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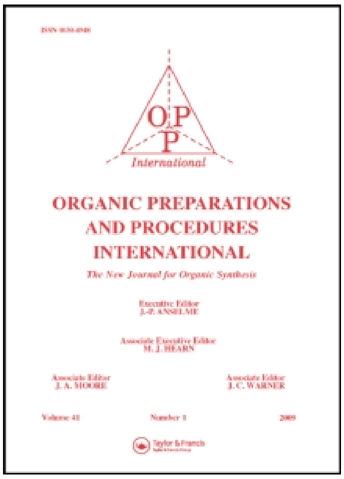

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THE SYNTHESIS OF 1*H*, 3*H*-NAPHTHO[1,8-*cd*]PYRAN-1-ONE, 1,8-DIMETHYL-1, 2,3,4TETRAHYDRONAPHTHALENE, 1,3,3a,4,5,6-HEXAHYDRONAPHTHO[1,8-*cd*] PYRAN, AND 1,2,3,4-TETRAHYDRO-8-METHYL-1-NAPHTHALENEMETHANOL

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ORGANIC PREPARATIONS AND PROCEDURES INT. 4(1), 35-42 (1972)

THE SYNTHESIS OF 1*H*,3*H*-NAPHTHO[1,8-*cd*]PYRAN-1-ONE, 1,8-DIMETHYL-1,2,3,4-TETRAHYDRONAPHTHALENE, 1,3,3a,4,5,6-HEXAHYDRONAPHTHO[1,8-*cd*]PYRAN, AND 1,2,3,4-TETRAHYDRO-8-METHYL-1-NAPHTHALENEMETHANOL

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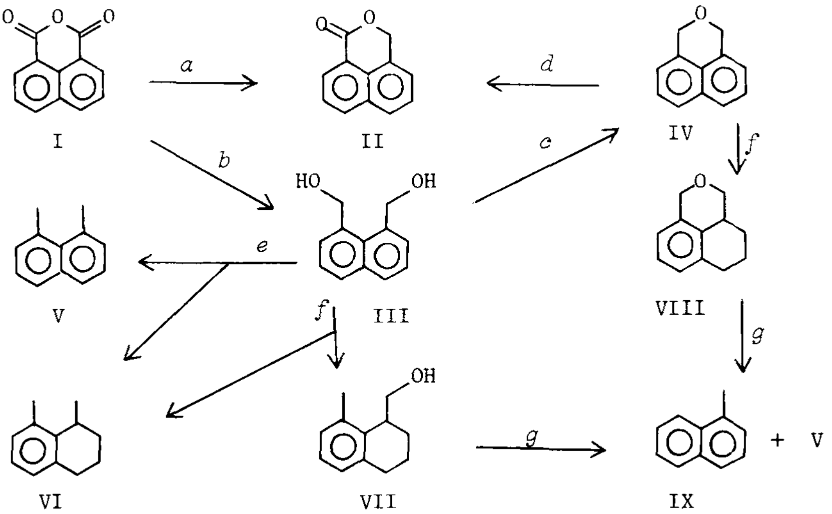
The synthesis of 1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one (II) and 1,8-dimethylnaphthalene (V) from 1,8-naphthalic anhydride (I) have been described.[2,3] The former has been prepared as a mixture of products by high-pressure copper chromite hydrogenation of I in an unspecified yield.[2a] We have found that addition of diisobutylaluminum hydride (DIBAH)[4] to a slurry of I in toluene at 10° gives II in 86% yield as the sole product. It is of interest that reduction of I with sodium borohydride in dimethylformamide, a reagent reported to convert anhydrides selectively to lactones, gave a complex mixture of products.[5]

Earlier syntheses of 1,8-dimethylnaphthalene (V) have utilized 1,8-naphthalenedimethanol (III)[2b,c] or the corresponding dichloride.[3] We chose Pd/C hydrogenolysis of III for the preparation of V and found the reaction to be remarkably smooth. The hydrogenolysis of III has been described[2b] but the experimental details are meager and the side products of the reaction were not mentioned. We have found that depending upon reaction conditions,[6] III may be converted to a mixture of V and VI or of VI and 1,2,3,4-tetrahydro-8-methyl-1-naphthalenemethanol (VII). The diol



$^a(C_4H_9)_2AlH$:I (2:1) in toluene. $^b(C_4H_9)_2AlH$:I(4:1) in benzene or $NaAl(C_2H_5)_2H_2$:I (2:1) in xylene. ^{c}Amberlyst-15 in benzene at reflux. ^{d}Dilute CrO_3 in acetic acid. $^eH_2$, Pd/C in acetic acid and hydrochloric acid at room temperature and one atmosphere. $^fH_2$, Pd/C in 95% ethanol at 50 psi at 60°. ^{g}Pd/C, Δ.

III may be hydrogenated to a mixture of VI:VII (55:45) in ethanol and in the absence of mineral acid.

Since traces of IV were observed as a product in all hydrogenations of III, it became of interest to prepare IV and subject it to the same hydrogenation conditions to determine whether it may serve as an intermediate to V, VI, or VII. Under hydrogenation condition *e* of the scheme, there was no apparent reaction and IV was recovered unchanged. However, more vigorous conditions (*f* of the scheme) gave the hexahydronaphtho-[1,8-*cd*]pyran (VIII) in 84% yield. Therefore, we do not consider IV to be a hydrogenation or hydrogenolysis intermediate in the formation of V, VI, or VII. Also, the rapidity with which III is reduced (*f* of the scheme) to VI and VII militates against regarding IV as an intermediate.

It is of interest that dehydrogenation of VII provides the expected V but in addition, IX is formed as the major product, the V:IX ratio being 7:93. It is assumed that dehydrogenation of VII to an aldehyde takes place and then decarbonylation ensues.[7] We have no evidence that VII may be an intermediate in the dehydrogenation of VIII to IX.

EXPERIMENTAL

DIBAH Reduction of Naphthalic Anhydride (I). A. To II. To a 12-l. vessel[9] fitted with stirrer and a dropping funnel with wide-bore Teflon stopcock, and equalizing sidearm was added 4 l. of dry toluene and 400 g. (2 mole) of I. The reaction mixture was cooled in an ice bath to 5-10° and held in this temperature range during addition of 579 g. (4.1 mole) of neat DIBAH[4] over 2 hr. The direct addition of DIBAH from 1-l. storage bottles to the dropping funnel was readily accomplished through use of a simple adapter.[10] The reaction mixture was then poured onto 4 kg. of ice and water. The salts were decomposed with 2 l. of conc. hydrochloric acid. Three l. of ether were added and the resulting mixture was filtered through Dicalite to remove a small amount of suspended material. A second 2-2-l. ethereal extract was combined with the first extract and these were dried ($MgSO_4$), filtered, and concentrated to 362 g. of crude solid, yellow lactone (98%). It was purified by dissolving in 10% sodium hydroxide and extracting with ether to remove neutral material. On acidification to pH 8-9, the lactone crystallized as colorless II (316 g., 86%): mp. 154-157° [lit.[2a] 152-155°]; mass spectrum (70 eV) *m/e* (rel intensity) 184 (66), 183 (38), 156 (19), 155 (100), 127 (70), 126 (22); nmr ($CDCl_3$) δ 8.30 (d, 1, ArH ortho to carbonyl), 8.13-7.21 (m, 5, ArH), 5.72 (s, 2, $ArCH_2$).

B. To 1,8-Naphthalenedimethanol (III). The above apparatus was used for reduction of I to III. A slurry of 600 g (3 mole) of I in 2500 ml. benzene was added over 2 hr. to 1850 g. (13 mole) of neat DIBAH[4] in 1.5 l. of dry benzene. During addition, the reaction temperature rose until reflux resulted (20 min) and was held at this temperature by addition of the remainder of I. After addition was complete, reflux was maintained for 17 hrs. at which time a sample was withdrawn. Glc studies[8a,11] showed that I had been consumed. Ethyl acetate (2 mole) was added to consume excess DIBAH. The reaction mixture was added to ice and water. Concentrated hydrochloric acid (2200 ml.) was added to the gel-like suspension. The white crystals which formed were filtered and dried and then added to 3500 ml. of 95% ethanol. The boiling ethanol suspension was diluted with 10 l. of water and allowed to cool to room temperature, then the layer of crystals (546 g.) was skimmed from the solution. These were recrystallized from 2 l. of hot 95% ethanol to give 525 g. (94%) of colorless III: mp 154.5-155° [lit.[2b] 158°]; mass spectrum (70 eV) *m/e* (rel intensity) 188 (M^+, 15), 170 (96), 169 (100), 153 (26), 142 (36), 141 (92), 115 (39). An nmr analysis was attempted but a suitable solvent was not found. Compound III is very insoluble in common solvents at room temperature. Reduction of I to III may also be conveniently carried out with $NaAl(C_2H_5)_2H_2$ in xylene.[4]

Cyclization of III to 1*H*,3*H*-Naphtho[1,8-*cd*]pyran (IV) with Amberlyst-15. The dehydration of III to IV was carried out by azeotropic distillation of water from a magnetically stirred mixture of 47 g. (0.25 mole) of III, 500 ml. of benzene and 5 g. of Amberlyst-15[12] during 2 hr. The catalyst was filtered, the filtrate was concentrated to 250 ml., and 250 ml. of petroleum ether[13] was added. The mixture was passed through a basis alumina column (2 cm. x 17 cm.). The colorless filtrate was further concentrated and on cooling, the filtrate gave 39 g. (92%) of IV: mp. 81-82° [lit.[14] 80-81°]; mass spectrum (70 eV) *m/e* (rel intensity) 168 (72), 167 (29), 142 (55), 141 (100), 139 (28), 115 (41); nmr (CCl_4) δ 7.72-6.98 (m, 6, ArH), 4.95 (s, 4, $ArCH_2O$).

Chromic Acid Oxidation of IV to II. To a stirred mixture of 13.6 g. (0.08 mole) of IV in 750 ml. of acetic acid at 11° was added 107 ml. of oxidizing mixture (190 ml. acetic acid, 10 ml. water, and 21 g. CrO_3) at one time.[15] The temperature ranged from 11° to 19°. The reaction mixture was stirred for 100 min., poured into 5 l. of water, and extracted with 2 x 750 ml. of ether. The combined extracts were filtered to remove 0.6 g. of I. The filtrate was stirred with 500 ml. of 10% NaOH to remove II (as the salt of the hydroxy acid). The ethereal layer yielded 4.6 g. of IV. The alkali layer was acidified with conc. hydrochloric acid (cyclization back to II) and extracted to give 6.1 g. (63%) of crude II which was purified by dissolving in benzene-petroleum ether (1:1) and then filtering through basic alumina to give 5.7 g. (59%) of II: mp 155-157° [lit.[2a] 152-155°].

Pd/C Hydrogenolysis of III to 1,8-Dimethylnaphthalene (V) and 1,8-Dimethyl-1,2,3,4-tetrahydronaphthalene (VI). A 94-g. (0.5 mole) sample of III in 750 ml. of acetic acid and 2 ml. of conc. hydrochloric acid in the presence of 1.6 g. of 10% Pd/C was hydrogenated at atmospheric pressure for 4 hr. at 25° using a Paar Model 3920 hydrogenation apparatus. The catalyst was filtered through a bed of Dicalite. Water (2 l.) was added to the filtrate and the mixture was extracced with ether (2 x 500 ml.). The extract was washed with water and 10% sodium hydroxide, dried ($MgSO_4$), and concentrated by rotary evaporation to give 77 g. of a mixture of dark crude solid V:VI (9:1) containing less than 1% of VII. These crystals were dissolved in 400 ml. of petroleum ether[13] and the solution was decolorized by elution through a 1.5 x 5 in. column of basic alumina. The petroleum ether was removed to give 70 g. (88%) of a colorless mixture of V and VI. The mixture was dehydrogenated at 265° in the presence of 2 g. of 10% Pd/C to give after filtration 69 g. (82% from I) of V:[16] mp. 63.5-64° [lit.[2b] 62-63.5°]; mass spectrum (70 eV) *m/e* (rel intensity) 156 (M^+, 100), 155 (29), 153 (15), 141 (65), 115 (16), 76 (13); nmr (CCl_4) δ 7.67-7.46 (m, 2, ArH peri), 7.30-7.08 (m, 4, ArH), 2.28 (s, 6, $ArCH_3$).

Pd/C Hydrogenolysis of III to VI and 1,2,3,4-Tetrahydro-8-methyl-1-naphthalenemethanol (VII). A 47-g. (0.25-mole) sample of III in 750 ml. of 95% ethanol in the presence of 1.2 g. of 10% Pd/C was hydrogenated at 50 psi and 60° for 4 hr. Filtration through Dicalite and concentration by rotary evaporation gave 41 g. of yellow oil which was shown by glc[8a] to be VI:VII (1.2:1.0). Addition of 50 ml. of petroleum ether,[13] refrigeration and filtration gave 16 g. (35%) of VII free of VI: mp. 72.5-73°; mass spectrum (70 eV) *m/e* (rel intensity) 176 (M^+, 12), 146 (14), 145 (100), 130 (13), 129 (12), 128 (12); nmr ($CDCl_3$) δ 7.20-6.82 (m, 3, ArH), 3.74-3.42 (m, 2, $ArCH(C\underline{H}_2OH)$), 3.28-2.98 (m, 1, $CH_2O\underline{H}$), 2.89-2.67 (m, 2, $ArCH_2$), 2.33 (s, 3, $ArCH_3$), 2.29-1.46 (envelope, 5, $ArCH_2C\underline{H}_2C\underline{H}_2C\underline{H}<$).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.74; H, 9.06.[17]

The filtrate containing VI:VII (46:1) was distilled to give 20 g. (40%) of VI: bp 60° (0.5 mm); mass spectrum (70 eV) *m/e* (rel intensity) 160 (M^+, 20), 146 (12), 145 (100), 129 (9), 128 (11), 115 (13); nmr (CCl_4) δ 6.94-6.74 (m, 3, ArH), 3.20-2.87 [m, 1, $ArC\underline{H}(CH_3)$], 2.86-2.58 (m, 2, $ArCH_2$), 2.27 (s, 3, $ArCH_3$), 1.98-1.58 [m, 4, $CH_2C\underline{H}_2C\underline{H}_2CH(CH_3)$], 1.16 [d, 3, $ArCH(C\underline{H}_3)$].

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.14; H, 10.17.[17]

Pd/C Hydrogenation of IV to VIII. An 8.5 g. (0.05 mole) sample of IV was hydrogenated in the presence of 0.85 g. of 10% Pd/C in 75 ml. of 95% ethanol at 50 psi and 60° for 7 hr. The product was 8.5 g. of crude VIII which showed about 2% VII. Recrystallization from cold petroleum ether[13] gave 7.4 g. (84%) of VIII: mp. 40-42°, bp 105° (1.1 mm); mass spectrum (70 eV) *m/e* (rel intensity) 174 (21), 145 (28), 144 (100), 129 (59), 128 (27), and 115 (24); nmr (CCl_4) δ 7.06-6.51 (m, 3, ArH), 4.66 (s, 2, ArC$\underline{H}_2$O), 4.04-3.04 (m, 2, ArCH$_2$OC$\underline{H}_2$), 2.96-2.38 (m, 3, ArC$\underline{H}_2$CH$_2$CH$_2$C$\underline{H}$), 2.04-0.78 (m, 4, ArCH$_2$C$\underline{H}_2$C$\underline{H}_2$).

Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.60; H, 8.12.[17]

Pd/C Dehydrogenation of VII to V and 1-Methylnaphthalene (IX). A 1.76-g. (0.01 mole) sample of VII under a N_2 atmosphere was dehydrogenated at 260° in the presence of 0.3 g. of 10% Pd/C for 2 hr. Filtration and distillation gave 1.3 g. of a mixture of V and IX (7:93).

The identity of IX, obtained by preparative glc, was established by comparing the nmr and ir spectra with those of an authentic sample.

Pd/C Dehydrogenation of VIII to IV, V, and IX. The above procedure was applied to VIII, which gave 1.3 g. of IV:V:IX (3:1:21).

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(b) Nmr spectra were obtained with a Varian XL100 spectrometer. We thank Mr. Cecil Dickson, Texas A&M University, for spectra of IV, V, VI, and VII.

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