Electrochemical Reactions. Part II.[1] The Structure of an Unusual Product from the Reduction of 1-Acetylnaphthalene

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Electro-reduction of 1-acetylnaphthalene in alkaline solution gave the substituted tetrahydro-1,4-methano-3-benzoxepin (I) and not the expected pinacol. The structure of this compound is deduced from its spectral properties and its conversion into 1-(4-acetyl-1-naphthyl)-1-(1-naphthyl)ethane (II) on treatment with acid. The reduction of 1-acetylnaphthalene in neutral medium also gave (I). In acid medium 1-ethylnaphthalene and an organomercury compound were formed.

ELECTROLYTIC reduction in alkaline solution of aromatic aldehydes and ketones is a useful route to the corresponding pinacols [1,2] which has been applied to many benzenoid and heterocyclic carbonyl compounds. However, reduction of 1-acetylnaphthalene at a mercury cathode gives a substance, m. p. 183°, which is not the expected pinacol. The evidence which leads us to propose structure (I) for this reduction product is presented here.

The mass spectrum of the product showed the molecular ion peak at *m/e* 342, and from this and other analytical data the molecular formula is established as $C_{24}H_{22}O_2$. This is the molecular formula of the expected pinacol, but the infrared spectrum showed no evidence for the presence of a hydroxy-group. There was an absorption band at 1720 cm.$^{-1}$, which suggested the presence of a carbonyl function; this was confirmed by the preparation of a mono-dinitrophenylhydrazone with an ultraviolet absorption maximum at 364 mμ, which indicated it to be the derivative of a compound containing an unconjugated carbonyl function.[3] The second oxygen function in the reduction product appeared to be an ether. From the ^{1}H n.m.r. spectrum the 22 protons in this substance could be assigned as 11 aromatic pro-

[1] Part I, J. Grimshaw and J. S. Ramsey, *J. Chem. Soc.* (*C*), 1966, 654.

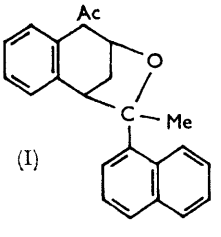
[2] Fr. Fichter, 'Organische Elektrochemie,' Theodor Steinkopff, Dresden and Leipzig, 1942, p. 224.

[3] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 1945, 498.

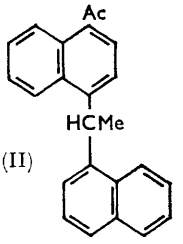
tons, two uncoupled methyl groups (one at τ 7·71, probably part of an acetyl group, and the other at τ 8·53), and 5 other aliphatic protons whose line positions and coupling constants, confirmed by double resonance experiments, are given in the Experimental section.

It was concluded that the substance was formed from two 1-acetylnaphthalene residues and contained one naphthalene ring intact and one reduced, probably to a tetralin system. One acetyl group remained as an unconjugated ketone whilst the other appeared to have been transformed into an ether function.

When warmed with sulphuric acid in acetic acid solution the substance was smoothly transformed into another ketone, m. p. 158°, which had the correct analysis for $C_{24}H_{20}O$. This showed an absorption, $\nu_{max.}$ 1675 cm.$^{-1}$, due to a conjugated carbonyl function. The ^{1}H n.m.r. spectrum indicated the presence of 13 aromatic protons and two methyl groups, one of which (τ 7·32) could be assigned to an acetyl group attached to an aromatic ring. The second methyl resonance appeared as a doublet with centre at τ 8·11 (J = 7 c./sec.) coupled to a single proton which gave rise to a quartet with centre at τ 4·32. From this spectral evidence the ketone (m. p. 158°) is most likely to be one of the isomeric acetyldinaphthylethanes. Since this series of substances was prepared from 1-acetylnaphthalene, the number of possible structures for the ketone (m. p. 158°) is reduced and the most likely appeared to be (II), which was therefore synthesised by an alternative route.



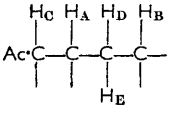
(I)



(II)

1,1′-Di(1-naphthyl)ethylene was prepared by dehydrating the tertiary alcohol obtained from the action of 1-naphthylmagnesium bromide on ethyl acetate.[4] Catalytic reduction gave the corresponding dinaphthylethane, which showed the tertiary aliphatic proton magnetic resonance as a quartet with centre at τ 4·38 (J = 7 c./sec.) almost in the same position as the corresponding ^{1}H n.m.r. signal of the ketone, m. p. 158°. Friedel–Crafts acetylation of the dinaphthylethane afforded its monoacetyl derivative, identical with the ketone (m. p. 158°) previously obtained. This ketone has been prepared both from a known di-1-naphthyl derivative and from 1-acetylnaphthalene, so it must have structure (II). 1-Alkylnaphthalenes, *e.g.*, 1-benzylnaphthalene,[5] are known to acylate preferentially in the 4-position.

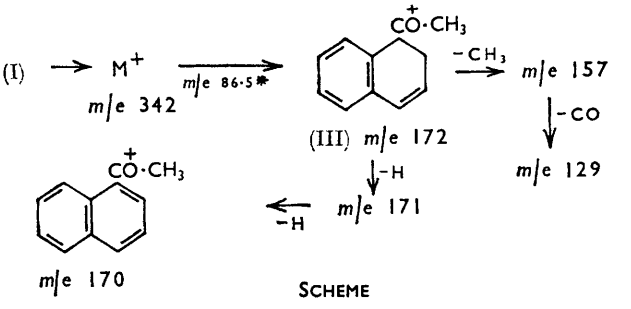
Conversion of the reduction product, m. p. 183°, into this acetyldinaphthylethane involves loss of water with concomitant aromatisation of the ring bearing the acetyl group. This reduced benzene ring bears five protons (H_{A-E}) the ^{1}H n.m.r. spectrum of which has to be explained. Recrystallisation of the ketone (m. p. 183°) from dioxan and deuterium oxide in the presence of a trace of sodium deuteroxide resulted in the loss, in the 1H n.m.r. spectrum, of the acetyl resonance and the resonance of H_C at τ 6·20. In addition the quartet due to H_A with centre at τ 5·02 had collapsed to a doublet. Thus H_C must be attached to the carbon bearing the acetyl group and be adjacent to H_A. The signal for H_D appears as a multiplet owing to coupling with H_A, H_B, and H_E. The signals due to H_D and H_E have the correct positions, with centres at τ 7·84 and 8·23, respectively, and the large coupling constant (J_{DE} = 12 c./sec.), for two non-equivalent methylene protons. This methylene group must be flanked by H_A and H_B in order to account for the coupling constants J_{AD} and J_{BD}. The signal from H_E is a doublet with observable coupling only to H_D. The arrangement of these five protons as



will thus account for the observed ^{1}H n.m.r. spectrum and when this is combined with the need to accommodate (II) as the product of acid treatment, structure (I) can be deduced for the ketone, m. p. 183°. The conversion of (I) into (II) in the presence of acid would be expected.

The mass spectrum of the ketone, m. p. 183° (see Scheme), shows fragmentation to an ion *m/e* 172 with the appropriate metastable peak visible. This can be interpreted as fragmentation to 1-acetylnaphthalene and the molecular ion of a dihydroacetylnaphthalene (III) (no definite position for the olefinic bond is intended). Further fragmentation of this ion with successive loss of CH_3 and CO would account for the peaks at *m/e* 157 and 129. Loss of hydrogen from any of these ions to give the naphthalene system accounts for the other important

Mass spectrum of (I) (principal peaks): *m/e* 342 (18%) (M^+), 173 (8), 172 (58), 171 (42), 170 (15), 157 (10), 156 (6), 155 (20), 130 (15), 129 (100), 128 (52), 127 (22), 43 (42).



SCHEME

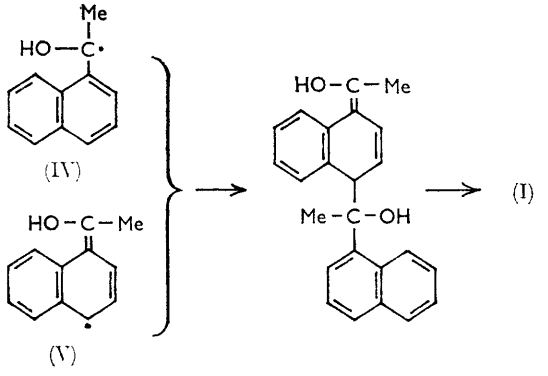
[4] P. Pfeiffer and P. Schneider, *J. prakt. Chem.*, 1931, [2] **129**, 136.

[5] K. Dziewonski and J. Moszew, *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1930, *A*, 66.

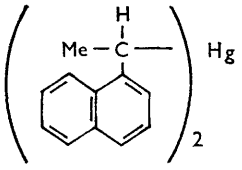
peaks observed. The molecular ion of 1-acetylnaphthalene could also be formed directly from (I) and then undergo successive loss of CH_3 and CO.

The conformation of the tetralin system in (I) is fixed because of the 1,3-bridged structure, and since the ketone is prepared in alkaline solution we can assign the acetyl substituent to the least hindered pseudo-equatorial position. The tetralin ring therefore has all the substituents in a *cis* relationship. The 1,3-bridge also has an asymmetric centre and can have either the methyl or the naphthyl group *endo* with respect to the benzene ring of the tetralin system. Some effect of the magnetic anisotropy of the benzene ring on the methyl ^{1}H n.m.r. signal would be good evidence for their *endo* configuration. Recently [6] it has been found that such effects are modified in the presence of tetranitromethane, so that a line shift observed on addition of this reagent would be evidence for the existence of the anisotropy effect. The shift observed for this methyl resonance in ketone (I) on addition of tetranitromethane was from τ 8·53 to 8·48, which is too small to confirm the existence of any interaction. The lack of any interaction does not necessarily allow us to conclude that the methyl group is *exo* with respect to the tetralin benzene ring, so the stereochemistry at this centre remains uncertain.

The formation of (I) has to be rationalised. Reduction of aromatic aldehydes and ketones gives a resonance-stabilised hydroxybenzyl radical as the first product. The radical first formed from 1-acetylnaphthalene can be written in several canonical forms, including (IV) and (V). Dimerisation of this radical in the forms (IV) and (V) will give the enol of an intermediate αβ-unsaturated ketone which can undergo intramolecular addition of the hydroxyl group across the olefinic bond to give (I) as the final product.



Compound (I) is the major product of reduction of 1-acetylnaphthalene in alkaline and in neutral solution. In strongly acid solution, however, reduction at a mercury cathode gives 1-ethylnaphthalene and an unstable oil which deposits mercury. This is probably the dialkylmercury (VI). Reduction for short periods gives a greater yield of (VI). Prolonged reduction gives more 1-ethylnaphthalene probably by way of hydrolysis



(VI)

of the dialkylmercury which is formed first. The mercury compound results from attack of the radical (IV) on the electrode surface followed by further reduction in a manner analogous to the Clemmensen reaction.[7] Such reactions [8] have been observed before at a mercury cathode.

EXPERIMENTAL

Except where otherwise stated, i.r. spectral data relate to dispersions in potassium bromide discs, u.v. data to solutions in ethanol, and ^{1}H n.m.r. data to solutions in carbon tetrachloride containing tetramethylsilane as internal standard. The n.m.r. data were obtained with a Varian HR 100 instrument. In the description of n.m.r. spectra the following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet); coupling constants are given in c./sec. Mass spectra were measured on an A.E.I. MS 9 mass spectrometer with an ionising beam of 70 ev.

Electro-reductions were carried out with a potentiostat like that designed by Palmer and Vogel [9] connected to a cell like that described by Pasternak [10] and according to the general directions given in a previous Paper.[1] Light petroleum had b. p. 60—80°.

Polarographic Reduction of 1-*Acetylnaphthalene*.—Solutions were prepared by mixing methanolic 1-acetylnaphthalene (5×10^{-4}M; 50 ml.), McIlvaine's buffer [11] of required pH (20 ml.), potassium chloride (1·0M; 10 ml.), and water (20 ml.). The solution of pH 13 was prepared by mixing methanolic 1-acetylnaphthalene (2×10^{-5}M; 50 ml.), potassium chloride (1·0M; 10 ml.), potassium hydroxide (1·0M; 10 ml.), and water (30 ml.). A silver–silver chloride anode was used and the polarographic waves were obtained by polarising the dropping mercury electrode with a Southern Analytical Manual D.C. polarograph A 1650. Over the range observed, 1-acetylnaphthalene showed one reduction wave with $E_{\frac{1}{2}}$ given below:

pH	6·5	7·3	8·3	13·1
$E_{\frac{1}{2}}$ (v)	−1·44	−1·44	−1·55	−1·69

The e.m.f. of a cell formed between the silver–silver chloride anode used here and a saturated calomel electrode was 0·008v, with mercury the positive pole.

Reduction of 1-*Acetylnaphthalene*.—(*a*) This was carried out at a mercury pool cathode maintained at a potential of

[6] C. R. M. Butt, D. Cohen, L. Hewitt, and I. T. Millar, *Chem. Comm.*, 1967, 309.
[7] T. Nakazayashi, *J. Amer. Chem. Soc.*, 1960, **80**, 3900.
[8] T. Arrai and T. Oguri, *Bull. Chem. Soc. Japan*, 1960, **33**, 1018.
[9] J. Grimshaw and R. K. Quigg, *Analyst*, 1966, **91**, 667; J. F. Palmer and A. I. Vogel, *ibid.*, 1953, **78**, 428.
[10] R. Pasternak, *Helv. Chim. Acta*, 1948, **31**, 735.
[11] H. T. S. Britton, 'The Hydrogen Ions,' Chapman and Hall, London, 1956, 4th edn., vol. 1, p. 352.

−1·8 v relative to a saturated calomel electrode. The catholyte was a solution of 1-acetylnaphthalene (10 g.) in ethanolic potassium hydroxide (2N; 250 ml.). The anolyte was 2N-ethanolic potassium hydroxide and a lead anode was used. Reduction was carried out at room temperature, and after about 70 hr. the current between the working electrodes had fallen to a negligible value. The catholyte was then separated and diluted with water, and the ethanol was evaporated off under reduced pressure. The residue was extracted with dichloromethane and the organic phase was separated, washed with water, and dried ($MgSO_4$); the solvent was removed. The resulting oil gave *5-acetyl-1,2,4,5-tetrahydro-2-methyl-2-(1-naphthyl)-1,4-methano-3-benzoxepin* (I) as needles (5·9 g.), m. p. 182—183° (recrystallised from methanol and sublimed at 165°/0·05 mm.) (Found: C, 84·2; H, 6·5. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·5%), $\nu_{max.}$ 1720 cm.$^{-1}$, τ 1·8—3·0m. (11H), 5·02q (H_A), 6·09d (H_B), 6·20d (H_C), 7·84m (H_D), 8·23d (H_E), (J_{AC} = 2·5, J_{AD} = 6·0, J_{BD} = 3·5, J_{DE} = 12), 7·71s (3H), and 8·53s (3H). The couplings listed were confirmed by double-resonance spectrometry.

The 2,4-*dinitrophenylhydrazone* gave yellow needles, m. p. 217—219° (from methanol–benzene) (Found: C, 68·8; H, 5·1; N, 10·7. $C_{30}H_{26}N_4O_5$ requires C, 68·95; H, 5·0; N, 10·7%), $\lambda_{max.}$ 364 mμ (log ε 4·16). A sample of the ketone was recrystallised from dioxan–deuterium oxide in which a small portion of sodium had previously been dissolved. The recrystallised sample showed, *inter alia*, the following ^{1}H n.m.r. signals: τ 5·02d (H_A), 6·09d (H_B), 7·84m (H_D), 8·23d (H_E), (J_{AD} = 6·0, J_{BD} = 3·5, J_{DE} = 12), and 8·53s (3H).

(*b*) Electro-reduction was carried out at pH 5·5—6 at a mercury pool cathode maintained at a potential of −1·8 v relative to a saturated calomel electrode. The catholyte was a solution of 1-acetylnaphthalene (2 g.) and lithium chloride (12 g.) in methanol (135 ml.), 2N-trisodium citrate solution (92 ml.), and 2N-hydrochloric acid (22 ml.). The pH was checked during reduction, after the working electrodes were first disconnected, with a glass electrode–saturated calomel electrode arrangement and a Beckman zeromatic pH meter standardised against aqueous buffer solutions. 2N-Hydrochloric acid was added as required to maintain the correct pH during a reduction. The anolyte was a solution of lithium chloride (11 g.) in methanol (90 ml.) containing aqueous trisodium citrate (2N; 90 ml.,) and hydrochloric acid (2N; 20 ml.), and a silver anode was used. When reduction was complete the catholyte was separated and the methanol removed under reduced pressure. The residue was extracted with dichloromethane, the organic phase was washed with water and dried ($MgSO_4$), and the solvent was removed. The residue was chromatographed on alumina to yield the ketone (I), eluted with benzene–ether (3 : 1), and 1-(1-naphthyl)ethanol, m. p. 65—66°, eluted with benzene–ether (1 : 3), in a ratio of 1 : 1; the overall yields varied from 15 to 30%. No further crystalline material, other than starting material, could be isolated.

(*c*) Electro-reduction in 45% aqueous sulphuric acid was carried out at a mercury cathode maintained at −1·5 v, with a platinum anode. The catholyte was a suspension of 1-acetylnaphthalene (2 g.) in sulphuric acid (250 ml., 45%). After reduction, the catholyte was poured on to ice and the product was extracted with dichloromethane. The organic layer was washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$), and the solvent was removed. The oily residue was chromatographed on alumina to yield an unstable mercury compound (eluted with light petroleum) which deposited mercury, and 1-ethylnaphthalene [eluted with light petroleum–benzene (3 : 1)], characterised as its picrate, m. p. 98—99°. A reduction time of 24 hr. gave these products in a ratio of 2 : 1; a 48 hr. reduction time gave a ratio of 1 : 2 (total yield 40%).

1-(4-acetyl-1-naphthyl)-1-(1-naphthyl)ethane (II).—(*a*) Ketone (I) (1·5 g.) was dissolved in a mixture of acetic acid (50 ml.) and concentrated sulphuric acid (10 ml.). The solution was refluxed for 30 min.; its colour gradually darkened. The cooled mixture was diluted with water and extracted with dichloromethane. The organic layer was washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$), and the solvent was removed to leave an oil (1·5 g.) which was chromatographed on alumina. Elution with benzene afforded the *ketone* (II), which was recrystallised from methanol and sublimed as needles (1·0 g.), m. p. 157—158° (Found: C, 89·1; H, 6·5. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%), $\nu_{max.}$ 1690 cm.$^{-1}$, τ 1·2—3·0m (13H), 4·32q (J = 7·0, 1H), 7·32s (3H), and 8·11d (J = 7·0, 3H).

(*b*) Catalytic hydrogenation of 1,1′-di-(1-naphthyl)-ethylene [4] in acetic acid at room temperature and pressure over Adams catalyst afforded the dinaphthylethane which gave needles, m. p. 135—136° (from ethanol) (lit.,[12] 136°), τ (*inter alia*) 4·38q (J = 7·0, 1H) and 8·15d (J = 7·0, 3H).

The dinaphthylethane (0·80 g.) was dissolved in carbon disulphide (10 ml.), and a suspension of aluminium chloride (0·45 g.) in carbon disulphide (20 ml.) and acetyl chloride (0·30 g.) were added. The solution was refluxed for 3 hr. then cooled and poured into dilute hydrochloric acid; the organic layer was collected, washed with water, and dried ($MgSO_4$). Removal of the solvent left a yellow oil (0·83 g.) which was chromatographed on alumina. Elution with benzene afforded the *ketone* (II) (0·19 g.) which crystallised from methanol and sublimed at 145°/0·05 mm. to give needles, m. p. and mixed m. p. with product of (*a*) 155—156° (Found: C, 89·0; H, 6·2%). The two samples of this ketone had identical infrared spectra.

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[12] R. Quelet, C. Borgel, and R. Dwand, *Compt. rend.*, 1955, **240**, 1900.