solid which separated was recrystallized from an ethanol–water mixture to give dark-yellow cubes not melting below 300°.

*Anal.* Calcd. for $C_{26}H_{22}N_8O_{14}$: C, 46.57; H, 3.31; mol. wt., 670. Found: C, 46.51; H, 3.62; mol. wt.,[19] 658 ± 13.

**2,3-Bis-(N,N-dimethylamino)-pleiadane (XIII).**—To a solution of 4.88 g. of 2,3-pleiadanedicarbohydrazide in 200 ml. of 0.5 *N* hydrochloric acid solution held at 0° there was added a solution of 2.5 g. of sodium nitrite in 50 ml. of water. The solid diazide which separated was collected, pressed dry as well as possible and dissolved in 250 ml. of dry benzene at 10°. The diazide was then dried completely by azeotropic distillation under reduced pressure keeping the temperature of the flask below room temperature. The concentrated solution (about 100 ml.) was boiled under reflux at atmospheric pressure for 5 hours to effect decomposition of the diazide and rearrangement to the corrresponding diisocyanate. At this point 34 ml. of a 1.27 *N* ethereal solution of lithium aluminum hydride was added and the mixture was boiled an additional 13 hours under reflux. After the excess of lithium aluminum hydride had been decomposed by addition of water, the organic solvents were removed under reduced pressure and 200 ml. of a 30% aqueous potassium hydroxide solution was added to dissolve the lithium and aluminum hydroxides. The resulting solution was extracted with ether and the ethereal extracts were dried and concentrated. This gave 3.06 g. of crude 2,3-bis-(N-methylamino)-pleiadane (XII) as an oil (see below). The crude oil was taken up in a mixture of 10 g. of 90% formic acid and 4.0 g. of formalin (37% solution of formaldehyde in water) and the mixture was heated on a steam-bath for 20 hours. When the solution had been made basic, it was extracted with ether and the ethereal extracts were dried and concentrated. Distillation of the residue at 0.3 mm. gave 2.51 g. (57% over-all yield) of an oil which solidified to a waxy solid, m.p. 56–62°.

*Anal.* Calcd. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01. Found: C, 80.63; H, 8.92.

**2,3-Bis-(N-methylamino)-pleiadane (XII).**—When, in the preceding experiment, a sample of the crude 2,3-bis-(N-methylamino)-pleiadane was heated at 0.1 mm., it yielded through sublimation a slightly pink solid, m.p. 63–67°.

*Anal.* Calcd. for $C_{16}H_{20}N_2$: C, 79.93; H, 8.39. Found: C, 79.94; H, 8.42.

A dipicrate of XII readily formed in ethanol and was obtained, after recrystallization from a dioxane–water mixture, as bright yellow crystals, m.p. 206–209°.

*Anal.* Calcd. for $C_{28}H_{26}N_8O_{14}$: C, 48.14; H, 3.75; mol. wt., 699. Found: C, 47.93; H, 3.95; mol. wt.,[19] 710 ± 14.

**2,3-Bis-(N,N,N-trimethylammonio)-pleiadane Diiodide (XIV).**—A solution containing 5.66 g. of 2,3-bis-(N,N-

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[16] M. H. Beeby, G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 1922 (1950).

[17] C. A. Bischoff and C. Rath, *Ber.*, **17**, 2781 (1884).

[18] W. H. Perkin, Jr., *J. Chem. Soc.*, **53**, 10 (1888).

[19] K. G. Cunningham, W. Dawson and F. S. Spring, *ibid.*, 2305 (1951).

dimethylamino)-pleiadane, 9.0 g. of methyl iodide and 2.0 ml. of methanol was boiled under reflux for 4 hours. After addition of more methanol to aid in filtration, the precipitated solid was collected and dried, yielding 9.13 g. (73%) of a light tan solid, m.p. 206–210°. An analytical sample was obtained, after recrystallization from ethanol, as colorless needles, m.p. 210–211°.

*Anal.* Calcd. for $C_{20}H_{30}N_2I_2$: C, 43.49; H, 5.48. Found: C, 43.86; H, 5.56.

**Pleiadiene** (I).—To a solution of 2.30 g. of sodium in 50 ml. of absolute ethanol there was added 800 mg. of 2,3-bis-(N,N,N-trimethylammonio)-pleiadane diiodide and the resulting mixture was boiled under reflux for 15 min. After dilution with 300 ml. of water, the mixture was carefully extracted with hexane. The combined hexane extracts were dried, concentrated and chromatographed over alumina. The eluate fraction containing the first orange band was collected and rechromatographed over alumina. From the second chromatogram there was isolated 192 mg. (74%) of a bright red solid, m.p. 87–89°, in satisfactory purity for further use. An analytical sample was obtained by recrystallization from pentane as bright red bars, m.p. 87–90°.

*Anal.* Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.01; H, 5.67.

**Hydrogenation of Pleiadiene.**—To a suspension of 40 mg. of prereduced platinum oxide in 5 ml. of ethanol there was added a solution of 43.6 mg. of pleiadiene in 15 ml. of ethanol and the mixture was subjected to hydrogenation at room temperature and atmospheric pressure. Hydrogen uptake was complete in about 15 min. and corresponded to the absorption of two moles of hydrogen. After removal of the catalyst and solvent, the residual oil was taken up in hexane and chromatographed over alumina. From the eluate a white solid was obtained in excellent yield. This was further purified by two recrystallizations from an ethanol–water mixture to give flat, white plates, m.p. 57–58° (Gilmore and Horton[9] give the m.p. of pleiadane as 55–57°).

*Anal.* Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.83.

Treatment of 8.4 mg. of pleidane with ethanolic picric acid gave orange needles. These, after two recrystallizations from ethanol, melted at 114–116°, undepressed on admixture of an authentic sample of pleiadane picrate.[9]

**Acepleiadylene** (III).—A solution of 1.000 g. of acepleiadiene[3] in 30 ml. of mesitylene containing 500 mg. of a 30% palladium-on-charcoal catalyst[20] was boiled under reflux for two hours. Only about 10% of the expected quantity of hydrogen was evolved. The catalyst and solvent were then removed and the residue was taken up in hexane and chromatographed over alumina. From the first colorless, but fluorescent, eluate there was isolated 230 mg. of a solid having a slight orange tint. This was set aside and its characterization is discussed under the paragraph on acepleiadene. The second eluate fraction containing a nonfluorescent orange band yielded 365 mg. of crystals, m.p. 105–117°, which was shown by the method of mixed melting points to be unchanged acepleiadiene. The third eluate fraction containing a fluorescent orange band gave 196.3 mg. (20%) of crystalline acepleiadylene. The analytical sample was obtained from hexane as beautiful red cubes, m.p. 156–162°. Because of the deep color of the crystals and their tendency to soften before melting, an exact melting point range is hard to describe.

*Anal.* Calcd. for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 94.86; H, 5.29.

**Hydrogenation of Acepleiadylene.**—A mixture of 13.7 mg. of acepleiadylene and 20 mg. of prereduced platinum oxide in 5.2 ml. of ethanol was subjected to hydrogenation at room temperature and atmospheric pressure in an apparatus designed to measure quantitatively the uptake of hydrogen. Hydrogen absorption essentially stopped after 25 minutes and corresponded to 90% of the calculated quantity for three double bonds. Removal of the catalyst and concentration of the solvent gave white crystals, m.p. 136–138° (acepleiadane[3,21] (XVI) is reported to melt at 138°).

As further confirmation a sample of acepleiadiene was hydrogenated in the same manner and shown to take up two moles of hydrogen yielding acepleiadane as white crystals, m.p. 136–138°. A mixture of the two samples of acepleiadane, thus prepared, showed no depression of melting point.

**Acepleiadene** (XV).—The solid obtained from the first eluate fraction in the previous experiment was dissolved in hexane and rechromatographed over alumina. The solid recovered from the eluate was then recrystallized from ethanol to give white crystals, m.p. 85–86°. The ultraviolet absorption spectrum of acepleiadenes show absorption maxima at 342 (log $\epsilon$, 4.0), 320 (log $\epsilon$, 4.1) and 236 m$\mu$ (log $\epsilon$, 4.6). Since the ultraviolet absorption spectrum of perinaphthene has maxima at 350, 320 and 233 m$\mu$ and that of acenaphthylene shows maxima at 339, 324 and 230 m$\mu$, it is not possible to make a choice of whether the aliphatic double bond is in the five- or seven-membered ring although the correspondence appears to be slightly better for the five-membered ring unsaturation.

*Anal.* Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.25; H, 7.10.

**Hydrogenation of Acepleiadene.**—The hydrogenation of acepleiadene was carried in the same manner as described for acepleiadylene. Hydrogen absorption corresponded to 110% of that required for one double bond and gave in excellent yield white crystals, m.p. 136–138°. These were shown by the method of mixed melting points to be identical with acepleiadane.

**Diels–Alder Addition of Maleic Anhydride to Pleiadiene.**—A solution of 20.0 mg. of pleiadiene and 15.0 mg. of freshly-sublimed maleic anhydride in 1 ml. of benzene was boiled under reflux until the red color of the hydrocarbon disappeared. This required 10 hours of heating. The solid remaining after removing all volatile material was recrystallized from benzene to give 15.2 mg. (49%) of crystals, m.p. 249–251°. After an additional recrystallization from benzene a sample was obtained as compact white crystals, m.p. 252–253°.

*Anal.* Calcd. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.10; H, 4.66.

**Diels–Alder Addition of Maleic Anhydride to Acepleiadiene.**—A solution of 45.8 mg. of acepleiadiene and 30 mg. of maleic anhydride in 2.0 ml. of benzene required heating for 2.5 days before the red color of the hydrocarbon disappeared. When the solution was cooled, there separated 50 mg. (74%) of white crystals, m.p. 267–270°.

*Anal.* Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.27; H, 4.64.

**Attempted Diels–Alder Addition of Maleic Anhydride to Acepleiadylene.**—A solution of 45.3 mg. of acepleiadylene and 40 mg. of maleic anhydride in 2.0 ml. of benzene was boiled under reflux for 8.5 days with no appreciable change in the appearance of the solution. After removal of the benzene, the residue was taken up in pentane and on concentration the pentane solution yielded 35.0 mg. of unchanged acepleiadylene.

**Nitration of Pleiadiene.**—To a solution of 34 mg. of cupric nitrate trihydrate in 20 ml. of acetic anhydride cooled in a Dry Ice–acetone-bath there was added 50 mg. of pleiadiene. The mixture was stirred for one hour in the cold and then allowed to warm to room temperature and stand overnight. After addition of sufficient water to hydrolyze the excess acetic anhydride and bring the total volume to 200 ml., the mixture was extracted carefully with methylene chloride. The combined methylene chloride extracts were washed with aqueous bicarbonate solution, then with water and finally dried. Concentration of the solution gave a thick dark oil which was taken up in a 50% hexane–methylene chloride mixture and chromatographed over alumina. From the first eluate fraction there was isolated 14.5 mg. of a reddish-brown solid. The later eluate fraction did not yield any characterizable materials. The reddish-brown solid was again dissolved in hexane and twice more chromatographed over alumina using methylene chloride in hexane to elute the columns. In this way there was obtained 4.0 mg. of brick-red crystals, m.p. 120–122°. The infrared spectrum of these crystals show strong absorption bands at 6.47, 7.56 and 7.65 $\mu$ in agreement with the absorption bands usually assigned to the nitro group.[12]

*Anal.* Calcd. for $C_{14}H_9NO_2$: C, 75.32; H, 4.06. Found: C, 74.64; H, 4.05.

**Nitration of Acepleiadylene.**—To a solution of 60 mg. of cupric nitrate trihydrate in 40 ml. of acetic anhydride cooled

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[20] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).

[21] L. F. Fieser and M. A. Peters, THIS JOURNAL, **54**, 4347 (1932).

in a Dry Ice–acetone-bath there was added 100 mg. of acepleiadylene and the resulting mixture was stirred in the cold for the three hours. The mixture was then allowed to warm to room temperature and stirring was continued for an additional three hours. The solution was then diluted to a volume of 200 ml. with water and extracted with methylene chloride. After the methylene chloride extracts had been washed with aqueous bicarbonate and water, they were dried and concentrated to give a dark solid residue. This was taken up in a 20% methylene chloride in hexane solution and chromatographed over alumina. From the eluate there was isolated 36.7 mg. of deep red crystals. These were recrystallized from a methylene chloride–hexane mixture and yielded dark red needles, m.p. 162–170°. Further recrystallization did not sharpen the melting point. The infrared spectrum of these crystals showed absorption bands at 6.58, 7.54 and 7.65 μ as expected for a nitro group.[12] The maxima and log ε values for the ultraviolet and visible spectrum of nitroacepleiadylene are 556 (3.20), 510 (3.42), 476 (3.42), 400 (3.53), 324 (4.35), 312 (4.40) and 250 mμ (4.30).

*Anal.* Calcd. for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.67. Found: C, 77.55; H, 4.01; N, 5.53.

After elution of the red needles of nitroacepleiadylene, a 50% methylene chloride–hexane solution was passed over the column and from the eluate there was isolated 16 mg. of black crystals, m.p. 210–212°. Satisfactory characterization of this material could not be made although its infrared spectrum showed absorption typical of the nitro group.

**Nitration of Acepleiadiene.**—A 100-mg. sample of acepleiadiene was nitrated following the same procedure described previously for pleiadiene and acepleiadylene. From the methylene chloride–hexane eluate from the chromatogram there was isolated 17 mg. of a yellow solid melting above 300°. Its infrared spectrum showed absorption at 6.57, 7.45 and 7.56, indicating the presence of a nitro group. Its ultraviolet absorption spectrum showed a broad maximum at 390 mμ (log ε 3.62) with no further absorption at longer wave lengths. This would suggest the presence of a substituted nitronaphthalene as the absorbing system. This is in agreement with the possibility that this product is a dimer of the Diels–Alder type.

*Anal.* Calcd. for $C_{32}H_{22}N_2O_4$: C, 77.09; H, 4.45; mol. wt., 498. Found: C, 77.61; H, 4.98; mol. wt. (Rast camphor), 456.

ROCHESTER, NEW YORK

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

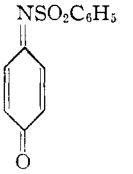
# Quinone Imides. XXXIX. Adducts of Quinone Monoimides and Conversion of Active Methylene Adducts to Benzofurans

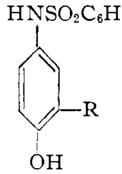
BY ROGER ADAMS AND LEROY WHITAKER[1]

RECEIVED JUNE 13, 1955

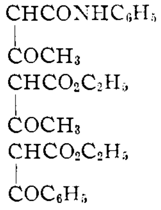
Hydrazoic acid, benzenesulfinic acid and several active methylene compounds have been added to *p*-quinonemonobenzenesulfonimide. The latter adducts are converted by means of acid to benzofuran derivatives. 1,4-Naphthoquinonemonobenzenesulfonimide adds the same reagents and, unlike the benzene analog, also reacts with piperidine, morpholine and aniline to give crystalline adducts.

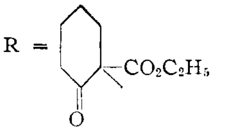
The addition of active methylene compounds to quinone diimides[2] and the conversion of the adducts to indoles by treatment with acids[3] have been reported. Active methylene compounds have now been added to quinone monoimides and the adducts have been converted to benzofurans by treatment with acids. Acetylacetone, acetoacetanilide and the ethyl esters of acetoacetic acid, benzoylacetic acid, cyclohexanone-2-carboxylic acid and malonic acid were allowed to react with *p*-quinonemonobenzenesulfonimide (I) to form the substituted phenols IIa–IIf. All these products except IIf were obtained in good yield.


I


II

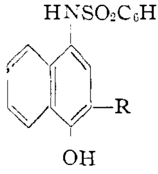
a, R = $CH(COCH_3)_2$


b, R = $\underset{COCH_3}{CHCONHC_6H_5}$
c, R = $\underset{COCH_3}{CHCO_2C_2H_5}$
d, R = $\underset{COC_6H_5}{CHCO_2C_2H_5}$

e, R = 

f, R = $CH(CO_2C_2H_5)_2$
g, R = $SO_2C_6H_5$
h, R = $N_3$
i, R = $NH_2$
j, R = $NHCOCH_3$

No isolable products resulted from the following reactions: I with dimedone, nitromethane, dibenzoylmethane and the ethyl esters of acetylsuccinic acid, cyclopentanone-2-carboxylic acid, cyanoacetic acid, methylmalonic acid, propionylmalonic acid, α,α′-dimethyl-β-ketoglutaric acid and thiolacetic acid; *p*-quinonemonomethanesulfonimide with acetylacetone, acetoacetanilide and ethyl acetoacetate; 1,4-naphthoquinonemonobenzenesulfonimide with diethyl malonate. 3-(4-Benzenesulfonamido-1-hydroxynaphthalene-2)-2,4-pentanedione (IIIa) was obtained in an impure state from the reaction of acetylacetone with 1,4-naphthoquinonemonobenzenesulfonimide.



IIIa, R = $CH(COCH_3)_2$
b, R = $N(CH_2)_5$
c, R = $N(CH_2CH_2)_2O$
d, R = $NHC_6H_5$
e, R = $SO_2C_6H_5$

The additions were effected successfully in dioxane using sodium methoxide as the catalyst. The addition of the catalyst caused the reaction mixture to turn dark. The speed and degree of decolorization usually could be used as a measure of the success of the reaction. The desired adduct was obtained from only one addition that did not decolorize and then in a yield of only 18%. Tar formation

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[1] An abstract of a thesis submitted by Leroy Whitaker to the Graduate College of the University of Illinois, 1955, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Eastman Kodak Company Fellow, 1952–1954; American Cyanamid Company Fellow, 1954–1955.

[2] R. Adams, *et al.*, THIS JOURNAL, **74**, 5557, 5872 (1952); **75**, 3403 (1953); **76**, 2763 (1954).

[3] R. Adams and W. P. Samuels, Jr., *ibid.*, **77**, 5375 (1955).