# Reaction of chloral with naphthalene, and the synthesis of α-methoxynaphthylacetic acids from naphthyl(trichloromethyl)carbinols

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From the Friedel-Crafts reaction of chloral and naphthalene, others have reported the isolation of only 2-naphthyl(trichloromethyl)carbinol. Our reexamination of this reaction has shown that a mixture of 1- and 2-naphthyl(trichloromethyl)carbinols is obtained and that 80 to 90% of the product consists of the 1-naphthyl(trichloromethyl)carbinol. The 1- and 2-naphthyl(trichloromethyl)carbinols, their acetates, and their methyl ethers differ in their nuclear magnetic resonance (n.m.r.) spectra in that the signal of the  $\alpha$ -hydrogen of the side chain of the 1-naphthyl isomer always occurs 0.8 p.p.m. downfield compared to the signal of the  $\alpha$ -hydrogen of these compounds are in the region between the 1- and 8-positions of the naphthalene ring and subject to the ring currents of both benzenoid rings.

The mixture of crude naphthyl(trichloromethyl)carbinols was converted to the mixture of  $\alpha$ -methoxynaphthylacetic acids, and these were separated. A small amount of  $\alpha, \alpha'$ -dimethoxy-1,5-naphthalenediacetic acid was also obtained, demonstrating that a certain amount of 1,5-substitution occurred in the Friedel–Crafts reaction of naphthalene and chloral.

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The study of the reaction of chloral with naphthalene is of some interest because substitution might occur in either the 1- or 2-positions. For instance, acetyl chloride in a Friedel–Crafts reaction with naphthalene gives predominantly the 1-isomer when carbon disulfide is the solvent; but with nitrobenzene as the solvent the 2-isomer is formed preferentially, presumably because the solvent forms a larger complex with the oxocarbonium ion and steric considerations strongly favor attack of this larger complex on the more open 2-position (for a review, consult ref. 1). Since the chloral molecule is certainly larger than the acetyl group, one might expect that substitution in the 2-position would be favored.

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In the aluminium chloride catalyzed reaction of naphthalene with chloral, the amount of aluminium chloride employed is a critical factor in determining the nature of the products formed. Under optimum conditions, a mixture of the 1- and 2-naphthyl(trichloromethyl)carbinols is formed. With more aluminium chloride, or under more severe reaction conditions, the reaction proceeds beyond the carbinol stage to form a mixture of trichlorodinaphthylethanes and dehydrohalogenated products; with less aluminium chloride, the reaction is incomplete. The first studies on the reaction of naphthalene with chloral were carried out with excessive amounts of aluminium chloride and none of the naphthyl-(trichloromethyl)carbinols were obtained (2). More recently, two groups have studied this

reaction and worked out the conditions for obtaining the naphthyl(trichloromethyl)carbinols in 24 to 28 % yields and they reported the isolations of only the 2-naphthyl isomer (3–5). This was contrary to the results we were obtaining at about the same time which showed the reaction product to be a mixture of the 1-naphthyl and 2-naphthyl isomers with the 2-naphthyl(trichloromethyl)carbinol the minor component.

Our work had involved the reaction of naphthalene with chloral and aluminium chloride, with nitrobenzene or carbon disulfide as solvents, and the conversion of the naphthyl(trichloromethyl)carbinols to the corresponding mixture of  $\alpha$ -methoxy-1- and 2-naphthylacetic acids. These could be separated semiquantitatively and formed the basis for our conclusion that the reaction occurred predominantly at the 1-position of naphthalene. We have now repeated our work and the work of the French workers, analyzed the carbinol mixture obtained under their and our experimental conditions by nuclear magnetic resonance (n.m.r.) spectra, and shown conclusively that under all reaction conditions, the major product is the 1-naphthyl(trichloromethyl)carbinol. Our results are summarized in Table I.

It is apparent that under all conditions, the substitution occurs between 80 and 90% in the 1-position, and that the choice of solvent does play a real but minor role within this range.

The n.m.r. spectra are of unusual interest

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Friedel-Crans reaction of chlorar with haphthalene to form 1- and 2- $C_{10}H_7$ -ChOr-CCI <sub>3</sub>							
Naphthalene (mole)	Chloral (mole)	AlCl <sub>3</sub> (mole)	Solvent	Reaction temperature	Carbinol mixture		
					Yield (%)	Ratio 1-/2- substitution	Method of analys
0.2	0.4	0.06	Nitrobenzene	0°	61	7 to 1	*
0.2	0.4	0.06	Nitrobenzene	0°	61	6 to 1	†
0.2	0.4	0.06	Carbon disulfide	0°	56	9 to 1	*
0.2	0.4	0.04‡	Cyclohexane	0°	39‡	4 to 1	†

TABLE I anhthalana

Cyclohexane \*By conversion to a mixture of  $\alpha$ -methoxy(1- and 2-naphthyl)acetic acids, and by separation of these.

<sup>†</sup>By nuclear magnetic resonance. ‡Reaction conditions followed Broquet-Borgel (5) including the use of freshly sublimed aluminium chloride.

because of certain consistent and pronounced differences in the spectra of the 1- and 2-substituted naphthalene compounds. Considering first the naphthyl(trichloromethyl)carbinols, the side chain  $\alpha$ -hydrogen for the 1-substituted naphthalene (1) is found to be shifted almost 0.8 p.p.m. downfield relative to the  $\alpha$ -hydrogen in the 2substituted naphthalene (2). The same downfield shift is observed with the acetates and also the methyl ethers of the two carbinols; in each of these cases the  $\alpha$ -hydrogen signal occurs slightly over 0.8 p.p.m. downfield in the 1-substituted naphthalene relative to the 2-substituted naphthalene. This also occurs in the isomeric  $\alpha$ methoxynaphthylacetic acids to the extent of 0.4 p.p.m. This consistent behavior can be explained by placing the hydrogen attached to the side chain  $\alpha$ -carbon of the 1-substituted naphthalenes in the region between the 1- and 8-positions of the naphthalene ring where the ring currents from both rings have a maximum effect and cause the larger downfield shift. A study of models shows that the 1-substituted naphthalenes must have this conformation since the larger groups are excluded from this position by steric considerations.



The isomeric methylnaphthalenes exhibit a similar pattern of chemical shifts (6), but the differences in the chemical shifts of the two methyl groups is less than one quarter of that observed with the carbinols and their derivatives.

With the 1- and 2-naphthyl(trichloromethyl)carbinols showing such different chemical shifts for the side chain hydrogen, mixtures of the isomeric carbinols could be unambiguously and accurately analyzed by comparing areas under these two peaks.

Our study of the naphthalene-chloral Friedel-Crafts reaction was originally undertaken in the expectation of forming the 2-naphthyl(trichloromethyl)carbinol and converting this to  $\alpha$ methoxy-2-naphthylacetic acid by reaction with methanolic potassium hydroxide (7). This methoxy acid might serve as a source of additional 2-naphthyl compounds difficult to obtain by other methods. The sodium hydrogen di-(amethoxy-2-naphthylacetate) is the least soluble of the known sodium acid salts of the  $\alpha$ -methoxy acids (8) and was being studied as a reagent for sodium. While the composition of the mixture of isomeric carbinols was not as expected, the positive achievements of this part of the work were the elucidation of the reaction conditions so that the mixture of carbinols could be obtained in 61% yield, the conversion of the mixture of carbinols to the corresponding mixture of the isomeric α-methoxynaphthylacetic acids, and the semiquantitative separation of these isomeric acids.

The optimum conditions for the reaction of naphthalene with chloral involved treating a nitrobenzene solution of 1 mole of naphthalene and 2 mole of chloral with 0.3 mole of aluminium chloride at 0 °C. The conversion of the carbinol mixture to the mixture of isomeric  $\alpha$ -methoxynaphthylacetic acids was accomplished by the usual procedure involving treatment with methanolic potassium hydroxide at 50 °C (7) (Reaction Scheme 1). Their separation was accomplished semiquantitatively by taking advantage

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of the fact that the  $\alpha$ -methoxy-2-naphthylacetic acid forms a *normal* sodium salt insoluble in 2.3 N sodium hydroxide solution; under the same conditions, the isomeric 1-naphthyl salt remains in solution. The compositions of the carbinol mixtures determined by this two-step chemical method are in agreement with the later n.m.r. analyses.

Although the  $\alpha$ -methoxy-2-naphthylacetic acid forms an insoluble sodium *acid* salt and the pure 1-naphthyl isomer does not (8), this difference could not be used in their separation. When both acids were present, they coprecipitated as a nonstoichiometric sodium acid salt mixture from which acetone would extract the 1-naphthyl isomer only incompletely. Repeated reprecipitation of the sodium acid salt mixture only partially eliminated the 1-naphthyl isomer.

Since the sulfonation of naphthalene is a reversible reaction, and some Friedel–Crafts reactions are reversible, attempts were also made to convert the 1-naphthyl(trichloromethyl)carbinol into its 2-naphthyl isomer by heating at 200 °C for 2 h both with and without hydrogen chloride being present. No isomerization was detected. Likewise, no isomerization was detected on stirring a carbon disulfide solution of the 2-naphthyl(trichloromethyl)carbinol (0.0036 mole) with aluminium chloride (0.001 mole) for 24 h at 25 °C.

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From a large scale run with 5 moles of naphthalene, 15 g of a crude high-melting acid crystallized from a benzene extract of the mixture of isomeric acids, and from this by repeated recrystallization from several solvents, 1.5 g of pure  $\alpha, \alpha'$ -dimethoxy-1,5-naphthalenediacetic acid was obtained. The structure was assigned on the basis of analytical data, the infrared spectrum which agrees with that of disubstituted naphthalenes having a symmetrical structure with three adjacent unsubstituted positions in each ring (9), and the n.m.r. spectrum which clearly showed both side chain  $\alpha$ -hydrogens to be equivalent in that they give only a single signal at  $\delta$  5.57. For comparison purposes, the  $\alpha$ -hydrogen of  $\alpha$ -methoxy-1-naphthylacetic acid gives a signal at  $\delta$  5.5 and the corresponding signal for the  $\alpha$ -methoxy-2-naphthylacetic acid occurs at  $\delta$  5.05. It clearly follows from this and from the infrared spectra that the disubstituted acid must have the naphthalene ring symmetrically substituted in the  $\alpha$ -positions, and must therefore be either 1,5 or 1,8. The latter can be eliminated because 1,8 substitution does not occur with 1-substituted naphthalenes; also, two side chain  $\alpha$ -hydrogens could not both fit into the same region between the 1- and 8-positions and the n.m.r. signals observed would be therefore either a singlet or a doublet upfield from the characteristic  $\delta$  5.5 position.

Tetralin has been reported to condense with chloral exclusively in the 2-position (3, 5) and our work confirms this. Treatment of the 5,6,7,8tetrahydro-2-naphthyl(trichloromethyl)carbinol with methanolic potassium hydroxide yielded the oily  $\alpha$ -methoxy-1,2,3,4-tetrahydronaphthalene-6acetic acid which formed an insoluble sodium acid salt. Attempts to dehydrogenate the carbinol and also the sodium salt of the methoxy acid to the naphthalene analogues were unsuccessful.

# Experimental

All melting points are corrected. Nuclear magnetic resonance (n.m.r.) spectra were recorded with a Varian A-60A. Analyses were performed by Mrs. Kathryn G. Baylouny, Mrs. Jane R. Ratka, and Dr. Franz J. Kasler.

## 1-Naphthyl(trichloromethyl)carbinol

To an ether-benzene solution of 1-naphthylmagnesium bromide, prepared from 100 g (0.48 mole) of 1-bromonaphthalene and 12 g of magnesium, were added 73 g (0.48 mole) of anhydrous chloral over a 3 h period. The reaction mixture was maintained at ice-bath temperature during the addition and then stirred at room temperature for 4 h before working up in the usual way. There was obtained 77 g (58% of theory) of the crude carbinol as a yellow-orange oil, b.p. 170-190 °C at 6 mm. It was purified by conversion to the acetate.

The acetate was prepared by refluxing 10 g of the crude carbinol with 75 ml of acetic anhydride for 3 h, after which the reaction mixture was poured into 400 ml of an ice and water mixture and stirred vigorously for 30 min. The oily layer was separated and allowed to dry; it then solidified. Recrystallization from ethanol-water gave 8 g of white crystalline *1-naphthyl(trichloromethyl)methyl acetate*, m.p. 82–83 °C. The infrared (i.r.) spectrum (KBr pellet) showed absorption bands at 3045, 2980, 1730, 1360, 1190, 1025, 920, 875, 770, 725, 665, 625, and 605 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (in CCl<sub>4</sub>) appeared

at  $\delta$  8.5 to 7.1, multiplet (7 ring protons); 7.28, singlet (--CH(OAc)--); 2.13, singlet (3 protons, --CH<sub>3</sub>).

Anal. Calcd. for  $C_{14}H_{11}O_2Cl_3$ : C, 52.93; H, 3.49; Cl, 33.49. Found: C, 53.09; H, 3.40; Cl, 33.20.

The acetate was hydrolyzed by refluxing for 8 h a solution of 3 g of the acetate in 10 ml of ethanol, 15 ml of water, and 10 ml of concentrated hydrochloric acid. After separating and drying the yellow-brown oil in a vacuum oven, it slowly solidified; 2 g were obtained. Recrystallization from cyclohexane gave white *1-naphthyl(trichloromethyl)carbinol*, m.p. 59 °C in agreement with the literature value (4, 5). The infrared spectrum of the oil showed absorption bands at 3525 (shoulder), 3340, 3055, 2920, 2845, 1600, 1510, 1395, 1350, 1260, 1230, 1205, 1165, 1075, 1015, 975, 870, 820, 790, 770, 730, 660, 635, and 600 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (in CCl<sub>4</sub>) appeared at  $\delta$  8.2 to 7.1, multiplet (7 ring protons); 5.97, singlet (--CHOH--); 3.42, broad singlet (--CHOH--).

The carbinol was converted to its methyl ether by treating 5 g of the crude product dissolved in 25 ml of methyl iodide with 5 g of silver oxide (for preparation, see ref. 10) at 0 °C for 20 h. The oily product solidified; recrystallization from aqueous ethanol gave 3 g of methyl *1-naphthyl(trichloromethyl)methyl ether* melting at 76 °C. The infrared spectrum (KBr pellet) showed absorption bands at 3060, 2990, 2910, 2820, 1590, 1510, 1440, 1225, 1190, 1160, 1100, 1010, 875, 800, 775, 730, 675, 640, 615, and 550 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (compound dissolved in CCl<sub>4</sub>) appeared at  $\delta$  8.33 to 7.27, multiplet (7 ring protons); 5.52, singlet (—CH=); 3.40, singlet (3 protons of —OCH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>OCl<sub>3</sub>: C, 53.91; H, 3.83; Cl, 36.72. Found: C, 53.70; H, 3.70; Cl, 36.60.

## 2-Naphthyl(trichloromethyl)carbinol

This was prepared in the same way as the above carbinol. From 45 g of 2-bromonaphthalene, there was obtained 22 g (37% of theory) of the oily carbinol, b.p. 180–190 °C at 2 mm. This solidified and was recrystallized from petroleum ether giving 14 g of the pure carbinol, m.p. 101–102 °C in agreement with the literature value (4, 5). The infrared spectrum (KBr pellet) showed absorption bands at 3470 (broad), 1590, 1355, 1290, 1230, 1160, 1120, 1070, 990, 950, 905, 880, 860, 810 to 840, 745, 720, 660, 615, 565, 515, and 475 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (in CCl<sub>4</sub>) appeared at  $\delta$  8.0 to 7.3, multiplet (7 ring protons); 5.2, doublet (J = 4 c.p.s.) (—CHOH—); and 3.37, doublet (J = 4 c.p.s.) (—CHOH—).

The acetate was prepared by refluxing 4 g of the carbinol with 40 ml of acetic anhydride for 12 h. On pouring into ice-water, 5.5 g of the solid acetate was obtained. The 2-naphthyl(trichloromethyl)methyl acetate melted at 110–112 °C after recrystallization from aqueous ethanol. The infrared spectrum (KBr pellet) showed absorption bands at 3050, 2940, 1750, 1370, 1210, 1170, 1125, 1060, 930, 905, 865, 840, 820, 790, 740, and 675 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (in CCl<sub>4</sub>) appeared at  $\delta$  8.2 to 7.3, multiplet (7 ring protons); 6.43, singlet (1 proton of -CHOAc); 2.18, singlet (3 protons of --CH-(OCOCH<sub>3</sub>)--).

Anal. Calcd. for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>Cl<sub>3</sub>: C, 52.93; H, 3.49; Cl, 33.49. Found: C, 52.75; H, 3.62; Cl, 33.30.

The methyl ether was prepared from the carbinol by methylation with excess methyl iodide and silver oxide as in the previous case. The *methyl 2-naphthyl(trichloro-* methyl)methyl ether melted at 49–50 °C after crystallization from ethanol. The infrared spectrum (KBr pellet) showed absorption bands at 1600, 1450, 1330, 1265, 1190, 1100, 1000, 905, 880, 865, 840, 810, 750, 725, 670, 625, 570, 510, and 475 cm<sup>-1</sup>. Signals in the n.m.r. spectrum (in CCl<sub>4</sub>) appeared at  $\delta$  7.9 to 7.2, multiplet (7 ring protons); 4.70, singlet (1 proton of  $-CH(OCH_3)-$ ); 3.43, singlet (3 protons of  $-CH(OCH_3)-$ ).

Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>OCl<sub>3</sub>: C, 53.91; H, 3.83; Cl, 36.72. Found: C, 54.20; H, 3.97; Cl, 36.43.

# Mixture of 1- and 2-Naphthyl(trichloromethyl)carbinols

To a solution of 25.6 g (0.20 mole) of naphthalene and 60 g (0.40 mole) of anhydrous chloral in 50 ml of nitrobenzene, there was added with stirring over a 3 h period a solution of 7.8 g (0.06 mole) of aluminium chloride in 50 ml of nitrobenzene. The temperature was maintained near 0 °C by means of an ice-bath. After standing overnight, the reaction mixture was washed three times with 6 Nhydrochloric acid to remove the aluminium chloride, then twice with 5% sodium carbonate solution to remove chloral polymers, and finally with water. The nitrobenzene was removed by distillation under reduced pressure. Five g of calcium carbonate were added to the residue to lessen decomposition, and the residue was rapidly distilled at 1 to 2 mm. The carbinol mixture distilled at 150-180 °C/2 mm as a pale-yellow, viscous oil weighing 34 g (61 % yield). The literature b.p. is 180 °C at 1.5 mm (5). The areas of the peaks in the n.m.r. spectrum at  $\delta$ 5.97 (1-naphthyl isomer) and 5.2 (2-naphthyl isomer) were in the ratio of 85 to 14. This indicates the mixture contained the 1-naphthylcarbinol and the 2-naphthylcarbinol in the ratio of 6:1. Another large peak at  $\delta$ 6.45 showed the presence of an unidentified impurity. Since the carbinol mixture was converted into the isomeric α-methoxynaphthylacetic acids (see below) in 76% yield, the amount of impurities was probably under 20%.

The experiments with carbon disulfide as a solvent were carried out in an analogous manner except that the aluminium chloride was added portionwise as a solid since it is insoluble in the solvent.

The experiments with cyclohexane followed the published experimental procedures (5). To a solution of 26 g (0.20 mole) of naphthalene and 60 g (0.40 mole) of anhydrous chloral in 150 ml of cyclohexane, there was added with stirring over a 3 h period, 5 g (0.04 mole) of freshly sublimed aluminium chloride. The temperature was maintained at 0 °C throughout the entire addition period. After the addition, the mixture was allowed to warm up to room temperature and stirring was continued for 8 h before decomposing the reaction mixture with cold 6 N hydrochloric acid. There was obtained 22 g (39% yield) of the mixture of carbinols as a yellow viscous oil distilling at 170 °C at 1 mm. The areas of the singlet peaks at  $\delta$  5.97 and 5.2 of the 1- and 2-naphthylcarbinols, measured as before, were in the ratio of 43:11, indicating these isomers to be present in the reaction mixture in the ratio of 4:1.

## $\alpha$ -Methoxynaphthylacetic Acids

To 27 g (0.1 mole) of the mixture of carbinols, prepared using nitrobenzene as the solvent, dissolved in 100 ml of methanol was added with stirring over a 3 h period 22.5 g (0.4 mole) of potassium hydroxide dissolved in 100 ml of methanol. The temperature was maintained between 45

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and 50 °C during the addition, and then allowed to cool slowly to room temperature while stirring was continued. The reaction mixture was allowed to stand overnight and then diluted with an equal volume of water. It was filtered to remove potassium chloride and some neutral material, and the filtrate was clarified by two treatments with activated carbon. The clear filtrate was then acidified with hydrochloric acid to a pH of 3.3, and enough sodium chloride added to half saturate the water present. After stirring and then standing overnight, 21 g of a lightbrownish solid were filtered off. Acidification and evaporation of the filtrate yielded only a trace of acidic material. The precipitate was triturated with three 50 ml portions of acetone and filtered. Upon evaporation of the acetone, 8 g of crude  $\alpha$ -methoxy-1-naphthylacetic acid, m.p. 130-145 °C, were collected. The white, insoluble material from the acetone trituration weighed 9 g and consisted of a mixture of the sodium acid salts of the  $\alpha$ -methoxy-1- and 2-naphthylacetic acids.

After further working up as described in the following sections, a total of 14.2 g (66% yield) of  $\alpha$ -methoxy-1-naphthylacetic acid, and 2.2 g (10% yield) of  $\alpha$ -methoxy-2-naphthylacetic acid was obtained. This approximates a 7:1 ratio of the two acids.

# Separation of $\alpha$ -Methoxy-1- and 2-naphthylacetic Acids

The 9 g mixture of sodium acid salts obtained above was dissolved in 36 ml of 20% potassium hydroxide solution. It was warmed on the steam bath to effect solution and then filtered to remove traces of alkaliinsoluble material. Enough water was added to the filtrate to make the concentration of the solution exactly 5.0% with respect to the mixture of 1-naphthyl and 2naphthyl salts. Exactly 10.0 N sodium hydroxide was then added with stirring to precipitate the sodium a-methoxy-2-naphthylacetate. For each ml of the 5% solution, 0.30 ml of the sodium hydroxide solution was used. (An excess causes the isomeric 1-naphthyl sodium salt to precipitate.) After the addition, the solution was allowed to stand for 10 min, and the insoluble sodium salt was then filtered off on a large Buchner funnel. The salt was washed with acetone, stirred with more acetone in a beaker, and filtered to yield 5 g of the crude sodium salt of  $\alpha$ -methoxy-2-naphthylacetic acid.

The filtrate from the sodium salt precipitation was cooled in an ice-bath and acidified with 6 N hydrochloric acid to yield the crude  $\alpha$ -methoxy-1-naphthylacetic acid.

## $\alpha$ -Methoxy-2-naphthylacetic Acid

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The above crude sodium salt was dissolved in 225 ml of hot water, the solution filtered and then cooled to 0 °C. The solution was poured into an excess of cold 6 N hydrochloric acid, seeded, and allowed to stand two days at 0 °C. The crystals (3 g) were filtered off, air-dried, and recrystallized from benzene. The yield was 2.2 g melting at 97–98 °C in agreement with the literature value of 99° (8). Signals in the n.m.r. spectrum (in DCCl<sub>3</sub>) appeared at  $\delta$  9.37, singlet (1 proton of -COOH); 7.93 to 7.17, multiplet (7 protons of ring); 4.9, singlet (1 proton of -CH(OCH<sub>3</sub>)-); 3.42, singlet (3 protons of -OCH<sub>3</sub>). In dimethyl sulfoxide, the last two signals were shifted slightly to  $\delta$  5.05 and 3.46 respectively.

Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>: C, 72.20; H, 5.59; -OCH<sub>3</sub>, 14.34. Found: C, 71.95; H, 5.80; -OCH<sub>3</sub>, 14.18.

## a-Methoxy-1-naphthylacetic Acid

The crude acid was obtained from the acetone extraction of the sodium acid salt precipitate and also by acidifying the filtrate after precipitating the sodium  $\alpha$ methoxy-2-naphthylacetate as described above. It was purified by recrystallization from benzene. A preliminary trituration with a small amount of cold ethyl acetate was necessary to remove colored material when undistilled carbinol was used in the reaction with the methanolic potassium hydroxide. The acid melted at 148–149 °C in agreement with the literature value (8). Signals in the n.m.r. spectrum (in DCCl<sub>3</sub>) appeared at  $\delta$  10.43, singlet (1 proton of —COOH); 8.4 to 7.1, multiplet (7 protons of ring); 5.35, singlet (1 proton of —CH(OCH<sub>3</sub>)—); 3.4, singlet (3 protons of —OCH<sub>3</sub>). In dimethyl sulfoxide, the last two signals were shifted slightly to  $\delta$  5.50 and  $\delta$  3.47. Anal Calcd for CretHaOQ: C 72 20: H 5 59:

Anal. Calcd. for  $C_{1_3}H_{1_2}O_3$ : C, 72.20; H, 5.59; -OCH<sub>3</sub>, 14.34. Found: C, 72.17; H, 5.54; -OCH<sub>3</sub>, 14.30.

## a,a'-Dimethoxynaphthalene-1,5-diacetic Acid

A condensation of chloral and naphthalene was carried out in a manner similar to the one described above using nitrobenzene as solvent, but scaled up 25-fold. During the workup, the nitrobenzene was distilled at 16 to 20 mm until the temperature of the liquid reached 180 °C, and the residual crude carbinol was used in the undistilled form. After reaction with methanolic potassium hydroxide, the aqueous alkaline solution was clarified by several treatments with activated carbon, acidified, and the oily acids which separated were extracted with benzene. From this benzene extract  $\alpha, \alpha'$ -dimethoxynaphthalene-1,5diacetic acid crystallized on washing the extract with water. The crude acid (15 g) was crystallized from acetone-water, ethyl acetate, and finally benzene. The 1.5 g of acid obtained melted at 233-234 °C. The infrared spectrum (Nujol mull) showed absorption bands at 2900, 1725, 1670, 1450, 1165, 1110, 794, 781, and 763 cm<sup>-1</sup>. Assignment of the 1,5 structure was based on the peaks at 781 and 763  $\text{cm}^{-1}$  (9) and on the n.m.r. spectrum. Signals in the n.m.r. spectrum (in DMSO- $d_6$ ) appeared at  $\delta$  8.6 to 8.2, multiplet (2 ring protons); 7.8 to 7.5, multiplet (4 ring protons); 5.55, singlet (2 protons, -CH-(OCH<sub>3</sub>)---); and 3.5, singlet (6 protons, ---CH(OCH<sub>3</sub>)---).

Anal. Calcd. for  $C_{16}H_{16}O_6$  (neutralization equivalent 152): C, 63.15; H, 5.30; —OCH<sub>3</sub>, 20.40. Found (neutralization equivalent, 154): C, 63.22; H, 5.62; —OCH<sub>3</sub>, 19.95.

#### a-Methoxy-1,2,3,4-tetrahydronaphthalene-6-acetic Acid

The preparation of the carbinol from chloral and tetralin using carbon disulfide as the solvent was analogous to the procedure given above for naphthalene. The 5,6,7,8-tetrahydro-2-naphthyl (trichloromethyl) carbinol distilled at 188–190 °C/2 mm and was obtained in 51 % yield.

Reaction of the carbinol with methanolic potassium hydroxide was carried out in the same way as described for the naphthyl(trichloromethyl)carbinols. The methoxy acid was isolated as *sodium hydrogen di(a-methoxy-1,2,3,-4-tetrahydronaphthalene-6-acetate)*. After washing with water and acetone, the material had a neutralization equivalent of 460; the theoretical value is 462. The *free acid* was an oil. Signals in the n.m.r. spectrum (free acid in DCCl<sub>3</sub>) appeared at  $\delta$  10.4, singlet (-COOH); 7.3 to 6.9, four peaks (3 protons of aromatic ring); 4.7, singlet (1

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proton of --CH(OCH<sub>3</sub>)--); 3.38, singlet (3 protons of  $-OCH_3$ ; 2.73, multiplet (4 protons of carbons 1 and 4); and 1.75, multiplet (4 protons of C-2 and C-3). Anal. Calcd. for  $C_{13}H_{16}O_3$ : C, 70.88, H, 7.31. Found:

C, 70.82; H, 7.36.

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