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PLEIADENE SYSTEMS—II

ON THE MECHANISM OF ACEPLEIADYLENE FORMATION—A VINYLOGOUS ELIMINATION IN THE ACENAPHTHENE SERIES

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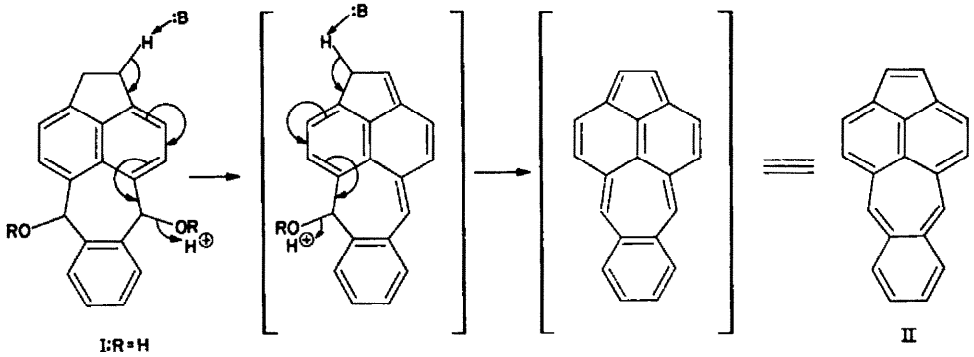
Abstract—A vinylogous dehydration mechanism is suggested for the formation of acepleiadylene from 5,10-dihydroacepleiadene-5,10-diol. Support for this mechanism is found in the conversion of 5-(α-hydroxybenzyl)acenaphthene to 5-benzylacenaphthylene by *p*-toluenesulphonyl chloride in pyridine solution. A hydride transfer mechanism for this reaction is ruled out by the observation that 4-(α-hydroxybenzyl)acenaphthene is not converted to an acenaphthylene derivative under the same conditions. Detailed syntheses of a number of acenaphthene derivatives are described.

IN THE first paper of this series it was shown that 5,10-dihydroacepleiadene-5,10-diol (I) is readily converted to the blue hydrocarbon acepleiadylene (II) by brief treatment with acid or by warming with *p*-toluenesulphonyl chloride in pyridine solution. The mechanism of this novel transformation appears to involve two consecutive vinylogous elimination steps as indicated below:



Supporting evidence for this mechanism has been sought in the study of a simpler model system containing only a portion of the dihydroacepleiadenediol structure. The model compound chosen was 5-(α-hydroxybenzyl)acenaphthene (III). It was anticipated that the latter alcohol would undergo vinylogous dehydration to the *p*-quinodimethane IV; prototropic rearrangement of this quinonoid intermediate would result in the formation of the fully aromatic 5-benzylacenaphthylene (V).

Synthesis and dehydration of 5-(*α-hydroxybenzyl)acenaphthene* (III). The previously reported 5-(α-hydroxybenzyl)acenaphthene (III)[1] was readily prepared starting from

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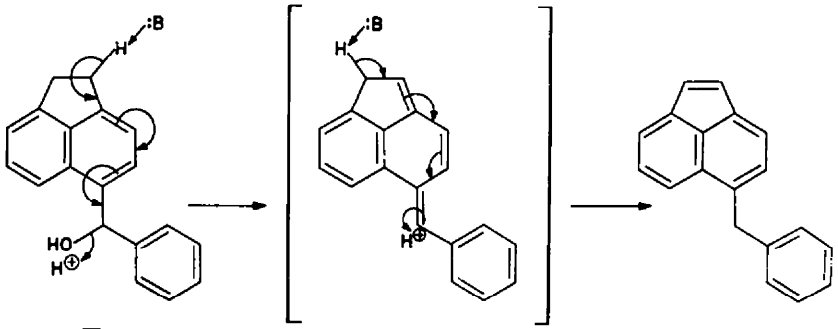
[1] K. Dziewonski and M. Rychlik, *Bull. intern. acad. polon. Sci. Ser. A.* 179 (1925); K. Dziewonski and M. Rychlik, *Ber. Dtsch. Chem. Ges.* **58**, 2239 (1925).



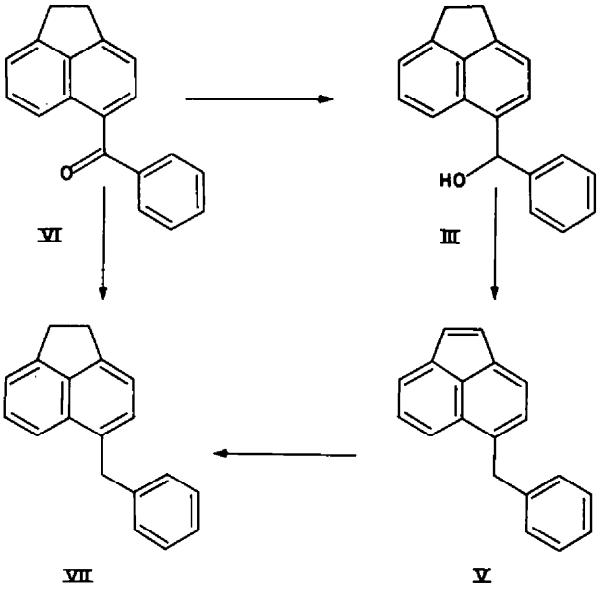
III IV V

acenaphthene. Thus, Friedel-Crafts acylation of acenaphthene with benzoyl chloride gave 5-benzoylacenaphthene (VI),[2] which was reduced conveniently by sodium borohydride to the desired alcohol III. Alcohol III was not affected by dilute mineral acid in dioxane solution; however, when the alcohol was refluxed for 24 hr in pyridine containing *p*-toluenesulphonyl chloride, there was isolated in 57% yield a bright yellow crystalline hydrocarbon, $C_{19}H_{14}$, m.p. 58°. This yellow hydrocarbon was assigned the structure of 5-benzylacenaphthylene (V) on the basis of the following evidence: (a) Its UV spectrum showed a typical acenaphthylene chromophore in the 300–350 mμ region, (b) its NMR spectrum showed only twelve aromatic protons below 3τ and two benzhydryl-type protons at 5·54 τ, and (c) one equivalent of hydrogen was absorbed readily on catalytic reduction to give the previously reported 5-benzylacenaphthene (VII).[1] 5-Benzylacenaphthylene (V) has been reported previously as a pale yellow compound (m.p. 104–105°) obtained by the copper catalysed dehydrogenation of 5-benzylacenaphthene (VII) at 600°.[3] Since hydrocarbon VII has a reported melting point of 111°,[1] it seems very likely that the substance obtained in the dehydrogenation reaction consisted of unchanged starting material coloured by a small amount of the desired 5-benzylacenaphthylene. In this regard we have noted that mixtures of hydrocarbons V and VII are essentially inseparable by crystallization. It was thus demonstrated that 5-(α-hydroxybenzyl)acenaphthene (III) could indeed be converted into 5-benzylacenaphthylene (V) by dehydration with *p*-toluenesulphonyl chloride and pyridine.

Synthesis and attempted dehydration of 4-(α-*hydroxybenzyl*)*acenaphthene* (VIII). If the dehydration of 5-(α-hydroxybenzyl)acenaphthene (III) to 5-benzylacenaphthylene (V) proceeds by way of the quinonoid intermediate IV, it may be predicted that the analogous dehydration of 4-(α-hydroxybenzyl)acenaphthene (VIII) to 4-benzylacenaphthylene (IX) would not occur. If, on the other hand, VIII were to undergo dehydration to IX, a hydride transfer mechanism involving carbonium ions could be invoked not only for this reaction, but also for the conversion of III to V. Evidence bearing upon this point was obtained by synthesizing alcohol VIII and observing its behaviour under mild dehydrating conditions.

The synthesis of 4-(α-hydroxybenzyl)acenaphthene (VIII) was achieved by means of a twelve-step synthesis from acenaphthene. The previously reported route to the

[2] C. Graebe, *Leibigs Ann.* **327**, 77 (1903).
[3] K. Dziewonski and K. Leonhard, *Bull. intern. acad. polon. Sci. Ser. A.* 99 (1928).



necessary intermediate, 4-aminoacenaphthene (X),[4] was found to be unsatisfactory in a number of respects for the preparation of large quantities of this amine; an improved procedure was developed involving the following steps:

(a) Nitration of acenaphthene to 5-nitroacenaphthene (XI)[5] in 87% yield.

(b) Hydrazine and Pd-reduction of 5-nitroacenaphthene (XI) to 5-aminoacenaphthene (XII)[2] in 95% yield.

(c) Acetic anhydride acetylation of 5-aminoacenaphthene (XII) to 5-acetamidoacenaphthene (XIII)[2] in 95% yield.

(d) Nitration of 5-acetamidoacenaphthene (XIII) to 4-nitro-5-acetamidoacenaphthene (XIV) followed by acid hydrolysis to give 4-nitro-5-aminoacenaphthene (XV)[4] in 69% overall yield.

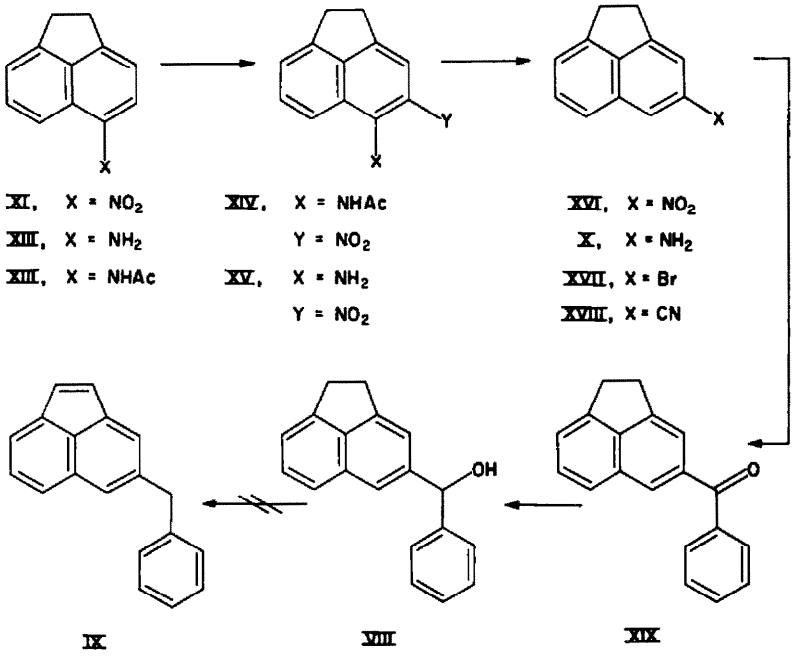
(e) Diazotization of 4-nitro-5-aminoacenaphthene (XV) followed by hypophosphorous acid deamination to give 4-nitroacenaphthene (XVI) in 60% yield and

(f) Hydrazine and Pd-reduction of 4-nitroacenaphthene (XVI) to 4-aminoacenaphthene (X)[4] in 96% yield.

4-Aminoacenaphthene (X) was best converted to 4-bromoacenaphthene (XVII) by the Schwechten method as utilized in the synthesis of 2-bromonaphthalene from 2-aminonaphthalene.[6] Thus, diazotization of amine (X) and dry pyrolysis of the mercuric bromide complex of the resulting diazonium salt afforded bromide XVII in 37% yield. Treatment of bromide XVII with cuprous cyanide in dry N-methylpyrrolidine gave 4-cyanoacenaphthene (XVIII) in 71% yield. Reaction of nitrile XVIII with phenylmagnesium bromide followed by acid hydrolysis of the resulting imine afforded 4-benzoylacenaphthene (XIX) in 82% yield. LAH reduction of ketone XIX gave 4-(α-hydroxybenzyl)acenaphthene (VIII) in 88% yield.

[4] G. T. Morgan and H. A. Harrison, *J. Soc. Chem. Ind.* **49**, 413T (1930).
[5] F. Quinke, *Ber. Dtsch. Chem. Ges.* **21**, 1454 (1888).
[6] M. S. Newman and P. H. Wise, *J. Amer. Chem. Soc.* **63**, 2847 (1941).

Like 5-(α-hydroxybenzyl)acenaphthene (III), 4-(α-hydroxybenzyl)acenaphthene (VIII) was stable to dilute mineral acid in dioxane solution. Unlike the 5-isomer, however, alcohol VIII was recovered unchanged in essentially quantitative yield after refluxing in pyridine with *p*-toluenesulphonyl chloride for 24 hr.[7]

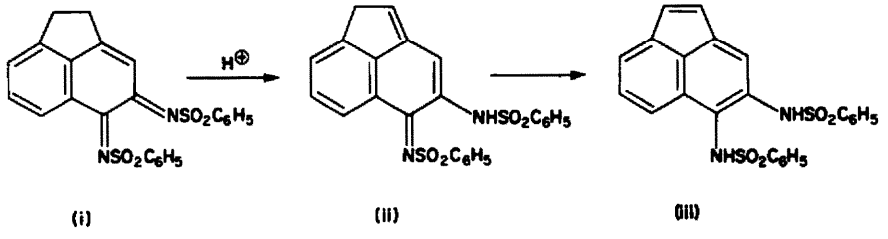


CONCLUSION

A vinylogous elimination hydration mechanism has been proposed for the conversion of 5,10-dihydroacepleiadene-5,10-diol (I) to acepleiadylene (II). Supporting evidence for this mechanism has been found in the dehydration of 5-(α-hydroxybenzyl)acenaphthene (III) to 5-benzylacenaphthylene (V) by tosyl chloride in pyridine, and in the stability toward dehydration of 4-(α-hydroxybenzyl)acenaphthene (VIII) under the same conditions.[8]

[7] It is most likely that alcohol VIII is converted *via* a tosylate to a pyridinium salt during this process, and that the resulting pyridinium salt is hydrolysed with the regeneration of the original alcohol in the course of the work-up.

[8] The acid catalysed rearrangement of the acenaphthene derivative (i) to the isomeric acenaphthylene derivative (iii) has been suggested to proceed by way of a *p*-quinonoid intermediate (ii): H. J. Richter and B. C. Weberg, *J. Amer. Chem. Soc.* **80**, 6446 (1958). This proposal is supported indirectly by the results described by us in this paper.



EXPERIMENTAL*

5-Benzoylacenaphthene (VI). Aluminium chloride (4·2 g) was added to a solution of acenaphthene (5·0 g) and benzoyl chloride (3·7 ml) in benzene (75 ml) during 15 min at room temp. The mixture was stirred for an additional 1 hr, and then poured into dil. HCl aq (100 ml). Extraction with ether followed by the usual work-up gave a brown oil which, after chromatography over alumina (Woelm, neutral, grade I, 100 g, benzene eluant) followed by crystallization from hexane, afforded colourless needles of VI (4·18 g, 49%), m.p. 100–102° (reported[3] 101°).

5-(α-Hydroxybenzyl)acenaphthene (III). A solution of $NaBH_4$ (0·5 g) and ketone VI (1·21 g) in a mixture of benzene (40 ml) and MeOH (30 ml) was stirred at room temp for 4 hr. Evaporation of the reaction mixture gave a white gel which became a granular solid on treatment with 10% NaOH aq. Crystallization of this material from cyclohexane gave white needles of III (1·15 g, 95%), m.p. 113–114° (reported[1] 113–114°).

5-Benzylacenaphthylene (V). A solution of alcohol III (0·1 g) and *p*-toluenesulphonyl chloride (0·1 g) in pyridine (20 ml) was refluxed for 20 hr under a N_2 atm. Evaporation of the reaction mixture gave a yellow oil, which was purified by chromatography over alumina (Woelm, neutral, grade I, 20 g, cyclohexane eluant). Crystallization from hexane afforded yellow needles of V (0·049 g, 58%), m.p. 58°; NMR spectrum ($CDCl_3$): 5·54τ (2H, benzhydryl), 2·95τ (2H, aromatic in five-membered ring); NMR spectrum of acenaphthylene ($CDCl_3$): 2·92τ (2H, aromatic in five-membered ring). Found: C, 94·06; H, 5·79. Calc. for $C_{19}H_{14}$: C, 94·18; H, 5·82%.)

5-Benzylacenaphthene (VII). A solution of hydrocarbon V (0·1 g) in EtOH (50 ml) was hydrogenated for 1 hr in the presence of 5% Pd–C (0·12 g). The reaction mixture was then filtered through Celite and evaporated to dryness under red. press. to give a solid residue. Crystallization of this material from hexane afforded VII as short white needles (0·1 g, 99%), m.p. 111° (reported[1] 110–111°).

Preparation of the comparison sample of VII. By use of a Soxhlet extractor, ketone VI (0.4 g) was introduced into a suspension of LAH (0·65 g) and $AlCl_3$ (6·3 g) in ether (300 ml) during a period of 2 hr. Decomposition of the reaction mixture with water (100 ml), followed by extraction with ether (200 ml) and work-up in the usual manner gave a tan solid residue. Crystallization of this material from hexane afforded VII as short white needles (3·5 g, 93%), m.p. 111°. The product obtained from the reduction of V was found to be identical to that obtained by the reduction of VI by direct comparison of IR spectra and by mixed m.p. determination.

5-Nitroacenaphthene (XI). To a rapidly stirred suspension of acenaphthene (100 g) in glacial acetic acid (800 ml) was added 70% HNO_3 aq (125 ml) during 15 min. After the addition of HNO_3 was complete, the reaction mixture was cooled and diluted to a volume of 2 l, with water. The yellow precipitate was filtered, dried, and crystallized from benzene to give light yellow needles of XI (111·2 g, 87%), m.p. 104° (reported[3] 106°).

5-Aminoacenaphthene (XII). A mixture of nitro compound XI (50·0 g), 10% Pd–C (2·5 g), 85% hydrazine hydrate (60 ml), and 95% EtOH (1·0 l) was refluxed for 45 min. The hot solution was then filtered through Celite, and water was added to the filtrate until crystallization of the reaction product was complete. On filtration there were obtained white prisms of XII (40·3 g, 95%), m.p. 104° (reported[3] 108°).

5-Acetoamidoacenaphthene (XIII). To a suspension of amine XII (83·0 g) in pyridine (85 ml) was slowly added acetic anhydride (85 ml). After standing for 20 min, water (400 ml) was added to the reaction mixture and the resulting suspension was cooled to 10°. Filtration afforded white needles of XIII (98·0 g, 95%), m.p. 190° (reported[3] 186°).

4-Nitro-5-aminoacenaphthene (XV). To a solution of amide XIII (10·0 g) in glacial acetic acid (900 ml) was added 70% HNO_3 aq (70 ml) during 15 min. After stirring for a further 30 min, the reaction mixture was diluted with water (2·0 l) and the crude nitration product was filtered. Without further purification, this material was hydrolyzed by refluxing it for 24 hr with a mixture of EtOH (600 ml) and 70% H_2SO_4 aq (80 ml). Evaporation of the hydrolysis mixture to one third of its original volume, followed by cooling the solution to 10°, afforded dark red needles of XV (13·94 g, 69%), m.p. 235° (reported[4] 224°).

4-Nitroacenaphthene (XVI). To a solution of $NaNO_2$ (6·0 g) in conc. H_2SO_4 (50 ml) was added a solution of XV (11·0 g) in glacial acetic acid (150 ml), and conc. H_2SO_4 (15 ml); the temp was

* Melting points are uncorrected.

maintained at 0–20° during the reaction. After standing for 1 hr at room temp, the resulting diazonium solution was added slowly to a mixture of hydrated cupric sulphate (14·0 g), 30% hypophosphorous acid (180 ml), and 95% EtOH (100 ml). After standing for 1 hr the reaction mixture was diluted with ice water (1·5 l.) and extracted with ethyl acetate (300 ml). Work-up of the extract in the usual manner gave material which was chromatographed over alumina (Woelm, neutral, grade II, 60 g, benzene eluant). Crystallization from benzene gave yellow needles of XVI (5·968 g, 60%), m.p. 130–132°. Found: C, 72·55, H, 4·34: N, 7·08. Calc. for $C_{12}H_9NO_2$: C, 72·35. H, 4·55: N, 7·03%.)

4-*Aminoacenaphthene* (X). A solution of (20·0 g), in a mixture of 85% hydrazine hydrate (30 ml) and 95% (1·0 l.) was refluxed for 2 hr with 10% Pd–C (2·0 g). The reaction mixture was then filtered through Celite and the filtrate was evaporated under red. press. to a volume of 100 ml. Water was then added until crystallization of the reaction product was complete. Filtration afforded white needles of X (16·4 g, 96%), m.p. 88–89° (reported[4] 88–89°).

4-*Bromoacenaphthene* (XVII). A slurry of X (10·0 g) in conc. HCl aq (25 ml) and water (115 ml) was diazotized at 0° by the addition of a solution of $NaNO_2$ (4·5 g) and water (50 ml). After stirring the diazonium mixture a further 1 hr, a solution of mercuric nitrate (10·0 g) and NaBr (15·0 g) in water (50 ml) was added. The resulting mercuric bromide complex was separated by filtration and air dried. Decomposition of the complex was carried out by heating it at 100° in the presence of powdered NaBr (50·0 g) for 30 min. Extraction of the decomposition residue with benzene, followed by chromatography over alumina (Woelm, neutral, grade II, 40·0 g; benzene eluant) gave a yellow solid; sublimation of this material afforded white needles of XVII (5·2 g, 37%), m.p. 65–66°. Found: C, 62·02; H, 3·85; Br, 34·14. Calc. for $C_{12}H_9Br$: C, 61·82: H, 3·89: Br, 34·29%.)

4-*Cyanoacenaphthene* (XVIII). A mixture of XVII (5·199 g), cuprous cyanide (3·6 g), and freshly distilled *N*-methylpyrrolidone (25 ml) was refluxed for 4 hr. The reaction mixture was then poured into a solution of $FeCl_3$ (10·0 g), water (15 ml), and conc. HCl aq (4 ml). After heating this mixture on the steam bath for 20 min, the organic product was extracted into $CHCl_3$ (300 ml) and the extract was worked up in the usual manner to give a dark brown oil. Chromatography of this oil over alumina (Woelm, neutral, grade I, 40 g, benzene eluant) followed by crystallization from cyclohexane gave XVIII as white needles (2·74 g, 71%), m.p. 106–107°. Found: C, 86·98; H, 4·98; N, 7·78. Calc. for $C_{13}H_9N$: C, 87·12; H, 5·06; N, 7·82%.)

4-*Benzoylacenaphthene* (XIX). To a solution of XVIII, (0·105 g) in ether (40 ml) was added a solution of 3M ethereal PhMgBr (3·0 ml). After stirring at room temp for 4 hr, the reaction mixture was poured into conc HCl aq (15 ml). The resulting yellow precipitate, which was identified by its IR spectrum as the imine hydrochloride of XIX, was filtered and then hydrolyzed by boiling it in EtOH. Chlorofrom (200 ml) was then added to the hydrolysis mixture and the precipitated NH_4Cl was separated by filtration. Evaporation of the filtrate afforded XIX as white needles (0·124 g, 82%), m.p. 97–98·5°, after crystallization from EtOH. Found: C, 87·68; H, 5·49. Calc. for $C_{19}H_{14}O$, C, 88·34; H, 5·46%.)

4-(α-*Hydroxybenzyl)acenaphthene* (VIII). A suspension of LAH (1·0 g), ketone XIX (1·0 g), and ether (125 ml) was stirred at room temp for 4 hr. Water (100 ml) was then added to the reaction mixture, which was worked up in the usual manner to give VIII as a white solid (0·88 g, 88%); crystallization from hexane gave white needles, m.p. 86–87°. Found: C, 87·38; H, 6·15. Calc. for $C_{19}H_{16}O$: C, 87·67; H, 6·19%.)

Attempted dehydration of alcohol VIII. A solution of VIII (0·1 g) and *p*-toluenesulphonyl chloride (0·15 g) in pyridine (20 ml) was refluxed under a N_2 atm. for 24 hr. After the usual work-up, a solid was obtained which crystallized from hexane as white needles (0·091 g), m.p. 84°. This substance was found to be starting material (VIII) by direct comparison of its IR spectrum and by a m.p. determination.

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