

Studies in Metal–Ammonia Reduction. Part 3.¹ Reduction and Reductive Methylation of Some Acetylnaphthalenes with Metal–Ammonia Solutions

By G. S. R. Subba Rao * and N. Shyama Sundar, Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

Birch reduction and reductive methylation of 1- and 2-acetylnaphthalenes have been examined. It has been found that, while 1-acetylnaphthalene is reduced to the 3,4-dihydro-compound, the 2-acetylnaphthalene gives the corresponding 1,2,3,4-tetrahydro-compound. However, anhydrous ferric chloride has been found to limit the reduction and reductive methylation to the dihydro-stage with 2-acetylnaphthalene. The factors influencing the mechanism of the reduction process have been discussed. Some of the intermediate compounds are useful substrates in synthesis.

METAL–AMMONIA reduction of naphthalene and its derivatives has been extensively investigated.^{2,3} It was shown that the course of reduction of naphthalenes depends upon the nature of the substituents in the ring. In general, electron-donating groups (OMe, Me, NMe₂) at the 1-position of naphthalene direct the reduction in the adjacent ring while 2-substituted naphthalenes are reduced in the ring containing the substituent. However, the presence of electron-withdrawing substituents (CO₂H) results in the reduction occurring in the ring containing the substituent. Mejer⁴ observed that the reduction of the naphthalene derivative (1) with sodium in ammonia afforded compound (2), while its isomer (3) gave compound (4). These results were rather surprising since, (i) the site of reduction in aromatic ketones is usually localised⁵ at the carbonyl group and should lead to the deoxygenated products,⁶ (ii) the influence of the carbonyl group is felt only in the reduction of ketone (1) and not in its isomer (3), and (iii) the unsaturated ketone (2) was isolated even with an excess of metal present during the reduction. In view of these unexpected observations we investigated this problem using 1-acetyl- and 2-acetyl-naphthalene as model compounds; the results^{7a} are described in this paper.

Reduction and Reductive Methylations of 1-Acetylnaphthalene.—Reduction of 1-acetylnaphthalene (5) with lithium, sodium, or potassium in liquid ammonia followed by quenching with ammonium chloride, sodium benzoate or absolute ethanol afforded 1-acetyl-3,4-dihydronaphthalene⁸ (6) in good yield. Reductive methylation of the acetylnaphthalene (5) with lithium and quenching with methyl iodide gave 1-acetyl-1-methyl-1,4-dihydronaphthalene (7), the structure of which was deduced from its spectral data. The i.r. spectrum of compound (7) showed absorptions due to a saturated carbonyl and an aromatic moiety; the ¹H n.m.r. spectrum showed two singlets at δ 1.2 and 2.20 (1-methyl and acetyl-methyl groups), a broad triplet at δ 3.55 (benzylic-allylic protons), two triplets at δ 5.70 and 6.05 (vinyl protons), and a multiplet at δ 6.70–7.10 (aromatic protons). Reductive methylation of compound (5) with an excess of sodium or potassium afforded a mixture of the disubstituted naphthalene (7) and 1-

methyl-1-propionyl-1,4-dihydronaphthalene (8), the structure of which was deduced from its analytical and spectral data. The i.r. spectrum of compound (8) showed absorptions due to a saturated carbonyl and an aromatic moiety, and the ¹H n.m.r. spectrum displayed a triplet centred around δ 0.9 (the methyl of the propionyl group), a quartet around δ 1.18–1.20 (methylene protons), a singlet at δ 1.25 (1-methyl), a triplet around δ 3.50 (benzylic-allylic protons), two triplets at δ 5.65 and 6.10 (two vinyl protons), and a broad singlet at δ 7.2 (aromatic protons). The absence of an acetyl-methyl signal and the appearance of a triplet at δ 0.9 indicated the presence of an ethyl group; this was confirmed by the mass spectrum which showed a (*M* – Et) peak.

Similar results were obtained for the reduction and reductive methylation of the acetylnaphthalene (5) with other metals, as indicated in Table 1.

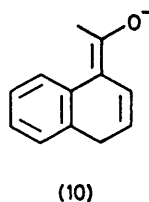
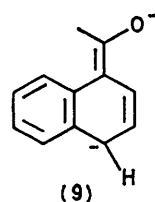
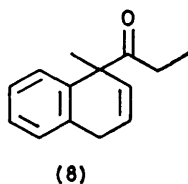
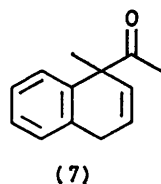
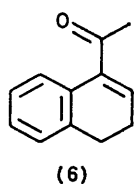
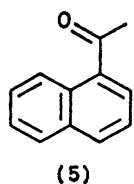
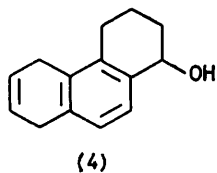
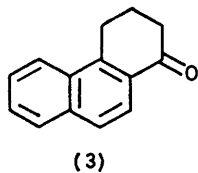
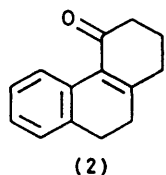
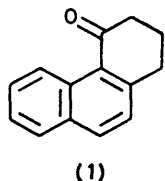
TABLE 1
Reduction and reductive methylation of
1-acetylnaphthalene (5)

Substrate ^a	Metal (g-atom/ mol of substrate)	Quenching agent	Products and yield [%]
(5)	Li (2,4,8)	Ammonium chloride or sodium benzoate ^b	(6) [75]
	Na (4,8)	Ammonium chloride or sodium benzoate ^b	(6) [70]
	K (2,4)	Ammonium chloride or sodium benzoate ^b	(6) [75]
(5)	Li (2,4,8)	MeI	(7) [75]
	Na (2); K (2)	MeI	(7) [70]
	Na (4); K (4)	MeI	Mixture of (7) [60] and (8) [40]

^a 10 Mmol in THF (20 ml) and liquid ammonia (100 ml).
^b No significant change in the yield.

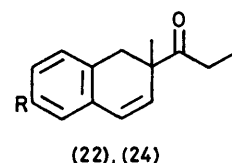
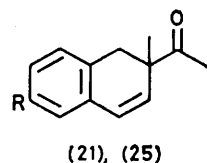
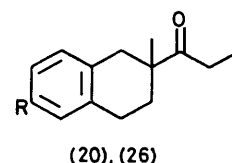
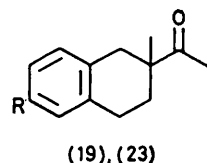
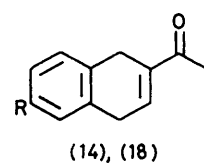
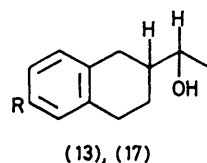
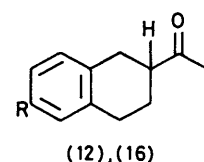
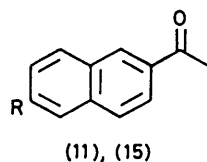
The mechanism of reduction probably involves the addition of two electrons to the substrate (5) giving the dianion (9) which is protonated by ammonia to give the anion (10). This anion (10), which is stable towards further reduction, affords the unsaturated ketone (6) on work-up while methylation results in the exclusive formation of the unsaturated compound (7) because of the significant⁹ charge density at the α -carbon. The

formation of the propionyl compound (8) during the reductive methylation of compound (5) with an excess of sodium or potassium in ammonia is due to further methylation at the α '-carbon of compound (7).



Reduction and Reductive Methylation of 2-Acetylnaphthalene (11) and 2-Acetyl-6-methoxynaphthalene (15).—Reduction of 2-acetylnaphthalene (11) with lithium or sodium in ammonia followed by quenching with ammonium chloride or sodium benzoate afforded an equimolar mixture of 2-acetyl-1,2,3,4-tetrahydronaphthalene¹⁰ (12) and the corresponding alcohol (13). The compounds (12) and (13) were separated by preparative layer chromatography (p.l.c.) and their structures deduced from the spectral data and confirmed by comparison with authentic specimens. Reduction of compound (11) with lithium or sodium in the presence of anhydrous ferric chloride, or with potassium in ammo-

nia, followed by quenching with ammonium chloride or sodium benzoate afforded 2-acetyl-1,4-dihydronaphthalene¹¹ (14) as the sole product, the structure of which was deduced from its spectral and analytical data. The i.r. spectrum showed absorptions due to an unsaturated carbonyl and the aromatic moiety; the ¹H n.m.r. spectrum showed a singlet at δ 2.15 (acetyl methyl), a broad singlet at δ 3.35 (four allylic-benzylic protons), and a multiplet at δ 6.9 integrating to five protons (four aromatic protons and a vinyl proton). Similar results were obtained from the reduction of 2-acetyl-6-methoxy-



Compounds (11)—(14) and (19)—(22) R = H. Compounds (15)—(18) and (23)—(26) R = OMe

naphthalene (15). The results of the reductions of compounds (11) and (15) with sodium or potassium in ammonia are presented in Table 2.

Reduction of 2-acetylnaphthalene (11) with lithium in ammonia followed by quenching with methyl iodide afforded mainly 2-acetyl-2-methyl-1,2,3,4-tetrahydronaphthalene (19), the structure of which was established from its spectral and analytical data. The i.r. spectrum of (19) had absorptions due to a saturated carbonyl and an aromatic moiety; the ¹H n.m.r. spectrum showed two singlets at δ 1.0 and 2.0 (2-methyl and the acetyl-methyl groups respectively) apart from a multiplet centred at δ 2.70 (benzylic protons), and a broad singlet at δ 7.10 (aromatic protons). Reductive methylation of compound (11) with lithium (4 or 6 g-atom) in the presence of

anhydrous ferric chloride afforded 2-acetyl-2-methyl-1,2-dihydronaphthalene (21) the structure of which was deduced from its spectral data. The i.r. spectrum of the product (21) had bands due to a saturated carbonyl and an aromatic moiety; the ^1H n.m.r. spectrum showed two singlets at δ 1.15 and 2.05 (2-methyl and acetyl-methyl groups respectively), two doublets at δ 2.6 and

were obtained in the reductive methylation of the methoxy-compound (15); the results are indicated in Table 3.

It is clear from the above data that the carbonyl group influences the reduction of 2-acetylnaphthalenes with metals in ammonia. Furthermore there is selectivity in the reduction process affording either the tetrahydro-

TABLE 2
Reduction of 2-acetylnaphthalene (11) and 2-acetyl-6-methoxynaphthalene (15)

Substrate	Metal (g-atom/ mol of substrate)	Quenching agent	Other additions	Products and yield [%]
(11)	Li (2,4,8)	Ammonium chloride or sodium benzoate ^a		Mixture of (12) and (13) in ratio 1 : 1
(11)	Na (2,4,8)	Ammonium chloride or sodium benzoate ^a		Mixture of (12) and (13) in ratio 1 : 1
(11)	K (2,4)	Ammonium chloride or sodium benzoate ^a		(11) [40] and (14) [60]
(11)	K (4,8)	Ammonium chloride or sodium benzoate ^a		(14) [80]
(11)	Li (4,6)	Ammonium chloride or sodium benzoate ^a	FeCl ₃	(14) [75]
(11)	Na (4,6)	Ammonium chloride or sodium benzoate ^a	FeCl ₃	(14) [70]
(11)	K (4,8)	Ammonium chloride or sodium benzoate ^a	FeCl ₃	(14) [75]
(15)	Li (2,4,8)	Ammonium chloride or sodium benzoate ^a		Mixture [90] consisting of (16) and (17) in ratio 1 : 1
	Na (4,6)	Ammonium chloride or sodium benzoate ^a		Mixture [90] consisting of (16) and (17) in ratio 1 : 1
	K (2)	Ammonium chloride or sodium benzoate ^a		(15) [60] and (16) [40]
	K (4,6)	Ammonium chloride or sodium benzoate ^a		(16) [70]
	Li (4,6)	Ammonium chloride or sodium benzoate ^a	FeCl ₃	(16) [65—65]
	Na (4,6)	Ammonium chloride or sodium benzoate ^a	FeCl ₃	(16) [65—65]

^a No significant change in the yields.

3.2 each integrating to one proton (two non-equivalent benzylic protons), two doublets at δ 6.0 and 6.4 each integrating to one proton (two non-equivalent vinylic protons), and a broad singlet at δ 7.0 (aromatic protons). Reductive methylation of compound (11) with sodium (4 g-atom) gave a mixture of tetrahydro-compounds which was separated by p.l.c. into the components (19) and (20), while, with an excess of sodium, only compound (20) was obtained. However, the reduction of the 2-acetylnaphthalene (11) with sodium in the presence of anhydrous ferric chloride yielded the compounds (21) and (22). The structures of the compounds (19)—(22) were deduced from their spectral data. Similar results

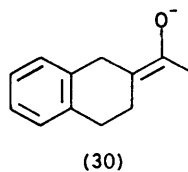
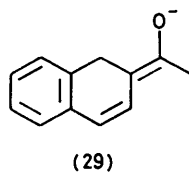
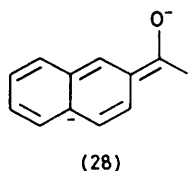
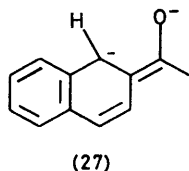
or the dihydro-compounds. The formation of the dihydro- or the tetrahydro-compounds can be rationalised by the mechanism involving 1,2-addition of two electrons to the substrate (11) giving the dianion (27) which is protonated to the dienolate anion (29). Under the experimental conditions, the dianion (28) would be less stable. Since the anion (29) has a double bond conjugated to the aromatic ring, unlike the dienolate dianion (9) obtained from 1-acetylnaphthalene, further reduction leads to the formation of the enolate anion (30). Protonation and alkylation of the anion (29) leads to the dihydro-products whereas the anion (30) yields the tetrahydro-products. Further alkylations at the α' -

TABLE 3
Reductive methylation of compounds (11) and (15)

Substrate	Metal (g-atom/ mol of substrate)	Quenching agent	Additives	Products and yield [%]
(11)	Li (4,8)	MeI		(19) [75,60]
	Li (4,8)	MeI	FeCl ₃	(21) [80]
	Na (4)	MeI		(19) [30] and (20) [70]
	Na (6)	MeI		(20) [60]
	Na (4,6)	MeI	FeCl ₃	(22) [55] and (21) [45]
	Na (6)	MeI	FeCl ₃	(22) [60]
	K (2)	MeI		(11) [40] and (21) [60]
	K (4)	MeI		(22) [65] and (21) [35]
	K (6)	MeI		(22) [60]
	K (6)	MeI		(23) [60]
(15)	Li (4,8)	MeI		(25) [50—60]
	Li (4,6)	MeI	FeCl ₃	(24) [80]
	Na (4)	MeI		(24) [55]
	Na (6)	MeI		(26) [80] and (25) [15]
	Na (4)	MeI	FeCl ₃	(26) [60]
	Na (6)	MeI	FeCl ₃	(15) [70] and (25) [30]
	K (2)	MeI		(26) [70] and (25) [30]
	K (4)	MeI		(26) [60]
	K (6)	MeI		(26) [60]
	K (6)	MeI		(26) [60]

carbon were observed only when one of the metals, sodium or potassium, was employed.

Anhydrous ferric chloride has been used for stepwise reduction¹² of polycyclic compounds since it induces the competing reaction between the metal and ammonia forming the metal amides. This was earlier observed¹³ in the reduction and reductive methylation of 2-naphthoic acids.



Since completion of our work,^{7a,b} Kapoor and Mehta¹⁴ reported the reduction of 2-acetyl-6-methoxynaphthalene (15), while Mejer and Marcinow¹¹ described the reduction and reductive alkylation of 1-acetyl- (5) and 2-acetyl-naphthalene (11). However, in both the cases the authors observed neither the product dependence on the nature of alkali metal used in reduction nor the influence of anhydrous ferric chloride on the course of metal-ammonia reduction of 2-acetylnaphthalenes.

EXPERIMENTAL

M.p.s are uncorrected. U.v. spectra were determined in 95% ethanol on a Unicam SP 700A spectrophotometer. I.r. spectra of liquids were measured as liquid films and those of solids were taken in Nujol on a Perkin-Elmer Infracord or model 237 spectrometer. ¹H N.m.r. spectra (chemical shifts in p.p.m. from SiMe₄) were recorded in CCl₄ solution on a Varian T-60 (60 MHz) spectrometer. T.l.c. and p.l.c. were carried out using silica gel (N.C.L. India). Tetrahydrofuran was distilled over lithium aluminium hydride and liquid ammonia was distilled from sodium before use; reductions were carried out at -33 °C. Whenever a mixture of compounds was obtained, separation of pure components was effected by p.l.c. followed by short-path distillation under reduced pressure; bath temperatures at which the components started to sublime are given. 2,4-Dinitrophenylhydrazones were prepared in the usual way and, unless otherwise stated, were crystallised from ethanol.

Reductions of Aryl Ketones using Metal-Ammonia.—To a well-stirred solution of the substrate (10 mmol) in ammonia (100 ml) and tetrahydrofuran or diethyl ether (20 ml) an appropriate quantity of the alkali metal was added in portions. After 30 min reaction was quenched by adding solid ammonium chloride, sodium benzoate, or absolute ethanol. The ammonia was evaporated off, water added, and the organic matter was thoroughly extracted with

diethyl ether. The ethereal solution was washed until neutral and dried (Na₂SO₄). The solvent was removed and the residue was purified further, either by p.l.c. or by distillation under reduced pressure.

For reactions in the presence of a proton source ethanol was used as co-solvent, and when studies were made on the effect of ferric chloride catalytic amounts of anhydrous ferric chloride (10 mg/1 g of the substrate) were added to the substrate solution prior to the addition of the reducing-agent.

Reductive Methylations of Aryl Ketones.—An appropriate quantity of the alkali-metal was added in portions to a well-stirred solution of the substrate (10 mmol) in tetrahydrofuran or diethyl ether (20 ml) and ammonia (100 ml), and the resultant deep-blue solution was agitated for 30 min. A solution of methyl iodide in diethyl ether was added dropwise until the blue colour of the solution was discharged; the pale-yellow reaction mixture was stirred for another 15 min. After evaporation of the ammonia the residue was worked-up in the usual manner.

1-Acetyl-3,4-dihydronaphthalene (6).—The dihydronaphthalene (6) was obtained as above, b.p. 130–135 °C at 5 mmHg; λ_{max.} 248 nm (ε 14 000); ν_{max.} 1 670, 1 610, 1 600, and 1 500 cm⁻¹; δ 2.15 (3 H, s, COMe), 2.60 (2 H, m, benzylic), and 6.60–7.20 (5 H, m, aromatic and vinylic) (Found: C, 83.5; H, 6.65. C₁₂H₁₂O requires C, 83.69; H, 7.02%). 2,4-Dinitrophenylhydrazone, m.p. 129–130 °C (Found: N, 15.8. C₁₈H₁₆N₄O₄ requires N, 15.9%).

2-Acetyl-1,2,3,4-tetrahydronaphthalene (12).—The tetrahydronaphthalene (12) was obtained *via* short-path distillation, b.p. 145–150 °C at 6 mmHg; λ_{max.} 214 nm (ε 16 800); ν_{max.} 1 700, 1 600, 1 500, 1 460, and 1 440 cm⁻¹; δ 1.20–1.40 (3 H, m, methylene and methine), 2.15 (3 H, s, COMe), 2.80 (4 H, m, benzylic), and 7.2 (4 H, br s, ArH) (Found: C, 82.85; H, 8.2. C₁₂H₁₄O requires C, 82.72; H, 8.10%). 2,4-Dinitrophenylhydrazone, m.p. 157–158 °C (Found: N, 15.65. C₁₈H₁₈N₄O₄ requires N, 15.81%).

2-(1-Hydroxyethyl)-1,2,3,4-tetrahydronaphthalene (13).—The hydroxyethyl substituted naphthalene (13) was obtained *via* short-path distillation, b.p. 155–160 °C at 3 mmHg; ν_{max.} 3 450, 1 590, 1 510, and 1 450 cm⁻¹; δ 1.20 (3 H, d, CHMe), 1.30–1.40 (3 H, m, methylene and methine), 2.60 (4 H, m, benzylic), 3.15 (1 H, m, CHOH), and 7.15 (4 H, m, ArH) (Found: C, 81.4; H, 8.85. C₁₂H₁₆O requires C, 81.77; H, 9.15%).

2-Acetyl-1,4-dihydronaphthalene (14).—The unsaturated naphthalene (14) was obtained *via* short-path distillation, b.p. 115–118 °C at 8 mmHg; ν_{max.} 1 650, 1 590, 1 490, and 1 440 cm⁻¹; δ 2.15 (3 H, s, COMe), 3.35 (4 H, br s, benzylic) and 6.9–7.2 (5 H, m, aromatic and vinylic) (Found: C, 83.6; H, 7.15. C₁₂H₁₂O requires C, 83.69; H, 7.02%). 2,4-Dinitrophenylhydrazone, m.p. 225–226 °C (Found: N, 15.7. C₁₈H₁₆N₄O₄ requires N, 15.90%).

2-Acetyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (16).—The tetrahydronaphthalene (16) was obtained *via* short-path distillation, b.p. 180–185 °C at 8 mmHg; ν_{max.} 1 705, 1 600, 1 590, 1 470, and 1 460 cm⁻¹; δ 1.61–1.98 (3 H, m, methylene and methine), 2.10 (3 H, s, COMe), 2.80 (4 H, m, benzylic), 3.75 (3 H, s, OMe) and 6.61–7.10 (3 H, m, ArH) (Found: C, 76.95; H, 8.4. C₁₃H₁₆O₂ requires C, 76.44; H, 7.90%). 2,4-Dinitrophenylhydrazone, m.p. 116–117 °C (Found: N, 14.1. C₂₀H₂₂N₄O₅ requires N, 14.06%).

2-(1-Hydroxyethyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene (17).—The hydroxyethyl derivative (17) was obtained *via* short-path distillation, b.p. 170–175 °C at

4 mmHg; ν_{\max} 3 500, 1 590, and 1 495 cm^{-1} ; δ 1.15 (3 H, d, CHMe), 1.30 (3 H, m, methylene and methine), 2.7 (4 H, m, benzylic), 3.2 (1 H, m, CHOH), 3.8 (3 H, s, OMe), and 6.6—7.1 (3 H, m, ArH) (Found: C, 75.65; H, 8.35. $\text{C}_{13}\text{H}_{18}\text{O}_2$ requires C, 75.69; H, 8.80%).

2-Acetyl-6-methoxy-1,4-dihydronaphthalene (18).—The dihydronaphthalene (18) was obtained, m.p. 55—56 °C (crystallised from methanol); ν_{\max} 1 660, 1 600, 1 510, and 1 480 cm^{-1} ; δ 2.20 (3 H, s, COMe), 3.4 (4 H, br s, benzylic), 3.8 (3 H, s, OMe), and 6.6—7.2 (4 H, m, aromatic and vinylic) (Found: C, 77.45; H, 7.5. $\text{C}_{13}\text{H}_{14}\text{O}_2$ requires C, 77.20; H, 6.98%). 2,4-Dinitrophenylhydrazone, m.p. 238—240 °C (crystallised from ethyl acetate) (Found: N, 14.55. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_5$ requires N, 14.65%).

1-Acetyl-1-methyl-1,4-dihydronaphthalene (7).—The 1,4-dihydronaphthalene (7) was obtained *via* short-path distillation, b.p. 120—125 °C at 5 mmHg; λ_{\max} 225 nm (ϵ 12 100); ν_{\max} 1 700, 1 600, 1 500, 1 470, and 1 450 cm^{-1} ; δ 1.2 [3 H, s, (C-1) Me], 2.0 (3 H, s, COMe), 3.55 (2 H, br t, benzylic), 5.7 (1 H, d, vinylic), 6.05 (1 H, m, vinylic), and 6.7—7.1 (4 H, br s, ArH) (Found: C, 83.75; H, 7.85. $\text{C}_{13}\text{H}_{14}\text{O}$ requires C, 83.83; H, 7.58%). 2,4-Dinitrophenylhydrazone, m.p. 132—133 °C (Found: N, 15.25. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$ requires N, 15.29%).

1-Methyl-1-propionyl-1,4-dihydronaphthalene (8).—The naphthalene derivative (8) was obtained *via* short-path distillation, b.p. 95—100 °C at 4 mmHg; λ_{\max} 223 nm (ϵ 12 300); ν_{\max} 1 710, 1 600, 1 490, 1 440, and 1 400 cm^{-1} ; δ 0.9 (3 H, t, H_2CMe), 1.18—1.20 (2 H, m, H_2CMe), 1.58 [3 H, s, (C-1)Me], 3.48 (2 H, t, benzylic), 5.65 (1 H, t, vinylic), 6.1 (1 H, t, vinylic), and 7.20 (4 H, br s, ArH); *m/e* 200 (M^+) and 171 ($M - \text{C}_2\text{H}_5$) (Found: C, 84.1; H, 8.15. $\text{C}_{14}\text{H}_{16}\text{O}$ requires C, 83.96; H, 8.05%). 2,4-Dinitrophenylhydrazone, m.p. 118—120 °C (Found: N, 14.35. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4$ requires N, 14.73%).

2-Acetyl-2-methyl-1,2,3,4-tetrahydronaphthalene (19).—Naphthalene derivative (19) was obtained *via* short-path distillation, b.p. 70—75 °C at 4 mmHg; ν_{\max} 1 705, 1 600, 1 510, and 1 480 cm^{-1} ; δ 1.0 [3 H, s, (C-2)Me], 2.0 (3 H, s, COMe), 2.7 (4 H, m, benzylic), 7.1 (4 H, br s, ArH) (Found: C, 83.25; H, 8.8. $\text{C}_{13}\text{H}_{16}\text{O}$ requires C, 82.93; H, 8.57%). 2,4-Dinitrophenylhydrazone, m.p. 176—177 °C (Found: N, 15.55. $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_4$ requires N, 15.21%).

2-Acetyl-2-methyl-1,2-dihydronaphthalene (21).—The dihydronaphthalene (21) was obtained *via* short-path distillation, b.p. 110—115 °C at 6 mmHg; ν_{\max} 1 705, 1 590, 1 480, and 1 450 cm^{-1} ; δ 1.15 [3 H, s, (C-2)Me], 2.05 (3 H, s, COMe), 2.6 (1 H, d, *J* 16 Hz, benzylic), 3.2 (1 H, d, *J* 16 Hz, benzylic), 6.0 (1 H, d, *J* 8 Hz, vinylic), 6.4 (1 H, d, *J* 8 Hz, vinylic), and 7.0 (4 H, br s, ArH) (Found: C, 83.95; H, 8.05. $\text{C}_{13}\text{H}_{14}\text{O}$ requires C, 83.83; H, 7.58%). 2,4-Dinitrophenylhydrazone, m.p. 142—143 °C (Found: N, 15.65. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$ requires N, 15.29%).

2-Methyl-2-propionyl-1,2,3,4-tetrahydronaphthalene (20).—The tetrahydronaphthalene (20) was obtained *via* short-path distillation, b.p. 90—95 °C at 4 mmHg; ν_{\max} 1 705, 1 590, 1 500, and 1 490 cm^{-1} ; δ 1.0 (3 H, t, CH_2Me), 1.20 (3 H, s, CMe), 1.30—1.6 (4 H, m, methylene), 2.8—3.0 (4 H, m, benzylic) and 7.1 (4 H, br s, ArH) (Found: C, 83.15; H, 9.1. $\text{C}_{14}\text{H}_{16}\text{O}$ requires C, 83.12; H, 8.97%). 2,4-Dinitrophenylhydrazone, m.p. 171—172 °C (Found: N, 14.35. $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_4$ requires N, 14.65%).

2-Methyl-2-propionyl-1,2-dihydronaphthalene (22).—The dihydronaphthalene (22) was obtained *via* short-path distillation, b.p. 100—105 °C at 6 mmHg; ν_{\max} 1 710,

1 600, 1 510, and 1 460 cm^{-1} ; δ 0.9 (3 H, t, CH_2Me), 1.10 [3 H, s, (C-2)Me], 2.0—3.0 (4 H, m, methylene), 5.9 (1 H, d, *J* 8 Hz, vinylic), 6.30 (1 H, d, *J* 8 Hz, vinylic), and 7.10 (4 H, br s, ArH) (Found: C, 83.4; H, 8.5. $\text{C}_{14}\text{H}_{16}\text{O}$ requires C, 83.96; H, 8.05%). 2,4-Dinitrophenylhydrazone, m.p. 126—127 °C (Found: N, 14.45. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4$ requires N, 14.73%).

2-Acetyl-6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene (23).—The tri-substituted hydronaphthalene (23) was obtained *via* short-path distillation, b.p. 160—165 °C at 6 mmHg; ν_{\max} 1 705, 1 600, 1 590, and 1 480 cm^{-1} ; δ 1.15 [3 H, s, (C-2)Me], 1.6—1.8 (2 H, m, methylene), 2.0 (3 H, s, COMe), 2.60 (4 H, m, benzylic), 3.75 (3 H, s, OMe), and 6.6—7.15 (3 H, m, ArH) (Found: C, 76.95; H, 8.25. $\text{C}_{14}\text{H}_{18}\text{O}_2$ requires C, 77.03; H, 8.31%). 2,4-Dinitrophenylhydrazone, m.p. 147—148 °C (Found: N, 14.1. $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_5$ requires N, 14.06%).

6-Methoxy-2-methyl-2-propionyl-1,2-dihydronaphthalene (24).—The dihydronaphthalene (24) was obtained *via* short-path distillation, b.p. 140—145 °C at 6 mmHg; ν_{\max} 1 705, 1 600, 1 570, 1 510, and 1 460 cm^{-1} ; δ 1.03 (3 H, t, CH_2Me), 1.08 [3 H, s, (C-2)Me], 1.80—3.20 (4 H, m, benzylic and CH_2Me), 3.74 (3 H, s, OMe), 5.9 (1 H, br s, vinylic), 6.3 (1 H, br s, vinylic), and 6.5 (3 H, m, ArH) (Found: C, 78.2; H, 8.15. $\text{C}_{15}\text{H}_{18}\text{O}_2$ requires C, 78.23; H, 7.88%). 2,4-Dinitrophenylhydrazone, m.p. 160—162 °C (Found: N, 13.45. $\text{C}_{21}\text{H}_{22}\text{N}_4\text{O}_5$ requires N, 13.65%).

2-Acetyl-6-methoxy-2-methyl-1,2-dihydronaphthalene (25).—The naphthalene derivative (25) was obtained *via* short-path distillation, b.p. 130—135 °C at 6 mmHg; ν_{\max} 1 710, 1 600, 1 510, and 1 490 cm^{-1} ; δ 1.0 [3 H, s, (C-2)Me], 2.0 (3 H, s, COMe), 2.2 (1 H, d, *J* 16 Hz, benzylic), 3.0 (1 H, d, *J* 16 Hz, benzylic), 3.75 (3 H, s, OMe), 5.8 (1 H, d, *J* 8 Hz, vinylic), 6.3 (1 H, d, *J* 8 Hz, vinylic), and 6.5—7.0 (3 H, m, ArH) (Found: C, 77.9; H, 7.3. $\text{C}_{14}\text{H}_{16}\text{O}_2$ requires C, 77.75; H, 7.46%). 2,4-Dinitrophenylhydrazone, m.p. 178—180 °C (Found: N, 14.3. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_5$ requires N, 14.14%).

6-Methoxy-2-methyl-2-propionyl-1,2,3,4-tetrahydronaphthalene (26).—The tetrahydronaphthalene (26) was obtained *via* short-path distillation, b.p. 115—120 °C at 4 mmHg; ν_{\max} 1 710, 1 605, 1 510, 1 470, and 1 460 cm^{-1} ; δ 1.0 (3 H, t, CH_2Me), 1.20 [3 H, s, (C-2)Me], 1.3—1.5 (4 H, m, methylene), 3.0 (4 H, m, benzylic), 3.8 (3 H, s, OMe), and 6.7—7.2 (3 H, m, ArH) (Found: C, 77.7; H, 8.6%; M^+ , 232. $\text{C}_{15}\text{H}_{20}\text{O}_2$ requires C, 77.55; H, 8.68%; M 232). 2,4-Dinitrophenylhydrazone, m.p. 135—136 °C (Found: N, 13.8. $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_5$ requires N, 13.59%).

[1/1304 Received, 13th August, 1981]

REFERENCES

- Part 2, G. S. R. Subba Rao and N. Shyama Sundar, *J. Chem. Res. (S)*, 1979, 282; (*M*), 3201.
- R. G. Harvey, *Synthesis*, 1970, 161.
- A. J. Birch and G. S. R. Subba Rao, *Adv. in Org. Chem.*, 1972, **8**, 1—65.
- S. Mejer, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 1962, **10**, 469 (*Chem. Abstr.*, 1963, **59**, 1553).
- M. Narisada and F. Watanabe, *J. Org. Chem.*, 1973, **38**, 3887.
- S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, 1971, **36**, 2558.
- (a) G. S. R. Subba Rao and N. Shyama Sundar, Abstracts of the Annual Convention of Chemists, Madurai (India), 1974, Org. II-6; (b) N. Shyama Sundar, Ph.D. Thesis, Indian Institute of Science, Bangalore (1976).
- A. J. Birch and R. Robinson, *J. Chem. Soc.*, 1944, 503.
- M. D. Bachi, J. W. Epstein, Y. Herzberg Minzly, and H. J. E. Loewenthal, *J. Org. Chem.*, 1969, **34**, 128.

¹⁰ M. S. Newman and J. Roger Mangham, *J. Am. Chem. Soc.*, 1949, **71**, 3324.

¹¹ S. Mejer and Z. Marcinow, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 1976, **24**, 175 (*Chem. Abstr.*, 1976, **85**, 94121).

¹² R. G. Harvey, *J. Org. Chem.*, 1967, **32**, 238.

¹³ G. S. R. Subba Rao, A. R. K. Murthy, and N. Shyma Sundar, *Indian J. Chem. Sect. B*, 1978, **16**, 1027.

¹⁴ V. M. Kapoor and A. M. Mehta, *Synthesis*, 1975, 471.