The Syntheses of Nuclearly Hydroxylated 1-Naphthyl Methylcarbamates

The 6- and 7-Isomers

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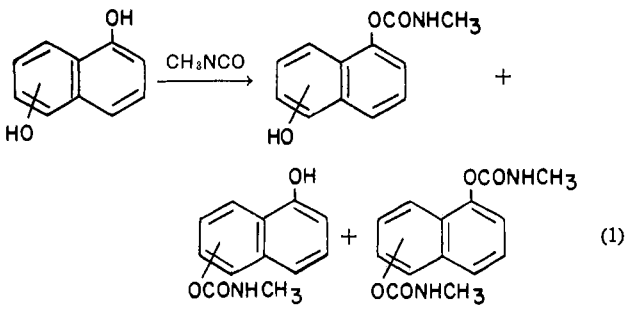
The unequivocal syntheses of 7-(and 6-)hydroxy-1-naphthyl methylcarbamate are described. The routes were developed in support of carbaryl insecticide (Sevin) plant metabolism studies and represent the first reported syntheses of β-hydroxycarbaryl derivatives. Infrared, nmr, and mass spectral data are presented for the compounds involved in these syntheses. The results of studies of the mono (methylcarbamoylation) of 1,β-dihydroxynaphthalenes is also discussed.

The synthesis of 4- and 5-hydroxy-1-naphthyl methylcarbamates, known plant and animal metabolites of carbaryl insecticide (Sevin, 1-naphthyl methylcarbamate) (Kuhr and Casida, 1967; Leeling and Casida, 1966) has been accomplished by the direct carbamoylation of 1,4- and 1,5-dihydroxynaphthalene (Knaak *et al.*, 1965). To date these are the only hydroxycarbaryl isomers whose syntheses have been reported in the literature.

Recent studies of the metabolism of carbaryl in bean plants have required the preparation of hydroxy-1-naphthyl methylcarbamates where the hydroxy group is in a β-position, *i.e.*, 3-, 6-, or 7-. Attempts to prepare these compounds by the direct carbamoylation of the corresponding 1,3-, 1,6-, and 1,7-dihydroxynaphthalene under conditions employed for the synthesis of 4- and 5-hydroxy isomers gave, in each case, a mixture of the desired product and the isomeric β-carbaryl derivative, together with small quantities of the starting diol and the bis(carbamate) (Equation 1). In the case of each dihydroxynaphthalene, the components of the product mixture were detected by tlc (Figure 1). Cochromatography with known diol and bis(carbamate) (Table I) served to identify the minor components of the various reaction mixtures, while the spots due to specific isomeric hydroxynaphthyl methylcarbamate were, in each case, identified through treatment of the chromatogram with Gibbs' reagent. This reagent, which reacts specifically with phenols (or naphthols) with open para positions, gave a positive reaction with the 1-hydroxy-β-naphthyl carbamate isomer, while the desired isomer was Gibbs negative.



(1)

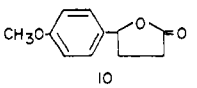
Also included in this study was 1,8-dihydroxynaphthalene which, predictably, gave only one monocarbamoylated product, presumably 8-hydroxy-1-naphthyl methylcarbamate. This product gave a positive reaction to the Gibbs reagent, but was not isolated in pure form.

The above reactions could serve to provide chromatographic standards for tentative identification of carbaryl metabolites, but for confirmation of structure, unequivocal syntheses were required. This paper reports syntheses of 6- and 7-hydroxy-1-naphthyl methylcarbamates (6- and 7-hydroxycarbaryl) which satisfy this criterion.

The preparation of 7-hydroxycarbaryl **1** was accomplished in the manner outlined in Figure 2.

The ketoacid **2** was obtained by the method shown, using nitrobenzene as solvent (Rao and Dev, 1957), but some difficulty was encountered in the removal of nitrobenzene from the product. Use of lower boiling solvents such as 2-nitropropane (Thomas and Nathan, 1948) or carbon disulfide circumvented the problem of solvent removal but, in our hands, resulted in decreased yields and, therefore, offered little advantage over the use of nitrobenzene.

The reduction of **2** to the butyric acid **3** has been accomplished catalytically (Fieser and Daudt, 1941; Horning and Reisner, 1949; House and McCaully, 1959) and by the Clemmenson reduction (Rao and Dev, 1957). These methods, together with the Wolff-Kishner technique (Huang-Minlon, 1946), were evaluated and it was found that the use of 10% Pd/C in acetic acid at a hydrogen pressure of 3 to 4 atmospheres gave consistently high yields in a reasonable period of time. In one experiment the reaction was stopped when approximately 50% of the required hydrogen had been absorbed to give 4-hydroxy-4-(4-methoxyphenyl)butyric acid lactone **10** in 62% yield. Lactone **10** could be reduced to **3**



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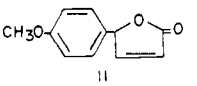

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under the conditions used for the conversion of **2** to **3**; **10** is a possible intermediate in the reduction of **2** to **3**. Lipovich and

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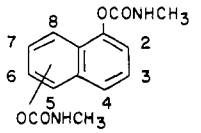
Table I. Bis(methylcarbamoyl) Derivatives of 1,X-Naphthalenediols



X	mp, °C	Yield %	Analyses: Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found	Nitrogen Calcd	Nitrogen Found
8-	243–247(d)	23	61.31	60.75	5.15	5.00	10.21	10.00
6-	181–183	41	61.31	61.42	5.15	4.90	10.21	10.11
3-	190–192	47	61.31	60.80	5.15	5.22	10.21	10.23
7-	183–184(d)	...	61.31	60.18	5.15	5.23	10.21	10.04

Sergievskaya (1951) have reported **10** as the product (49% yield) of the reduction of **2** with Raney Nickel alloy, and the conversion of **2** to the unsaturated lactone **11** has been reported (El-Assal and Shehab, 1961).

The cyclization of **3** to 7-methoxy-1-tetralone **4** was effected by the method of Rao and Dev (1957). The synthesis of **4** has also been reported by Autrey and Scullard (1968).

Demethylation of **4** to the corresponding phenol **5** was accomplished using an excess of 48% hydrobromic acid in acetic acid (Long and Burger, 1941). The yields in this reaction were somewhat variable (62 to 78%). The parameters which affect yield are not obvious, although there seems to be a relationship (inverse, after a point) with the volume of distillate removed during the reaction. A dark, gummy material frequently separated when the volume of the distillate exceeded 35 to 40% of the total solvent (48% hydrobromic acid plus acetic acid).

The progress of the demethylation was monitored by tlc (60:80 ether:hexane), the R_f values of **4** and **5** being 0.62 and 0.26, respectively, in this system. This reasonably facile reaction was probably complete in about 2 hr. However, all reaction times exceeded this because of a confusing shadow which developed and persisted just ahead of, and overlapping, the spot due to **4**. Although cochromatography showed that the shadow was almost certainly not due to unreacted starting material, reaction times were always extended until no change in the shadow occurred over a 30-min period.

The synthesis of **6** by the benzylation of **5** with benzyl chloride was studied under a variety of conditions. Use of sodium in ethanol or sodium methoxide in THF gave **6** in 61% yield, in each case. When benzyl chloride was used as the solvent for the reaction, with anhydrous potassium carbonate as the acid acceptor, **6** was formed in 42% yield, together with a byproduct (R_f = 0.36, 80:60 hexane:ether), tentatively identified by nmr as dibenzyl ether. When this reaction was carried out in acetone solvent, **6** was obtained in 80 to 90% yield. The reaction was followed by tlc in all cases, and generally required about 24 hr for completion. The byproduct formed in the reaction involving benzyl chloride solvent was not detected in most of the acetone-solvent reactions.

Conversion of **6** to 7-benzyloxy-2-bromo-1-tetralone **7** and the subsequent dehydrobromination of **7** to the naphthol **8** was accomplished by the general methods of Kasturi and Arunachalam (1968). Reaction of **8** with methyl isocyanate produced the carbamate **9**, which was reductively debenzylated in high yield to produce 7-hydroxy-1-naphthyl methylcarbamate **1** in high yield. The overall yield of **1** is 23.6%.

The debenzylation step was carried out under conditions which have been found to give reduction of the unsubstituted ring in the attempted debenzylation of 1-naphthyl benzyloxymethylcarbamate (Balba and Casida, 1968). Augustine (1965) has reported that under slightly acidic conditions (W2 Raney Nickel, ethanol, acetic acid), reduction of the unsubstituted ring occurred with 2-methoxynaphthalene at 3400 psig and 130° C. In addition, Augustine describes many other examples which indicate that in the conversion of **9** to **1** the mild conditions required for the hydrogenolysis of the benzyl group should not result in reduction of either ring, since both are substituted with an oxygen function. This expectation has been realized.

The structure of each compound described in this report has been established by infrared, nmr, and, in some cases (**5**, **6**, **7**, **8**, and **9**), by mass spectral studies, together with elemental analysis. The nmr spectra of certain of the compounds showed a pattern which deserves comment. In **4** and **5**, H-8 appeared as the anticipated doublet ($J \sim 3$ Hz) at the most downfield signal. However, the benzyl ethers **6** and **7** showed H-8 as either a doublet ($J \sim 3$ Hz) with a singlet superimposed or a partially collapsed doublet of doublets. To further investigate this observation, the compound **12** was synthesized by a route analogous to that employed for **6**. The nmr of **12**

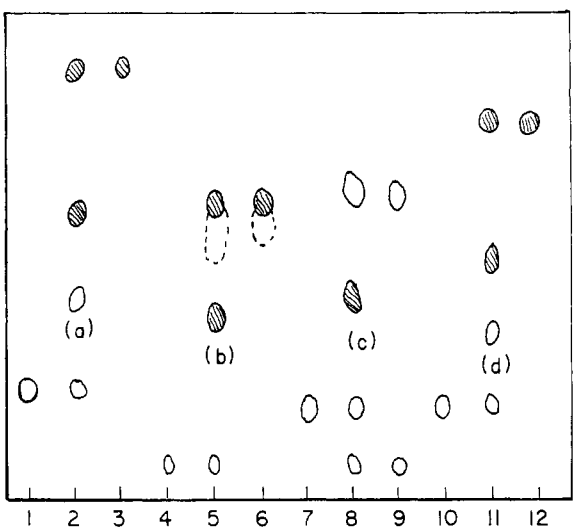


Figure 1. Tlc of the products from the reaction of 1,3-, 1,6-, 1,7-, and 1,8-dihydroxynaphthalene with one equivalent of methyl isocyanate. * The shaded spots indicate a positive reaction to Gibbs' reagent. (1) 1,6-bis(methylcarbamate); (2) 1,6-residue; (3) 1,6-diol; (4) 1,8-bis(methylcarbamate); (5) 1,8-residue; (6) 1,8-diol; (7) 1,3-bis(methylcarbamate); (8) 1,3-residue; (9) 1,3-diol; (10) 1,7-bis(methylcarbamate); (11) 1,7-residue; (12) 1,7-diol. (a) compound 13; (b) 8-hydroxy-1-naphthyl methylcarbamate; (c) 1-hydroxy-3-naphthyl methylcarbamate; (d) compound 1

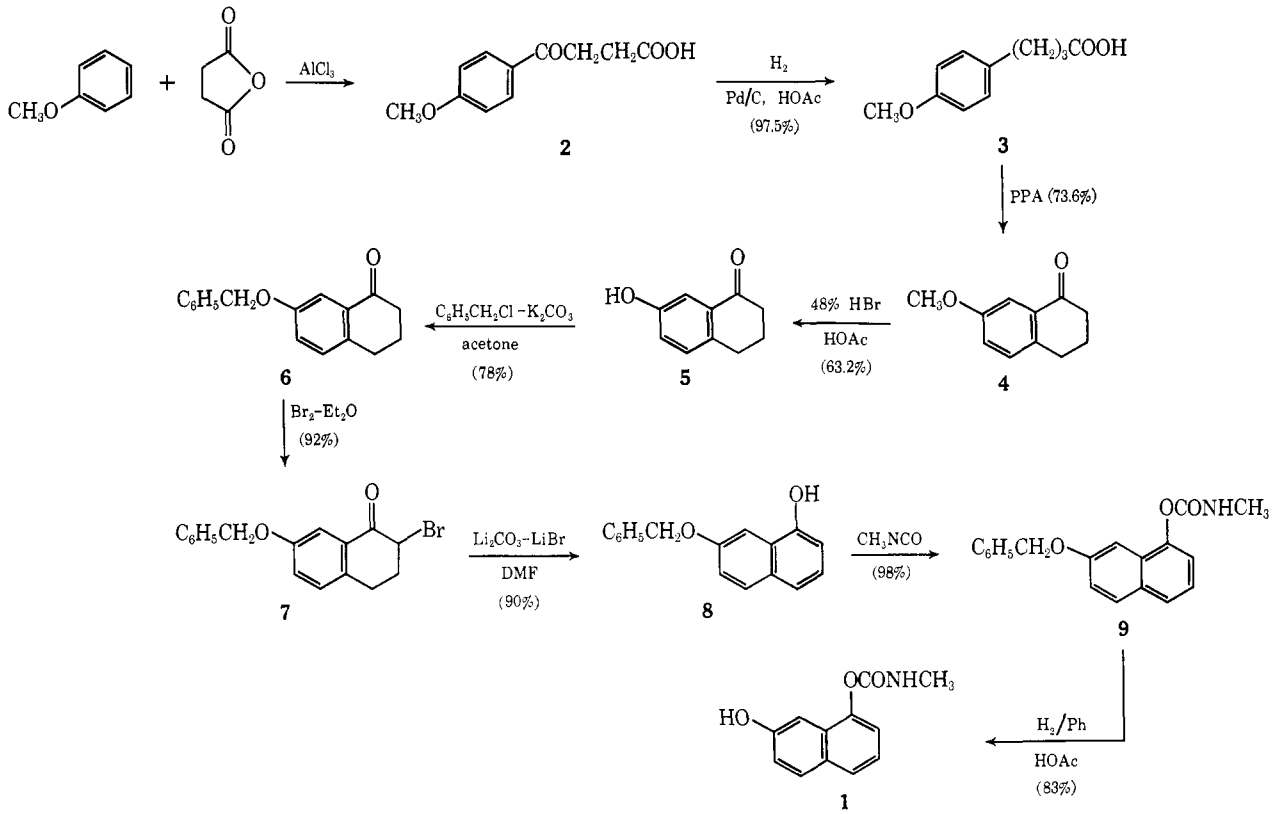


Figure 2. Synthesis of 7-hydroxy-1-naphthyl methylcarbamate

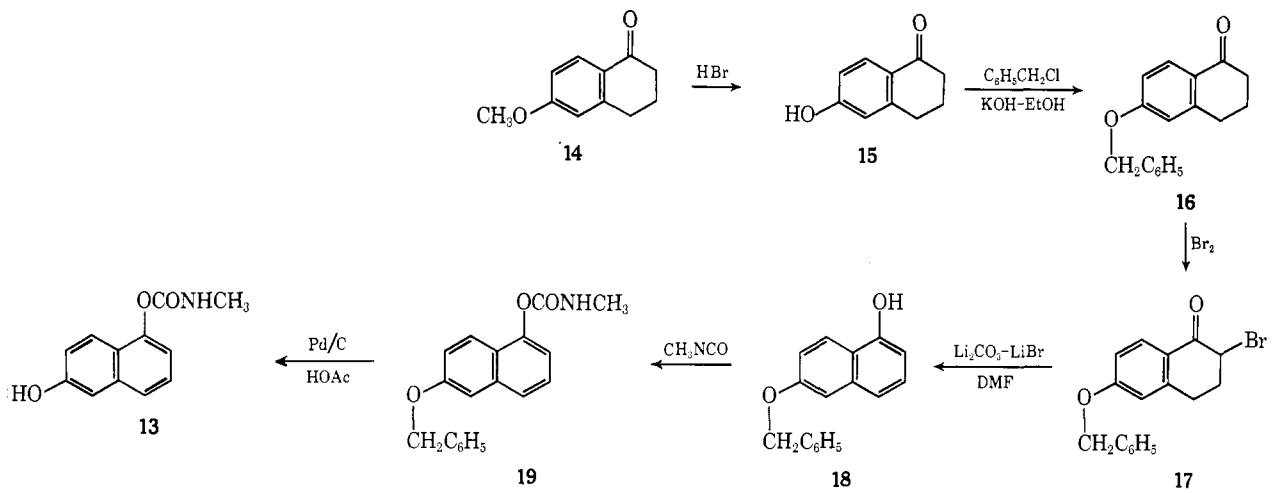
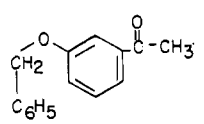


Figure 3. The synthesis of 6-hydroxy-1-naphthyl methylcarbamate

showed the isolated aromatic hydrogen as a pair of doublets



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($J \sim 3$ Hz), as might be anticipated. It is possible that the pattern observed for H-8 in **6** and **7** is related to the presence of the benzyl group.

The synthesis of 6-hydroxy-1-naphthyl methylcarbamate **13** from 6-methoxy-1-tetralone **14** was accomplished by a route analogous to that employed for **1** (Figure 3).

On comparison by tlc with the product mixture from the reaction of 1,6- and 1,7-dihydroxynaphthalenes with methyl isocyanate, compounds **13** and **1**, respectively, cochromatographed with the Gibbs negative isomer.

MASS SPECTRAL RESULTS

The mass spectra of the tetralones **6** and **7** and the naphthol derivatives **8** and **9** have been obtained. The salient features are summarized in Tables II and III, and for the purposes of visualization, various fragments are formalized in Figures 4 and 5. The molecular ion of **8** is apparently a key fragment in the breakdown of compounds **7** and **9**.

Many of the fragmentation pathways proposed for **7**, **8**, and **9** are supported by metastable species. Although the total portion of the ion current carried by many of these

Table II. Relative Intensities (%) of Various Fragments (*m/e*) Found in 6, 7, 8, and 9

Compound[a] No.	m/e/%[b] 332	330	307	252	251	250	224	160	159	133	132	131	115	105	103	102	92	91	77	65
9			2.2			46		1.6	3.3		1.1	18	2.7	0.38	5.8	5.9	25	100	53	20
8						13		0.55	1.1		0.39	3.3	0.8	0.39	1.1	1	83	100	3	7
7	6.8	6.9			5.9	4.5		1.2	3		1	3.4	3.5	3.7	7.1	2.3	54	100	15.4	43.1
6				23.4			0.63			0.74			1.4	2.5	1.1	0.5	21	100	5.1	19
				1.5			0.4			0.4				1.15	0.6	0.2	0.7	100	2.5	6.9

[a] Temperatures: **9**, 180° C; **8**, 265° C; **7**, 275° C; **6**, 240° C (upper), 180° C (lower). [b] In addition **6** shows the following fragments: *m/e* = 234, 0.22%, 0.16% rel. intensity; *m/e* = 223, 1.7% rel. intensity; *m/e* = 161, 2.3% rel. intensity; *m/e* = 162, 1.9% rel. intensity; *m/e* = 134, 1.6% rel. intensity.

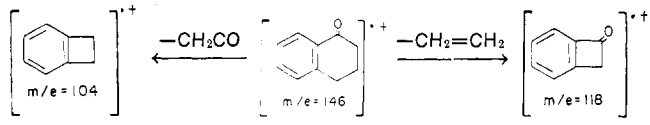
Table III. Major Metastable Species Encountered in The Mass Spectra of Various Compounds

Compounds Found In	Transition	Metastable Species (*m/e*) Calcd	Found 9	Found 8	Found 7	Found 6
9	*m/e* 307 → *m/e* 250	203.6	203.5	...	...	...
9, 8	*m/e* 250 → *m/e* 172	118.3	118.4	118.4	...	...
9, 8	*m/e* 159 → *m/e* 131	107.9	108	108	...	...
9, 8	*m/e* 132 → *m/e* 103	80.37	80.5	80.5	...	...
9, 8	*m/e* 131 → *m/e* 103	80.99	80.9	80.9	...	...
9, 8, 7	*m/e* 103 → *m/e* 77	57.6	57.6	57.6	57.6	...
9, 8, 7, 6	*m/e* 91 → *m/e* 65	46.4	46.4	46.4	46.4	46.4
9, 8, 7	*m/e* 250 → *m/e* 92	33.9	33.8	33.8	33.8	...
9, 8, 7	*m/e* 250 → *m/e* 91	33.1	33.0	33.0	33.0	...
6	*m/e* 252 → *m/e* 234	217.3	...	...	...	217
6	*m/e* 252 → *m/e* 224	199.1	...	...	...	199
6	*m/e* 252 → *m/e* 91	32.86	...	...	...	32.8
6	*m/e* 252 → *m/e* 92	33.58	...	...	...	33.6
6	*m/e* 105 → *m/e* 77	56.6	...	...	...	56 6
6	*m/e* 234 → *m/e* 144	88.6	...	...	...	88.6
7	*m/e* 330 → *m/e* 251	190.8	...	...	190.8	...
7	*m/e* 332 → *m/e* 251	189.8	...	...	189.8	...
6	*m/e* 252 → *m/e* 162	104.6	...	...	...	104.6
6	*m/e* 162 → *m/e* 134	110.5	...	...	...	110.6

fragments is small, they are nonetheless noted in Table II and Figure 4 because of the metastable peaks associated with them. Several features of the spectra of these compounds are noteworthy. None of them show a significant P-91 (loss of $C_6H_5CH_2$) peak, although in each case *m/e* 91 is the 100% peak. In the case of **7**, loss of Br (P-79, P-81) apparently occurs with facility, while with **9** the loss of CH_3NCO (P-57) is observed. These fragmentations lead to the molecular ion of **8**, and both are supported by metastable peaks. The decomposition of **8** generally involves loss of $C_6H_5CH_2$ (*m/e* 91) or the elements of $C_6H_5CH_3$ in the spectra of each of these materials. The *m/e* 172 fragment is minute in quantity and is noted only because the metastable peak at *m/e* 118.3 emphasizes its occurrence. The tropylium (*m/e* 91) to cyclopentadienium (*m/e* 65) step, a commonly encountered transformation (Budzikiewicz *et al.*, 1964), is supported by a metastable peak. The remaining steps shown in Figure 4 are analogous to those encountered in the fragmentation of 7-hydroxy-1-naphthyl methylcarbamate, **1** (Durden and Bartley, 1971).

The fragmentation of **6** apparently follows a somewhat different pattern from that of **7**, **8**, and **9**, and is visualized in Figure 5. The loss of $C_6H_5CH_2$ (P-91) and $C_6H_5CH_3$ (P-92) from the molecular ion is consistent with the structure of **6**, and both are supported by metastable peaks. Although the *m/e* 234 peak (P-18), visualized as 2-benzyloxynaphthalene, is quite small, as is the *m/e* 144 peak, both are indicated because metastable peaks at *m/e* 217.3 and 88.6 seem to support such transformations.

The mass spectrum of 1-tetralone (Bowie, 1966) shows the formation of a P-28 and P-42 fragment, formulated as shown below, with the P-28 ion being more important and, indeed, a predominant breakdown pathway. With **6**, only the P-28



peak (*m/e* 224) was detected and it was quite small. This peak could be analogous to the P-28 fragment described for 1-tetralone, but the fact that it was accompanied by a relatively more intense (though still small) P-29 (*m/e* 223) fragment (an analogous peak was not described in the work with 1-tetralone) led to the mass measurement of both of these fragments. The *m/e* 224 peak was a doublet, 95% $C_{16}C_{16}O$ (found: 224.120395; calcd: 224.120109) and 5% $C_{15}H_{12}O_2$ (found: 224.083605; calcd: 224.183724). The *m/e* 223 peak was also a doublet, 60% $C_{16}H_{15}O$ (found: 223.111966; calcd: 223.112204) and 40% $C_{15}H_{11}O_2$ (found: 223.075176; calcd: 223.075899). Thus, it would appear that the loss of C=O from **6** to give a fragment formulated as an indane derivative is more important than is the loss of either the elements of ethylene or ketene as described for 1-tetralone (Bowie, 1966), but in neither case are these decompositions for **6** as important as they are for 1-tetralone.

The peak of *m/e* 133 may be logically formulated as shown, although no mass measurement was performed. Such an assignment received support, since the *m/e* 105 peak was measured and found to be a doublet, 60% C_7H_5O (found: 105.034088; calcd: 105.034037) and 40% C_8H_9 (found: 105.070486; calcd: 105.070422). These are formulated as

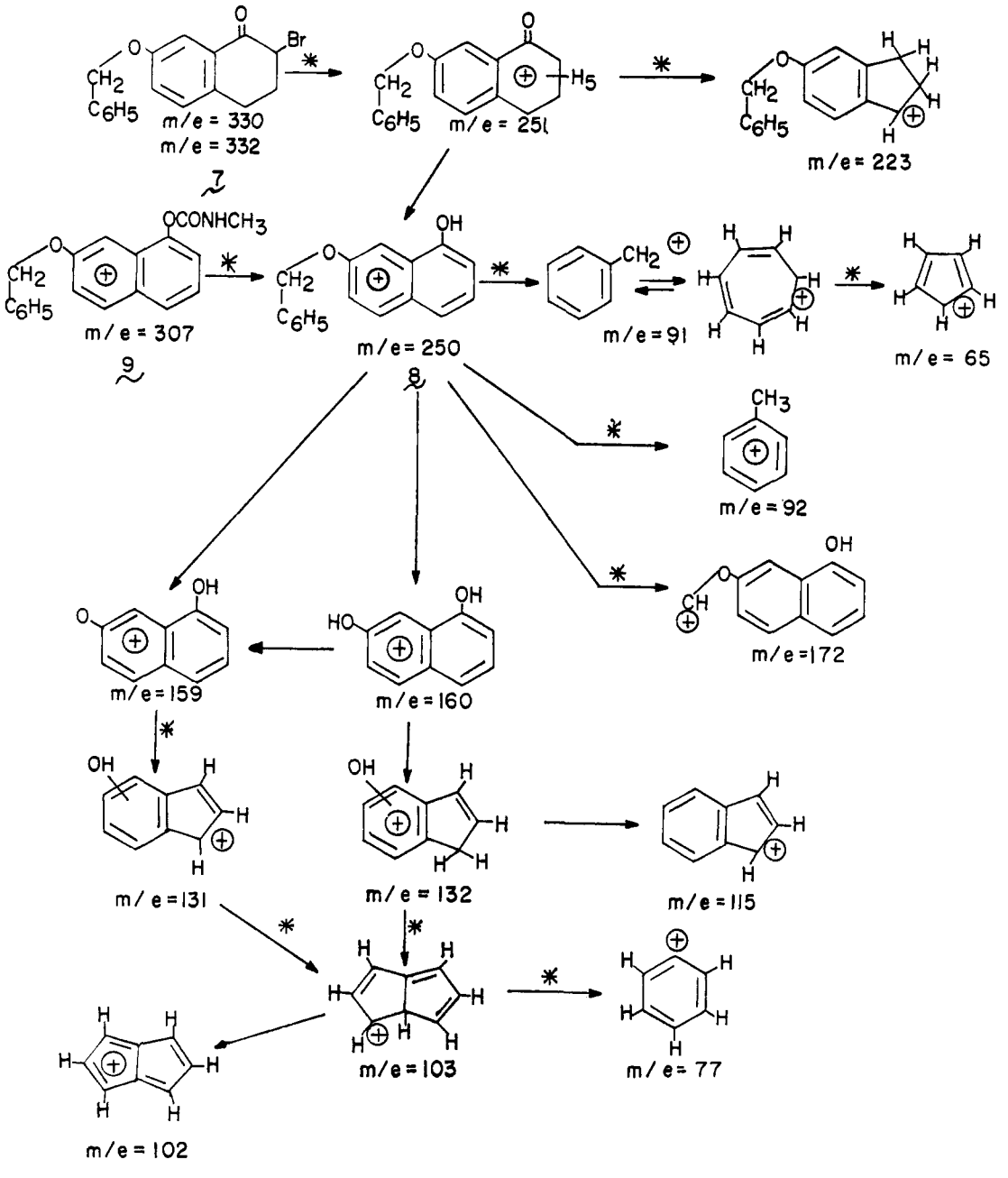


Figure 4. The fragmentation patterns of 7, 8, and 9. * Supported by a metastable species (Table III)

shown in Figure 3, and their decomposition to the *m/e* 77 fragment is supported by a metastable peak.

The mass spectrum of **6** also shows a peak at *m/e* 162, which is assigned the 7-hydroxy-1-tetralone structure, *i.e.*, the molecular ion of **5**. Such an assignment is supported by the presence of a weak metastable peak at 104.7 which may arise from the *m/e* 252 → *m/e* 162 transformation, as well as a metastable peak in the spectrum of **5**, assigned to the P-28 fragmentation of **5**. The *m/e* 134 fragment is present in the spectrum of **6**.

In each case the mass spectra support the assigned structures.

The mass spectra of **1** and **13** have been reported in detail (Durden and Bartley, 1971).

EXPERIMENTAL

The melting points are uncorrected. The mass spectra were obtained on an A.E.I. MS902b high-resolution mass spectrometer. The nmr spectra were determined on a Varian 60-cycle or 100-cycle instrument, and the infrared spectra were recorded by means of a Baird Atomic 4-55 spectrophotometer. The chemical shift assignments of the saturated ring protons in **4**, **6**, and **7** were verified by spin-spin decoupling experiments. Although some of the required 3-(4-methoxybenzoyl)-propionic acid was synthesized as described, the bulk of the material used in this effort was purchased from Aldrich Chemical Co. The 1,3-, 1,6-, 1,7-, and 1,8-dihydroxynaphthalenes were available commercially, as was 6-methoxy-1-tetralone. Thin-layer chromatograms were determined using Brinkmann silica-gel plates with fluorescent indicator.

General Procedure for the Preparation of the Crude X-Hydroxy-1-naphthyl Methylcarbamates, Equation 1. A solution of equivalent amounts of the naphthalenediol and methyl isocyanate (in the 0.01 to 0.03 mol range) in acetone was treated with one drop of triethylamine and left at room temperature overnight. Filtration of the mixture removed the solid bis(carbamate) which had formed and the filtrate was

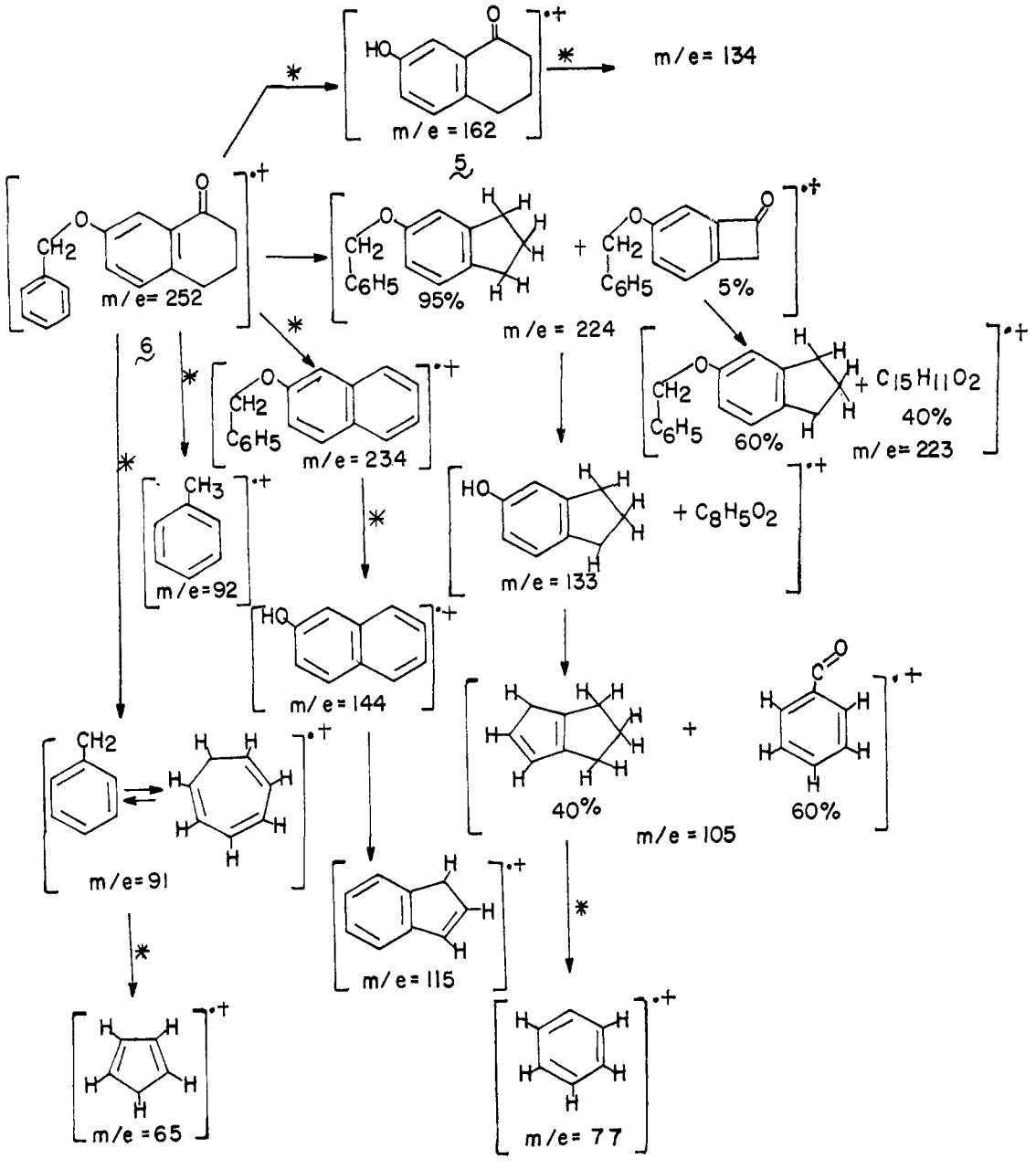


Figure 5. The fragmentation pattern of 6. * Supported by a metastable species (Table III)

concentrated *in vacuo* to give a residue which was shown by the examination (4:1 ether:hexane) to contain a spot, in each case, assignable to the hydroxycarbaryl desired from the particular diol (Figure 1). Gibbs reagent was employed to distinguish the various isomers.

The Synthesis of the Bis(methylcarbamate)s in Table I. To a solution of 0.5 to 1 g (0.003 to 0.006 mole) of the appropriate naphthalenediol in 15 ml of acetone in a small Erlenmeyer flask was added 1 ml (excess) of methyl isocyanate and 1 drop of triethylamine. The flask was stoppered and left at room temperature overnight. The solid which separated during this time was collected, air dried, and recrystallized from the appropiate solvent (1,8- from acetonitrile, the others from ethyl acetate) to give the products described in Table I.

4-(4-Methoxyphenyl)butyric Acid, 3. To a solution-suspension of 100 g (0.48 mole) of 3-(4-methoxybenzoyl)propionic acid (Rao and Dev, 1957; Aldrich Chem. Co.) in 650 ml of glacial acetic acid was added 8 g of 10% Pd/C and the mixture was hydrogenated at 56.5 psig at ambient temperatures. The required hydrogen was absorbed in 3.5 hr. The pressure during the hydrogenation was not allowed to fall below 27 psig. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo* to produce a liquid residue which was treated with 800 ml of water, followed quickly by vigorous shaking to suspend the organic material in the water. Slight scratching or seeding of this suspension produced fine white crystals which were collected after chilling to give, when dry, 90.6 g (97.5%) of product, mp 57–58° C (Krishna and Dev, 1957; report 61–61° C), λ_{max} (1% KBr) (μ): 3–4 (broad absorption from acid OH); 3.42, 3.51 (CH/CH_3); 5.93 (C=O); 6.22, 6.34, 6.64 (arom. C=C); 7.7, 8.1 (aryl—O and acid C—O); 9.75 (OCH_3); 10.8 (acid OH); 12.07, 12.32 (2 adjacent arom. H); nmr ($CDCl_3$) (ppm): 2.6, 2 H triplet, 8 Hz (—CH_2—CH_2—COOH), 1.94, 2 H quartet further split, 8 Hz (—$CH_2CH_2CH_2$); 2.34 2 H triplet further split, 8 Hz (aryl CH_2CH_2); 6.75 to 7.25, 4 H AB quartet, δ_A 6.80, δ_B 7.08, 9 Hz (arom. H); 3.75, 3 H singlet (OCH_3).

Occasionally it was necessary to distill the product, in which case using 4 in. unpacked column, a bp 149° C/0.5 mm was recorded.

7-Methoxy-1-tetralone, 4. The procedure generally described by Rao and Dev (1957) was employed to give from 272 g (1.4 moles) of **3**, 180.3 g (73.6%) of **4**, bp 126–132° C/1–1.5 mm. Crystallization of a small amount from hexane gave a mp 60–61° C [Rao and Dev (1957) report bp 130–132° C/0.5 mm, mp 66–67° C], tlc systems: R_f (**4**) = 0.67 (80:60 hexane:ethyl ether), λ_{max} (1% KBr) (μ): 3.25 shoulder (arom. CH); 3.4 (CH_2); 3.51 (OCH_3); 5.93 (C=O); 6.22, 6.38, 6.7 (arom. C=C); 7.8, 8.22 (aryl—O and conj. C=O); 9.71 (OCH_3); 11.42 (isolated arom. H); 12.24 (2 adjacent arom. H); nmr ($CDCl_3$) (ppm): 1.82 to 2.93, 6 H complex multiplet ($CH_2CH_2CH_2$); 3.75, 3 H singlet (OCH_3); 6.92 to 7.48, 2 H AB quartet $\delta_{H\text{-}6}$ 6.98, $\delta_{H\text{-}5}$ 7.12, $J_{5,6}$ = 8 Hz, with the 6 H peak further split $J_{6,8}$ = 2.5 Hz (arom. H-5 and H-6); 7.48, 1 H doublet $J_{8,6}$ = 2.5 Hz (arom. H-8).

7-Hydroxy-1-tetralone, 5. To a solution of 94.5 g (0.535 mole) of **4** in 500 ml of glacial acetic acid was added 500 ml of 48% hydrobromic acid. The stirred reaction mixture was heated to boiling as rapidly as possible and a distillate was slowly removed at a head temperature of 113 to 115° C. The reaction was followed by tlc (80:30 hexane:ethyl ether), and after 7 hr (100 ml of distillate) starting material (**4**) (R_f = 0.63) was just detectable, while **5** (R_f = 0.26) was clearly detectable and there was a small shadow at R_f = 0.5. In 1:1 benzene-ethyl ether R_f (**4**) = 0.82 and R_f (**5**) = 0.73. After 3 hr (250 ml of distillate) the reaction was discontinued, although the shadow at R_f = 0.5 was still present.

The reaction mixture was poured with vigorous stirring into 750 g of ice and 500 ml of water. The resulting solid was collected, resuspended in water, and after thorough agitation was recollected and air dried. After 1 hr the solid was dissolved in ether and the ether solution dried over Na_2SO_4 for 30 min. After filtration and concentration to ~800 ml, solid began to separate. Chilling produced 37.6 g of **5**, mp 163–165° C. The filtrate, after evaporation to 300 ml and chilling, gave an additional 15.6 g of **5**, mp 163.5–165° C, and this filtrate after similar treatment gave 2 g of **5**, mp 165–166° C; total yield 55.2 g (63.2%), λ_{max} (1% KBr) (μ): 3–4 (broad absorption due to phenolic OH); 3.4 (CH_2); 6.05 (C=O); 6.2, 6.37, 6.7 (arom. C=C); 7.37, 7.74, 8.13 (aryl—O, conj. C=O); 11.13, 11.2 (isolated arom. H); 12.22 (2 adjacent arom. H); nmr (d-acetone) (ppm): 2.05, 2 H complex multiplet ($CH_2CH_2CH_2$) plus some acetone H; 2.55, 2 H triplet 7 Hz, (aryl CH_2CH_2); 2.88 2 H triplet, 7 Hz (CH_2CH_2C=O); 6.3 to 7.23, 2 H AB quartet, $\delta_{H\text{-}5}$ = 7.17, $\delta_{H\text{-}6}$ = 7.0, $J_{5,6}$ = 8 Hz, with the H-6 peak further split, $J_{6,8}$ = 3 Hz (arom. H-5 and H-6); 7.4, 1 H doublet, $J_{8,6}$ = 3 Hz (arom. H-8), 8.35 1 H singlet (OH).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22; mole ion mass, 162. Found: C, 73.57; H, 6.25; mole ion mass, 162.

7-Benzyloxy-1-tetralone, 6. To a solution of 47 g (0.295 mol) of 7-hydroxy-1-tetralone and 76 g (0.6 mole) of benzyl chloride in 550 ml of anhydrous reagent grade acetone was added 83 g (0.6 mole) of anhydrous potassium carbonate, and the resulting mixture was heated at reflux with stirring and the reaction was followed by tlc (80:60 hexane-ether, $R_{f(5)}$ 0.26, $R_{f(6)}$ 0.61). After 1 hr a trace of product was evident and the mixture was cooled and stirred at room temperature overnight. After 16 hr at room temperature a tlc indicated that the reaction had proceeded to a considerable extent. After 6 hr at reflux, when no **5** could be detected, the mixture was cooled, filtered, and the filter cake was washed with acetone. The combined filtrates were concentrated *in vacuo* to a residue which was taken up in 450 ml of hot hexane and allowed to crystallize slowly after seeding. After chilling the solid was collected and air dried, 66.1 g of brown-yellow solid, mp 84.5–86° C. From the filtrate was obtained an additional 2 g. These combined solids were crystallized from 1 l. of isopropyl ether to give 58.1 g (78%) of white-yellow needles, mp 84.5–85° C, λ_{max} (1% KBr) (μ): 3.3 (arom. CH); 3.41, 3.48 (CH_2/OCH_3); 5.97 (C=O); 6.24, 6.7 (arom. C=C); 7.55, 7.84, 8.15 (aryl—O, conj. C=O); 9.92 (OCH_2—); 11.5 (isolated arom. H); 11.97, 12.05 (2 adjacent arom. H); 13.5 (monosubstit. arom.); nmr ($CDCl_3$) (ppm): 1.82 to 2.22, 2 H multiplet (—$CH_2CH_2CH_2$); 2.52, 2 H triplet, 6 Hz (perhaps further split) (aryl CH_2CH_2); 2.76, 2 H triplet, 6 Hz (CH_2CH_2CO); 4.98, 2 H singlet (aryl OCH_2–); 7.0 to 7.18, 2 H AB system, δ_A = 7.03, δ_B = 7.13, J_{AB} = 7 Hz (arom. H-5 and H-6); 7.20 to 7.49 (5 H multiplet) (C_6H_5-CH_2); 7.61, 1 H doublet, J ~ 3 Hz with a small singlet superimposed or a partially collapsed doublet of doublets (arom. H-8).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; mole ion, 252.1150218. Found: C, 80.96; H, 6.12; mole ion, 252.1145897.

7-Benzyloxy-2-bromo-1-tetralone, 7. To a suspension of 50.4 g (0.2 mole) of **6** in 600 ml of anhydrous ethyl ether containing a small amount of anhydrous hydrogen chloride in a flask wrapped in aluminum foil was added dropwise with stirring 32 g (0.2 mole) of bromine in 60 ml of chloroform. When only a few drops of the bromine solution had been added complete solution occurred, and when about three-quarters had been added a solid began to reappear. When the addition was complete the funnel was rinsed with 10 ml of chloroform. After 1 hr 200 ml of water was added to the reaction mixture and, after thorough stirring, the ether was removed *in vacuo*. To the remaining aqueous suspension was added 600 ml of methylene chloride, and the resulting methylene chloride solution was separated from the water layer. The aqueous layer was washed with 50 ml of methylene chloride and the combined organic layers were washed with $KHCO_3$ solution until neutral, and finally dried over sodium sulfate. Filtration followed by concentration *in vacuo* gave a solid residue which was dissolved in 1200 ml of boiling heptane, and the solution was decanted away from some pink gum. Concentration to 900 ml produced some reddish gummy material upon slight cooling; therefore 200 ml of heptane was added and the mixture was reheated. Decantation from the gum gave a clear solution which was allowed to *cool slowly* on the steam bath to produce 61 g (92%) of product, mp 105–106° C, λ_{max} (1% KBr) (μ): 3.25 (arom. CH); 3.36, 3.41, 3.48 (CH_2, OCH_2); 5.91 (C=O); 6.19, 6.34, 6.65, 6.85 (arom. C=C); 7.68, 7.73, 8.02, 8.01 (aryl—O, conj. C=O); 9.6, 9.76 (aryl—O–CH_2–); 11.21 (isolated arom. H); 13.35, 13.58 (monosubstit. arom.); nmr ($CDCl_3$) (ppm): 2.38, 2 H multiplet (CH_2CH_2CHBr); 2.76, 1 H pair of triplets, 17 Hz, 4 Hz (—CH—CH_2CHBr, H *trans* to Br); 3.18, 1 H pair of triplets (—CHCH$_2$CHBr, H *cis* to Br); 4.67, 1 H triplet, 4 Hz (CHBr); 5.01, 2 H singlet ($C_6H_5CH_2O$); 7.14, doublet, upfield member of AB system (2 Hz) and at 7.36 a broadened singlet which covers the downfield member of the AB pair, 7 H (arom. H-5 and H-6 and $C_6H_5CH_2$—), 7.63, 1 H doublet, J ~ 2 Hz, with singlet superimposed or partially collapsed doublet of doublets (arom. H-8).

Anal. Calcd for $C_{17}H_{15}BrO_2$: C, 61.64; H, 4.56; mole ion, 330.0255872. Found: C, 61.43; H, 4.46; mole ion, 330.025774.

7-Benzyloxy-1-naphthol, 8. To 27 g (0.081 mole) of **7** in 250 ml of DMF was added 14 g (0.16 mole) of lithium bromide and 16 g (0.24 moles) of lithium carbonate, and the mixture was heated to reflux with stirring under nitrogen over a period of 1 hr. The reaction was followed by tlc (1:1 hexane-ethyl ether, $R_{f(7)}$ = 0.65, $R_{f(8)}$ = 0.52) and in the time it takes to reach reflux the starting material had disappeared. After 2 hr at reflux the reaction mixture was poured with stirring into a mixture of 60 ml of concentrated HCl, 300 ml of water, and enough ice to make a volume of 1200 ml. The semisolid which separated was extracted into 400 ml of ethyl ether, and the residual aqueous layer was further extracted with two 200-ml portions of ether. The combined extracts were washed with water and then dried over Na_2SO_4. After filtration and concentration to 200 ml by boiling, 300 ml of heptane was added to the hot ether and concentration was continued until the ether was removed. The hot solution was seeded and allowed to cool *slowly* on a hot steam bath. The mixture was left at ambient temperature overnight and then chilled to give 18.2 g (90%) of product, mp 125.5–127° C. The filtrate was concentrated and tlc examination of the residue showed the presence of some **8**, together with some 7-benzyloxy-1-tetralone, **6**. The following spectral data relative to **8** were collected: λ_{max} (1% KBr) (μ): 2.95 (OH); 3.29 (arom. CH); 3.4, 3.48 (CH_2, OCH_2); 6.15, 6.25, 6.32 (arom. C=C); 7.26 (naphthalene OH); 8.22, 8.35, 10.0 (naphthalene—O—CH_2); 11.78 (isolated arom. H); 12.14, 12.2 (2 adjacent arom. H); 12.92 (3 adjacent arom. H); 13.6, 13.8, 14.44 (monosubstit. arom.); nmr (d-acetone) (ppm): 5.2, 2 H singlet (C_6H_5-CH_2O); 6.88 to 7.88, 11 H multiplet (arom. H).

Anal. Calcd mole ion mass $C_{17}H_{14}O_2$: 250.0994726. Found: 250.099024, 250.099753.

7-Benzyloxy-1-naphthyl Methylcarbamate, 9. To a solution of 70 g (0.25 mole) of 7-benzyloxy-1-naphthol and 17 g (0.3 mole) of methyl isocyanate in 200 ml of acetone in a 500 ml round-bottomed flask fitted with a dry ice condenser and a stirrer were added 2 drops of triethylamine. A moderately exothermic reaction took place. The mixture was stirred at ambient temperature for 16 hr and then was diluted with 200 ml of ice water with stirring. After 2 hr the solid was collected and air dried. A tlc (3:2 ethyl ether-chloroform, $R_{f(9)}$ = 0.56, $R_{f(8)}$ = 0.27, **9** showed some tailing in this system) indicated that the product was homogeneous. The product so obtained, 80 g (98%) mp 160–161° C was sufficiently pure for direct use in the subsequent reaction, λ_{max} (1% KBr) (μ); 3.0 (NH); 3.28 (arom. CH); 3.40, 3.58 (CH_2/CH_3); 5.85 (C=O); 6.12, 6.24 (arom. C=C); 6.55 (NH); 7.99, 8.08, 8.23, 8.34 (C—O); 11.47 (isolated arom. H); 12.03 (2 adjacent arom. H); 13.17 (3 adjacent arom. H); 13.82, 14.40 (monosubstit. arom.); nmr ($CDCl_3$) (ppm): 2.89, 3 H doublet, 5 Hz (NHCH_3); 5.17, 2 H singlet ($C_6H_5CH_2O$) with a broadened base (NH); 7.12 to 7.9, 11 H multiplet (aryl H).

Anal. Calcd molecular ion mass $C_{19}H_{17}NO_3$: 307.1208343. Found: 307.121203.

7-Hydroxy-1-naphthyl Methylcarbamate, 1. A solution of 10 g (0.033 moles) of **9** in 200 ml of glacial acetic acid containing 0.1 g of 10% Pd/C was shaken on a Parr hydrogenator at 50 psig for about 30 min when theory was absorbed. A tlc (3:2 ethyl ether-chloroform, $R_{f(9)}$ = 0.85, $R_{f(1)}$ = 0.55) indicated that the reaction was complete. The mixture was heated almost to boiling, filtered, and the filtrate concentrated *in vacuo* to about one-half volume. Cooling at room temperature for 3 hr produced crystals which were collected and air dried, 5 g. Further concentration of the filtrate with cooling at room temperature produced additional **1**, total yield 5.9 g (83%), mp 205–207° C, λ_{max} (1% KBr) (μ): 3.0 with some broadness in the 3μ region (OH, NH); 3.25 (arom. CH); 3.38 (CH_3); 5.9 (C=O); 6.09, 6.21, 6.35 (arom. C=C); 6.5 (NH); 7.9, 8.1, 8.3, 8.4 (C—O); 11.3 (isolated arom. H); 12.09 (2 adjacent arom. H); 13.35, 13.45 (3 adjacent arom. H); nmr (d-acetone) (ppm): 2.87, 3 H doublet, 4.8 Hz (NHCH_3); 7.77, 1 H doublet, $J_{5,6}$ 9 Hz (arom. 5-H); 7.63, 1 H doublet of doublets, $J_{3,4}$ 6.5 Hz, $J_{2,4}$ 3.5 Hz (arom. 4-H), 7.05 to 7.35, 4 H multiplet (arom. H).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45; mass molecular ion, 217.0738867. Found: C, 63.82; H, 5.16; N, 6.39; mass molecular ion, 217.074104.

4-(4-Methoxyphenyl)-4-hydroxybutyric Acid Lactone, 10. A solution of 19.2 g (0.1 mole) of 3-(4-methoxybenzoyl)-propionic acid (**2**) in 50 ml of glacial acetic acid containing 0.1 g of 10% Pd/C was hydrogenated at 40 psig (ambient temperature) until 0.1 mole of hydrogen was taken up (2 hr). The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to a solid residue. This residue was flash-distilled to give a fraction (bp 179–183° C/1 mm) which crystallized. This was recrystallized from 200 ml of boiling isopropyl ether to give 12 g (63%), mp 51–52° C (Lipovich and Sergievskaya, 1951; report mp 52–54° C); nmr (d-acetone) (ppm): 1.8 to 2.82, 4 H multiplet (CH_2CH_2C—O) also includes a small multiplet due to acetone at ~2 ppm; 3.78, 3 H singlet (OCH_3); 5.45, 1 H triplet (6 Hz) further split (1 to 2 Hz) [C_6H_5CH(—O—)—]; 6.76 to 7.5 4 H AB quartet δ_A = 6.95, δ_B = 7.33, $J_{A,B}$ = 9 Hz with further splitting (arom. H).

3-Benzyloxyacetophenone, 11. A mixture of 13.6 g (0.1 mole) of 3-hydroxyacetophenone, 25.2 g (0.2 mole) of benzyl chloride, and 27.8 g (0.2 mole) of potassium carbonate in 100 ml of acetone was heated at reflux with stirring for 24 hr when tlc [60:80 ethyl ether-hexane, $R_{f(11)}$ = 0.78, R_f (starting material) = 0.38] showed the reaction to be complete. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to a residue. The residue was dissolved in sufficient isopropyl ether to make 150 ml and this was diluted to 300 ml with hexane. This mixture was chilled to give 13.5 g (60%) of product, mp 28.5–29° C (Bolhofer, 1953; reports 29–30° C, bp 165–170° C/0.5 mm); λ_{max} (1% KBr) (μ); 3.26, 3.3 (arom. CH); 3.43, 3.49 (CH_3, CH_2, OCH_2—); 5.95 (C=O); 6.29, 6.34, 6.74 (arom. C=C); 7.9, 8.37 (aryl—O, aryl C=O); 9.77 (OCH_2—); 11.3, 11.46 (isolated arom. H); 12.73 (3 adjacent arom. H); 13.6 (monosubstit. arom.); nmr (CCl_4) (ppm): 2.38, 3 H singlet (CH_3C=O); 4.92 2 H singlet ($C_6H_5CH_2O$—); 6.86 to 7.5, 9 H multiplet (arom. H).

6-Hydroxy-1-tetralone, 15. A solution/suspension of 30 g (0.17 mole) of 6-methoxy-1-tetralone in 100 ml of 48% HBr was heated at boiling with stirring and slowly distilled for 4 hr, after which the reaction mixture was poured into 300 ml of ice water with stirring. The resulting solid was collected, thoroughly washed with water, and dried on the filter. Recrystallization from ethanol-water gave 22 g (80%) of product, mp 153–154.5° C (Papa *et al.*, 1949, report mp 150–152° C). The infrared spectrum was identical with a reference (Sadtler Spectrum No. 21263), nmr (d-acetone) (ppm) shows 6.83 and 7.92, 2 H pair of doublets (J = 8 Hz) (arom. H-7, H-8); 6.76 singlet with fine splitting (arom. H-5); 2.54, 2 H triplet with further splitting (J ~ 6 Hz) (CH_2CH_2CO); 2.1, 2 H complex multiplet (CH_2CH_2CO); 2.92, 2 H triplet (aryl CH_2CH_2); the OH peak falls under the 2.92 peak.

6-Benzyloxy-1-tetralone, 16. To a solution of 3.2 g (0.05 mole) of potassium hydroxide in 75 ml of 95% ethanol was

added 8 g (0.05 mole) of 6-hydroxy-1-tetralone and the mixture was stirred until solution was complete. To this solution was added dropwise with stirring over 10 min 6.3 g (0.05 mole) of benzyl chloride. After refluxing for 3 hr the mixture was chilled and poured into 200 ml of ice water. The resulting solid was collected, dried, and recrystallized from 100 ml of ethanol to give 7.5 g (60%) of product, mp 91–93° C (Smith, 1963; reports mp 96–99° C), λ_{max} (1% KBr) (μ); 3.28 (arom. H); 3.40, 3.47 (CH_2); 6.04 (C=O); 6.25 (arom. C=C); 8.05 (C—O—C); 11.49 (isolated arom. H); 12.12 (2 adjacent arom. H); nmr ($CDCl_3$) (ppm): 1.92–3.1, 6 H multiplet ($CH_2CH_2CH_2$); 5,12, 2 H singlet (OCH_2); 7.4, 5 H singlet (arom. H); 6.9, 8.09, 2 H, 2 pairs of doublets (arom. H-7, H-8); 6.82, 1 H singlet under 6.9 doublet (arom. 5-H).

This reaction has also been accomplished using sodium metal in ethanol with slightly improved yields.

6-Benzyloxy-2-bromo-1-tetralone, 17. To a solution of 2.52 g (0.01 mole) of 6-benzyloxy-1-tetralone in 100 ml of anhydrous ether was added 1 ml of ether saturated with hydrogen chloride. To this solution was then added dropwise with stirring over 15 min a solution of 1.6 g (0.01 mole) of bromine in 10 ml of carbon tetrachloride. During the addition of the bromine a solid separated, but upon continued stirring for about 2 hr after the addition was complete, the solid dissolved and hydrogen bromide was evolved. The solution was then washed with dilute aqueous potassium bicarbonate until neutral, dried over sodium sulfate, and, finally, concentrated *in vacuo* at 25–30° C to give 4 g (120%) of residual oil whose tlc (benzene) showed the presence of no unreacted starting material $R_{f(16)}$ = 0.15; $R_{f(17)}$ = 0.36 with a minor impurity at R_f = 0.57; nmr ($CDCl_3$) (ppm): 2.2 to 2.6, 2 H multiplet (arom. CH_2CH_2); 4.62, 1 H triplet (CHBr); 5.12, 2 H singlet ($ArCH_2O$); 7.5, 5 H singlet (C_6H_5); 6.8, 1 H broad singlet (arom. H-5); 6.9, 8.5, 2 H, pair of doublets (J = 8.5 Hz) (arom. H-7, H-8); the nmr spectrum supports the structure, although there are apparently small amounts of impurity present.

6-Benzyloxy-1-naphthol, 18. Using the procedure described for **8**, involving the above residual oil in 50 ml of DMF to which was added 2.1 g (0.025 mole) of lithium bromide and 1.8 g (0.023 mole) of lithium carbonate with 2 hr at reflux followed by 16 hr at ambient temperature there was obtained 0.4 g (16%) of **18**, mp 110–111° C (3:1 heptane-isopropyl ether), λ_{max} (1% KBr) (μ); 3.02 (OH); 3.29 (arom. CH); 3.45 (CH_2); 6.13, 6.25, 6.31, 6.59, 6.67 (C=C); 8.19 (ArOC); 11.75 (isolated arom. H); 12.06, 12.21 (2 adjacent arom. H); 12.93 (3 adjacent arom. H); nmr (d-acetone) (ppm): 5.26, 2 H singlet ($ArCH_2O$); 6.8 to 8.3, 11 H multiplet (arom. H).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.5; H, 5.6. Found: C, 79.79; H, 5.60.

6-Benzyloxy-1-naphthyl Methylcarbamate, 19. To a solution of 0.4 g (0.0016 mole) of 6-benzyloxy-1-naphthol in 10 ml of acetone was added 0.5 ml of methyl isocyanate (excess) and one drop of triethylamine, and the resulting solution was allowed to stand overnight in a stoppered flask. The solid which separated was collected and recrystallized from ethyl acetate to give 0.3 g of product, mp 156–158° C. The original filtrate was concentrated to a residue and recrystallized from isopropyl ether to give 0.1 g of product, mp 153–155° C, total yield, 80%. The two fractions were identical by tlc (2:1 benzene:ether), R_f = 0.68; λ_{max} (1% KBr) (μ); 3.01 (NH); 3.26 (=CH); 3.4, 3.47 (CH_2/CH_3); 5.83 (C=O); 6.13, 6.24, 6.64 (C=C); 6.54 (NH); 7.95, 8.09, 8.27 (Ar—O/C—O); 9.8 (Ar—O—CH_2); 11.7, 11.82 (isolated arom. H); 12.1 (2 adjacent arom. H); 12.6 (3 adjacent arom. H); nmr ($CDCl_3$) (ppm): 2.92, 2 H doublet (NCH_3); 5.2, 2 H singlet ($ArCH_2O$); 7.05 to 8.0, *ca.* 11 H multiplet (arom. H); mass spectrum shows a trace impurity at *m/e* 328 which corresponds to a 2-bromo-6-benzyloxy-1-naphthol.

Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56; mole ion, 307.120835. Found: C, 73.4; H, 5.68; N, 4.53; mole ion, 307.121203.

6-Hydroxy-1-naphthyl Methylcarbamate, 13. A solution of 5 g (0.013 mole) of 6-benzyloxy-1-naphthyl methylcarbamate in 40 ml of glacial acetic acid containing 0.2 g of 10% Pd/C was shaken on a Parr hydrogenation apparatus at 40 psig at room temperature for 1 hr when tlc (2:1 benzene:ether, $R_{f(13)}$ = 0.31, $R_{f(19)}$ = 0.56) indicated the reaction to be complete. After filtration the mixture was concentrated *in vacuo* to a residual solid which was heated in 75 ml of boiling chloroform while ethyl acetate was slowly added until solution was complete. Charcoal treatment and subsequent chilling gave 2 g (71%) of product, mp 159–160° C, nmr (d-acetone) (ppm): 2.83, 3 H doublet (J = 45 Hz) with superimposed singlet at 2.80 (NCH_3); 7.03 to 7.24, 7.41 to 7.54, 4 H multiplets (arom. H-2, H-3, H-4, H-5); 7.28, 7.85, 2 H pair of doublets (J = 8.5 Hz) (arom. H-7, H-8); λ_{max} (1% KBr) (μ); 3.00 (OH); 3.08 (NH); 3.28 (arom. H); 3.4 (CH_3); 5.85 (C=O); 6.12, 6.23, 6.45 (arom. C=C); 6.55 (NH); 7.9, 8.14, 8.28 (ArOC); 11.75 (isolated arom. H); 12.19 (2 adjacent arom. H); 12.7, 13.18 (3 adjacent arom. H).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45; mole ion, 217.17388. Found: C, 65.80; H, 4.94; N, 6.42; mole ion, 217.07432.

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