α-HALO KETONES IX.[1] A NEW FURAN-FORMING REACTION

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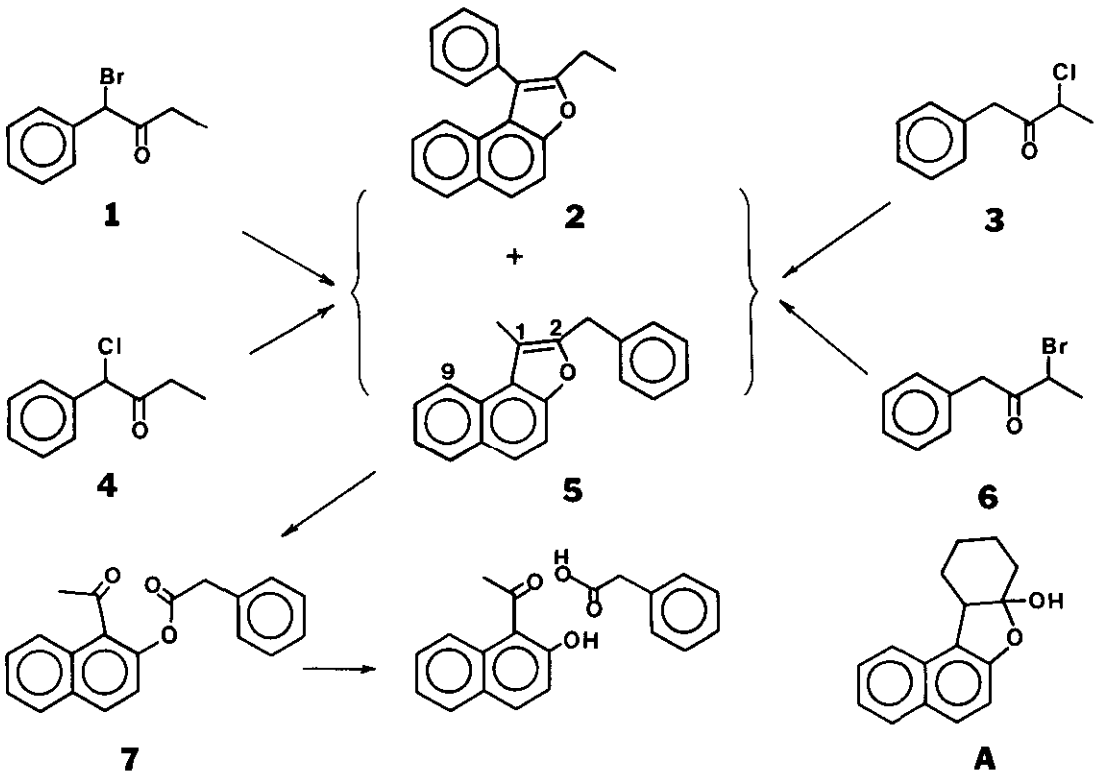
Some α-halo ketones react with 2-naphthol in the presence of strong acids to give naphtho[2,1-b]furans. A hydroxyallylic cation may be an intermediate in the reaction.

In the course of studying the α → α' rearrangement of α-halo ketones in acid, we have encountered a new furan-forming reaction. When a number of α-chloro and α-bromo ketones were treated at room temperature with strong acid in the presence of 2-naphthol (intended as a trap for cationic halogen species), naphthofurans were produced. The overall reaction is related to some other furan preparations, for example the Feist-Benary synthesis which employs α-halo ketones in a base-catalyzed reaction with β-dicarbonyl compounds.[2] A closer comparison is the reaction of 2-naphthol with 2-chlorocyclohexanone in the presence of K_2CO_3 to yield the furan precursor A.[3] However, we have not found previous mention of an acid-catalyzed process.[4-7]

The reaction is not strongly solvent dependent since it occurs in chloroform as well as acetic acid. The α-halogen may be either chlorine or bromine, and the strong acid may be HCl, HBr, or $HClO_4$. The ultraviolet spectra of the products were clearly characteristic of naphtho[2,1-b]furans,[8] and therefore C-C bond formation had taken place at the 1-naphthyl position. However, the reaction is not regiospecific in that more than one naphtho[2,1-b]furan can result. The best studied example is that of the α-halo-1-phenylbutan-2-ones. The same two naphtho[2,1-b]furans were formed from all four of the α-chloro and α-bromo isomers 1, 3, 4 and 6, whether the acid was HCl, HBr, or $HClO_4$.

The predominant product was 1-methyl-2-benzylnaphtho[2,1-b]furan 5. The methyl substituent on the naphthofuran skeleton was located at C-1 by the nuclear Overhauser enhancement of 6.7% in the C-9 proton signal when the methyl resonance was irradiated. More convincingly, the furan double bond was cleaved by chromic acid oxidation[9] to the keto ester 7 which was saponified to phenylacetic acid and 1-acetyl-2-naphthol.

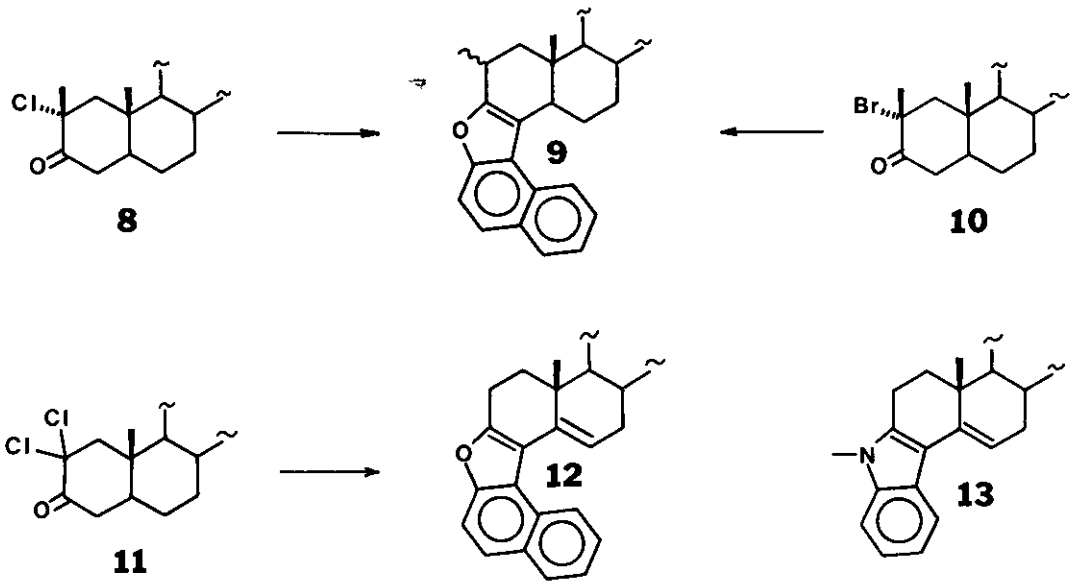
The minor naphthofuran 2 contained an ethyl side chain apparent in its ^{1}Hmr spectrum leaving



only phenyl for the other substituent. The phenyl group is placed at the more sterically crowded 1-position, where it cannot be coplanar, because of the lack of perturbation of the longer wavelength peaks in the ultraviolet spectrum and the shielding of the C-9 hydrogen in the ^{1}Hmr spectrum. This proton absorption is no longer at $\delta\sim8.3$ but instead has moved upfield to merge with the other aromatic protons.

From 2α-chloro- and 2α-bromo-2β-methyl-5α-cholestan-3-one 8 and 10, there were produced three isomeric naphtho[2,1-b]furans whose exact structures were not determined. In each the C-2 methyl group gave rise to a doublet in the ^{1}Hmr spectrum, and therefore the furan was presumably attached at C-3 and C-4 of the steroid nucleus. Two of the isomers would be expected to be C-2 epimers of structure 9, while the third might be an additional isomer of 9 resulting from restricted passage of C-6 of the steroid and C-9 of the naphthalene ring.

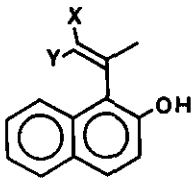
At 81°C 2,2-dichloro-5α-cholestan-3-one 11 gave an unsaturated chlorine-free naphthofuran which must be assigned structure 12. The ^{1}Hmr spectrum contained a single olefinic proton doublet at δ6.72 with the expected coupling to the adjacent methylene group. The C-2 methylene absorption is deshielded to δ3.04 by the furan ring. In fact the ^{1}Hmr spectrum is quite similar to that of the closely related nitrogen analog 13.[10]



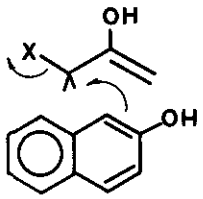
Some α-halo ketones, such as 5α-chloro-3β-acetoxycholestan-6-one, gave no reaction with 2-naphthol and acid under these conditions. On the other hand chloro- and bromoacetone reacted with 2-naphthol in the presence of HCl or HBr to give propenylnaphthols 14 from carbonyl condensation at the 1-naphthyl position. With bromoacetone and a number of other compounds, 2-naphthol did function as a cationic halogen trap in the presence of acid giving 1-bromo-2-naphthol (but no naphthofurans) from 1-bromobutanone, 1-bromopentan-2-one, 3-bromopentan-2-one, 1,1-dibromoacetone, 1,1-dibromobutanone, 2,2-dibromo-5α-cholestan-3-one, and 5α-bromo-3β-acetoxycholestan-6-one.

There are several ways in which naphthofurans might be formed from α-halo ketones, even with the provisos that a naphtho[2,1-b]furan be formed and that an acid catalyst is essential to its formation. For example (a) the 1-naphthyl position could serve as a nucleophile in an S_N2 displacement on an α'-enol allylic halide 15, or (b) the hemiketal or enol ether from 2-naphthol and an α-halo ketone could undergo intramolecular S_N2 displacement 16 or 17, or (c) the oxygen atom of 2-naphthol could act as a nucleophile in an S_N2 reaction on an α'-enol allylic halide 18 followed by acid-catalyzed carbonyl condensation at the 1-naphthyl position, or (d) 2-naphthol could react with a hydroxyallylic cation resulting from ionization of an α'-enol allylic halide 19.

Possibility (c) would give the wrong substituent pattern for the naphtho[2,1-b]furans from the α-halo-1-phenylbutan-2-ones. Mechanism (b) has the defect mentioned above that some α-halo ketones that should undergo the S_N2 reaction readily by this path do not give naphthofurans. Path (a) seems unlikely since several of the bromo ketones which give only 1-bromo-2-naphthol seem well suited for giving naphthofurans by this very route. Although the evidence is far from conclusive,



14 **a** X,Y= Cl,H
b X,Y= Br,H



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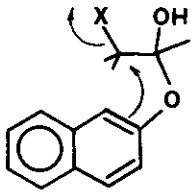

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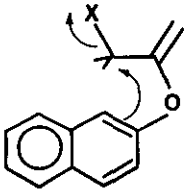

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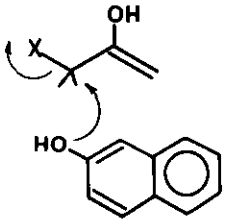

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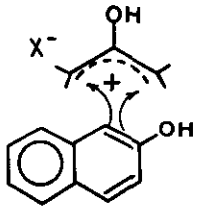

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so far the most attractive mechanism for naphthofuran formation is (d) 19. Those halo ketones which have been found to undergo $\alpha \rightarrow \alpha'$ halogen migration via ion pair rearrangement of an α'-enol allylic halide[1] are the ones that yield naphthofurans provided that steric hindrance is not too severe.[11] It would appear that those halo ketones which are reluctant to ionize to 19, whether because the halogen is on a primary carbon atom, or because the α'-enol does not form readily compared to the α-enol, or because reductive debromination is much faster, those ketones do not give naphthofurans. Moreover, the hydroxyallylic cation path (d) readily accommodates the formation of both naphthofurans 2 and 5 from each of the four halo-1-phenylbutan-2-ones. It also makes understandable the higher temperature required for the reaction of 2,2-dichloro-5α-cholestan-3-one, which probably rearranges to 2α, 4α-dichloro-5α-cholestan-3-one before furan formation. Further work will be necessary to determine whether the naphthofurans really arise from hydroxyallylic cations.

EXPERIMENTAL

Melting points were taken on a Reichert Kofler microscope hot stage. Infrared spectra were obtained on Beckman IR5, IR5A, IR10 and Accu$_{lab}$ 4 spectrometers. The 60 MHz ^{1}Hmr spectra were taken on a Varian T-60 instrument; the 100 MHz ^{1}Hmr spectra were obtained by Heather Schroeder on a Varian XL-100 instrument. Mass spectra were determined by Doug Hairsine on a MAT 311A instrument. Ultraviolet spectra were recorded on a Cary 118 spectrophotometer. Merck GF 254 silica gel was used for thin and preparative layer chromatography. BDH 60-120 mesh silica gel was used for column chromatography. Organic solvents were removed at water aspirator vacuum on a rotating evaporator.

Reaction of 3-Bromo-1-phenylbutan-2-one with 2-Naphthol

A solution of 1.45 g (6.38 mM) of 3-bromo-1-phenylbutan-2-one and 1.93 g (13.4 mM) of 2-naphthol in 2 ml of HOAc plus 4.5 ml of 1M $HClO_4$ in HOAc was stirred at room temperature for 1.5 h and then at 60 - 70°C for 3.5 h. The cooled reaction mixture was neutralized with excess saturated aqueous $NaHCO_3$ and extracted with ether to give 2.78 g of a complex mixture which was chromatographed on a column of 250 g of silica gel. Benzene-hexanes (1:9) eluted 446 mg (25%) of crude 1-methyl-2-benzylnaphtho[2,1-b]furan 5 as an oil. Three recrystallizations from pentane gave colorless needles, mp 70.5 - 71.5°C; uv(MeOH): 217(40,000), 239(31,000), 247(36,000), 299(11,200), 306(9100), 312(10,200), 319(7200), and 325 nm (12,000); ir(CCl_4): no C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 2.57(3H,s,CH_3), 4.12(2H,s,CH_2Ph), 7.24(5H,s,PhHs), 7.2 - 7.6(4H,m,ArH), 7.88(1H,m,ArH), and 8.36 ppm (1H,m,C-9 ArH); m/e 272(M^+), 257(M^+-CH_3), and 195(M^+-Ph). Mol. ion calcd for $C_{20}H_{16}O$: 272.1201; found: 272.1202. Anal. calcd for $C_{20}H_{16}O$: C 88.20, H 5.92; found: C 88.17; H 5.93.

The earlier fractions from the column chromatography above contained 83 mg of less polar material. Preparative tlc of this oil on silica gel developed with pentane gave 44 mg (3%) of pure 1-phenyl-2-ethylnaphtho[2,1-b]furan 2 as an oil which did not crystallize, uv (MeOH): 216(34,000), 226(31,000), 247(22,000), 300(9100), 306(7900), 313(8100), 320(6000), and 327 nm (7600); ir(CCl_4): no C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 1.29(3H,t,J=7Hz,$CH_3[CH_2]$), 2.73(2H,q,J=7Hz,$CH_2[CH_3]$), 7.0 - 8.0 ppm (11H,m + tall s at 7.49,ArH); m/e 272(M^+) and 257(M^+-CH_3). Mol. ion calcd. for $C_{20}H_{16}O$: 272.1201; found: 272.1197.

Reaction of Other α-Halo-1-phenylbutan-2-ones with 2-Naphthol

(a) A solution of 110 mg of 1-chloro-1-phenylbutan-2-one 4 and 100 mg of 2-naphthol in 0.5 ml of HOAc saturated with anhydrous HCl was allowed to stand at room temperature. After 10 days 75% of a mixture of furans had been formed. Preparative layer separation on silica gel developed in benzene-hexanes (1:5) gave 5 (major) and 2 (minor) identical with the naphthofurans from 6.

(b) A solution of 112 mg of 1-bromo-1-phenylbutan-2-one 1 and 143 mg of 2-naphthol in 0.7 ml of 0.2 M anhydrous HBr in HOAc was allowed to stand at room temperature for 96 h. After neutralization and partitioning between ether and aqueous NaOH solution, the ether soluble fraction was separated by preparative layer chromatography developed in benzene-hexanes (1:5) to give 5 (major) and 2 (minor) identical with the naphthofurans from 6.

(c) A reaction of 114 mg of 1 and 146 mg of 2-naphthol in 0.7 ml of 1M $HClO_4$ in HOAc for 122 h gave 40% of 5 and a lesser amount of 2.

(d) A non-quantitative experiment with 3-chloro-1-phenylbutan-2-one 3 and 2-naphthol in HCl-saturated HOAc also gave the same two naphthofurans 5 (major) and 2 (minor).

Oxidative Cleavage of 1-Methyl-2-benzylnaphtho[2,1-b]furan 5

The procedure of Ishii et al. was used.[9] To a stirred (magnetic bar) solution of 83 mg of the major naphthofuran 5 in 28 ml of acetone cooled to 1°C was added dropwise 2.8 ml of Jones reagent prepared from 2.50 g of CrO_3, 2.25 ml of conc. H_2SO_4, and 7.5 ml of water. After a further 5 min. of stirring at 1°C, the reaction was quenched with 3 ml of MeOH.

After filtration through glass wool, the filtrate was partitioned between water and ether. Concentration of the ether extract gave two phases which were again partitioned between water and ether. Evaporation of the dried ($MgSO_4$) ether solution left 74 mg of orange oil that was then partitioned between aqueous $NaHCO_3$ (A) and ether (B). The $NaHCO_3$ solution (A) was acidified with aqueous HCl and extracted with ether to yield 9 mg of crude phenylacetic acid, mp 72 - 76°C after recrystallization from hexanes. Evaporation of the ether solution (B) left 56 mg of material which was separated on a silica gel thick layer plate developed in $CHCl_3$. The major product from the band at R_f 0.48 was 27 mg (29%) of crude 1-acetyl-2-phenylacetoxynaphthalene 7, ir(CCl_4): 1768 (ester C=O) and 1708 cm^{-1} (aryl C=O); ^{1}Hmr ($CDCl_3$) δ: 2.37(3H,s,CH_3C=O), 3.87(2H,s,O=CCH_2Ph) and 7.0 - 8.2 ppm (∿11H,m,ArH). Mol. ion calcd for $C_{20}H_{16}O_3$: 304.1099; found: 304.1104.

A solution of 26 mg of 7 and 41 mg of KOH in 1 ml of MeOH was kept for 2 h at room temperature and then for 2 h at reflux. After evaporation of MeOH, acidification with aqueous HCl, and then treatment with an excess of solid $NaHCO_3$ (C), the phenolic material was removed by extraction with ether to give 14 mg of non-crystalline 1-acetyl-2-naphthol; ir(CCl_4): 3200(OH) and 1627 cm^{-1} (chelated ArC=O); ^{1}Hmr ($CDCl_3$) δ: 2.79(s,CH_3C=O), 7.60(m,ArH), and 13.4 ppm (broad,ArOH...O=C). Mol. ion calcd for $C_{12}H_{10}O_2$: 186.0681; found: 186.0678.

The aqueous $NaHCO_3$ solution (C) was acidified with aqueous HCl and extracted with ether to give 10 mg of phenylacetic acid. Two recrystallizations from hexanes gave 4 mg of colorless flakes, mp 75 - 76.5°C, undepressed on admixture with an authentic specimen; ^{1}Hmr ($CDCl_3$) δ: 3.60 (2H,s,$ArCH_2$), 7.21(5H,bs,ArH), and 9.48 ppm (1H,broad,OH).

Reaction of 2α-Halo-2β-methyl-5α-cholestan-3-ones with 2-Naphthol

(a) 2α-Chloro + HCl. A solution of 87 mg (0.20 mM) of 8 and 128 mg (0.89 mM) of 2-naphthol in 0.5 ml of $CDCl_3$ plus 0.5 ml of 0.3 M anhydrous HCl in HOAc was allowed to stand at room temperature for 10.7 days. Partition of the bright orange solution between ether and aqueous $NaHCO_3$ gave 231 mg of ether soluble material. Column chromatography on 15 g of silica gel gave 91 mg (86%) of a yellow solid mixture of two naphthofurans containing minor contaminants (separation and purification are described below).

(b) 2α-Bromo + HBr. A solution of 49 mg (0.10 mM) of 10 and 73 mg (0.51 mM) of 2-naphthol in 0.25 ml of $CDCl_3$ plus 0.25 ml of 0.6 M anhydrous HBr in HOAc was allowed to stand at room temperature for 22 days. Evaporation of solvent left 113 mg of crude product. Column chromatography on 10 g of silica gel gave 40 mg (76%) of an oily mixture of two naphthofurans containing other minor contaminants. Crystallization of this material from ethanol gave 21 mg of yellow solid.

The solid material from each of the above two reactions contained the same two furans which were separated by preparative layer chromatography on silica gel developed in pentane. The least polar component (minor), R_f 0.50, was probably a 2-epimer of naphtho[2,1-b]furan structure 9, mp 176.5 - 178.5°C, uv (cyclohexane): 223(31,600), 247(24,500), 254(27,500), 305(9500), 317(9300), 324(7500), and 331 nm (10,700); ir (CCl_4): no OH or C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 1.29(d,J=6.5 Hz,CH_3[CH]), 2.04(∿4H,m), 3.16 (∿2H,m), 7.2 - 7.7(4H,m + s at 7.61,ArH), 7.91(1H,dd,ArH), and 8.12 ppm (1H,bd,C-9ArH). Mol. ion calcd for $C_{38}H_{52}O$: 524.4018; found: 524.4018.

The more polar naphtho[2,1-b]furan, R_f 0.44, was also probably a 2-epimer of structure 9, mp 87 - 90°C to a liquid crystal form (?) which cleared completely by 107°C, uv (cyclohexane):

222(32,000), 247(24,000), 254(25,000), 305(9700), 317(9300), 324(7500), and 331 nm (10,000); ir (CCl_4): no OH or C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 1.28(d,J=7Hz,CH_3[CH]), 2.79(2H,m), 3.08(1H,m, HC-5 or HC-2?), 7.2 - 7.7(4H,m+s at 7.58,ArH), 7.88(1H,dd,ArH), and 8.10 ppm (1H,dd,C-9 ArH). Mol. ion calcd for $C_{38}H_{52}O$: 524.4018; found: 524.4018. Anal. calcd for $C_{38}H_{52}O$: C 86.96, H 9.99; found: C 86.95, H 10.03.

(c) 2α-Bromo + $HClO_4$. A solution of 50 mg (0.10 mM) of 10 and 68 mg (0.47 mM) of 2-naphthol in 0.25 ml of $CDCl_3$ and 0.25 ml of 1M $HClO_4$ in HOAc was allowed to stand at room temperature for 1.3 h. Partition of the intensely yellow solution between ether and aqueous $NaHCO_3$ gave 113 mg of ether soluble material. Removal of naphthols by partition between ether and aqueous NaOH gave 55 mg of neutral material. *Preparative tlc on silica gel* (benzene-hexanes, 1:19) gave a major fluorescent band containing three naphthofurans which were separated by further preparative tlc on *silica gel* developed thrice in pentane into three bands, R_f 0.48 (minor), 0.42 (major), and 0.36 (major). The upper two bands contained the two previously described naphthofuran epimers of 9. The most polar band gave a third new naphtho[2,1-b]furan which was recrystallized twice from EtOH-EtOAc to give small granules, mp 161 - 165°C; uv (cyclohexane): 222(34,000), 248(25,700), 255 (29,500), 305(11,200), 318(11,200), 325(8900) and 332 nm (11,500); ir (CCl_4): no OH or C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 1.55(d,J=6.5Hz,CH_3[CH]), 2.80(2H,m), 3.11(1H,m), 7.2 - 7.7(4H,m+s at 7.60, ArH), 7.90(1H,dd,ArH), and 8.15 ppm (1H,bd,C-9 ArH). Mol. ion calcd for $C_{38}H_{52}O$: 524.4018; found: 524.4015.

Reaction of 2,2-Dichloro-5α-cholestan-3-one with 2-Naphthol

A solution of 600 mg (1.32 mM) of 2,2-dichloro-5α-cholestan-3-one and 200 mg (1.38 mM) of 2-naphthol dissolved in 8 ml of a saturated solution of HCl gas in $CHCl_3$ was sealed in a thick-walled glass tube and heated at 81°C for 27 h. *The clear pinkish reaction mixture was partitioned* between water and ether, and the ether solution was extracted with aqueous NaOH and water. Concentration *of the dried ethereal solution* left 717 mg of glassy product. Tlc on silica gel developed in EtOAc-hexanes (10:90) gave the major product as the least polar spot (R_f 0.70) plus 11 more polar spots. Thick layer chromatography under the same conditions yielded 188 mg (28%) of the major product unsaturated naphthofuran 12 as a white solid. Two recrystallizations from hexanes gave colorless needles, mp 172 - 175°C, uv (EtOH): 216(56,000), 227 inf. (26,000), 245(19,000), 281 min. (2400), 309(8900), 315(9700), 322(8900), and 329 nm (9400); ir (CS_2): 3100 cm^{-1} (aromatic CH), no C=O absorption; ^{1}Hmr ($CDCl_3$) δ: 1.19(s,19-Me), 3.04(2H,dd,C-2 CH_2), 6.72(1H,d,C=CH), 7.64 - 8.16(5H,m,ArH), and 9.04 ppm (1H,m,ArH). Mol. ion calcd for $C_{37}H_{48}O$: 508.3705; *found:* 508.3708.

Reaction of Chloroacetone with 2-Naphthol

A solution of 95 mg (1.0 mM) of chloroacetone and 147 mg (1.02 mM) of 2-naphthol in 0.5 ml of 0.5 M anhydrous HCl in HOAc was kept at 60°C for 144 h. *The colorless solution gradually changed* to yellow, then orange, and finally brown. The reaction was quenched by partition between ether and aqueous $NaHCO_3$ to *yield 174 mg of crude product. Preparative* layer chromatography on silica gel developed in benzene-hexanes (3:2) gave 53 mg of recovered 2-naphthol, 63 mg of Z (or E) and 27 *mg of E (or Z)* 1-chloro-2-(1'-(2'-hydroxynaphthyl))propene 14a.

The major propene, a light yellow oil R_f 0.33, had uv(MeOH): (Short λ_{max} off chart) 265(4800), 275(6000), 284(4800), 321(2700), and 330 nm (3000); ir (CCl_4): 3555(OH), 1622 and 1597 cm^{-1} (conj. naphthyl C=C); ^{1}Hmr ($CDCl_3$) δ: 2.18(3H,d,J=1.5Hz,CH_3[C=CH]), 5.39(1H,bs,OH), 6.21(1H,q,J=1.5Hz, HC=CMe) and 7.40 ppm (6H,m,ArH). Mol. ion calcd for $C_{13}H_{11}{}^{35}ClO$: 218.0498; found: 218.0501.

The minor propene, also a light yellow oil R_f 0.22, had uv (MeOH): (Short λ_{max} off chart)

265(3700), 275(4800), 287(3700), 318(2000), and 330 nm (2300); ir (CCl_4): 3560(OH), 1623 and 1598 cm^{-1} (conj. naphthyl C=C); ^{1}Hmr ($CDCl_3$) δ: 2.13(3H,d,J=1.5Hz,CH_3[C=CH]), 5.11(1H,bs,OH), 6.57(1H, q,J=1.5Hz,HC=CMe), and 7.44 ppm (6H,m,ArH). Mol. ion calcd for $C_{13}H_{11}{}^{35}ClO$: 218.0498; found: 218.0501.

Reaction of Bromoacetone with 2-Naphthol

A solution of 80 mg (0.50 mM) of bromoacetone and 147 mg (1.02 mM) of 2-naphthol in 0.5 ml of 0.6 M anhydrous HBr in HOAc was kept at room temperature for 74 h. The colorless solution slowly changed to a deep brown. The reaction was quenched by partition between ether and aqueous $NaHCO_3$ to yield 208 mg of crude product. Preparative layer chromatography of 166 mg of the product on silica gel developed in benzene-hexanes (3:2) gave 58 mg of 2-naphthol, 32 mg of 1-bromo-2-naphthol, 22 mg of Z (or E) and 14 mg of E (or Z) 1-bromo-2-(1'-(2'-hydroxynaphthyl))propene 14b.

The major propene, a slightly greenish oil R_f 0.33, had ir (CCl_4): 3545 and 3300(OH), 1624 and 1598 cm^{-1} (conj. naphthyl C=C); ^{1}Hmr ($CDCl_3$) δ: 2.22(3H,d,J=1.5Hz,CH_3[C=CH]), 5.34(1H,bs,OH), 6.34(1H,q,J=1.5Hz,HC=CMe), and 7.34 ppm (6H,m,ArH). Mol. ion calcd for $C_{13}H_{11}{}^{79}BrO$: 261.9993; found: 261.9989.

The minor propene, also a greenish oil R_f 0.24, had ir (CCl_4); 3555 and 3300(OH), 1625 and 1600 cm^{-1} (conj. naphthyl C=C); ^{1}Hmr ($CDCl_3$) δ: 2.15(3H,d,J=1.5Hz,CH_3[C=CH]), 5.13(1H,bs,OH), 6.66(1H,q,J=1.5Hz,HC=CMe), and 7.41 ppm (6H,m,ArH). Mol. ion calcd for $C_{13}H_{11}{}^{79}BrO$: 261.9993; found 261.9987.

ACKNOWLEDGEMENT

We would like to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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Received, 26th August, 1980