[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY; DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE; AND THE NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Determination of Double-bond Character in Cyclic Systems. IV. Tetrahydronaphthalene. Steric Facilitation of Chelation[1]

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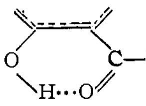
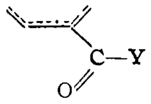
RECEIVED JANUARY 20, 1958

Infrared spectral measurements have led to the conclusion that there is no significant Mills–Nixon bond fixation in the aromatic ring of tetrahydronaphthalene. 2-Hydroxy-5,6,7,8-tetrahydro-1-naphthaldehyde and the corresponding methyl ketone and methyl ester are more strongly chelated than their 3,2-isomers, as shown by determination of $\Delta\nu$(C=O) values (which represent the lowering of the frequency of the C=O absorption band observed in going from the non-hydroxylated to the hydroxylated compounds). The average $\Delta\nu$(C=O) values for the 3,2-disubstituted tetrahydronaphthalenes are virtually identical with those determined earlier for the analogous *o*-disubstituted benzenes, the 5,6-disubstituted indans and the 4,5-disubstituted *o*-xylenes, showing that the ring bonds (bond B) between the chelated groups all have 50% double-bond character. The larger $\Delta\nu$(C=O) values for the 2,1-disubstituted tetrahydronaphthalenes, the 5,4-disubstituted indans and the 4,3-disubstituted *o*-xylenes are explained by assuming that the bulk of the adjacent methylene groups (in tetrahydronaphthalene and indan) or methyl groups (in *o*-xylene) pushes the carbonyl oxygen atom closer to the hydroxyl group than is the case with the first group of compounds. This effect (steric facilitation of chelation) affords a more satisfactory explanation of the higher $\Delta\nu$(C=O) values than would be obtained by assuming that the ring bonds (bond A) between the chelated groups have greater than 50% double-bond character. The concept of steric facilitation of chelation is shown to permit a refinement of the earlier interpretation of the $\Delta\nu$(C=O) values for naphthalene and phenanthrene. The steric effects of methyl groups and of alicyclic methylene groups are compared. N-Methylformanilide reacts with 2-methoxy-5,6,7,8-tetrahydronaphthalene to produce the symmetrical methoxyaldehyde. Depending on conditions, the haloform reaction on 3-methoxy-5,6,7,8-tetrahydro-2-acetonaphthone produces either 4-chloro-3-methoxy-5,6,7,8-tetrahydro-2-naphthoic acid or methyl 3-methoxy-5,6,7,8-tetrahydro-2-naphthoate. Syntheses of certain known tetrahydronaphthalenes are improved, and proofs of structure are offered which are independent of earlier work.

Introduction

Earlier work[3] in these laboratories has shown that the strength of an intramolecular hydrogen bond in an aromatic system such as I varies with the amount of double-bond character exhibited by the ring bond between the carbon atoms bearing the chelated substituents. The strength of such a hydrogen bond is measured by $\Delta\nu$(C=O), defined as the shift to lower frequency exhibited by the C=O absorption band (in the infrared) in going from II to the corresponding I. Thus, $\Delta\nu$(C=O) has a characteristic value for each carbon-to-carbon bond in an aromatic ring. A linear relationship has been observed between $\Delta\nu$(C=O) and Pauling's percentage double-bond character (obtained by averaging the most stable structures contributing to resonance) for the ring bonds in benzene,[3a] naphthalene[3a] and phenanthrene.[3b]


I


II

Y = –H, $-CH_3$ and $-OCH_3$

This paper records the results of a study of the bond structure of tetrahydronaphthalene and a comparison of these results with our earlier work on indan and *o*-xylene,[3c] thus permitting a rather comprehensive evaluation of the Mills–Nixon type of bond fixation. What is believed to be a novel steric effect on intramolecular hydrogen bonding also will be described.

Work on the Mills–Nixon effect has been reviewed by Badger.[4] Most of the experimental work done in this field has involved a study of comparative chemical reactivities and hence is subject to the severe limitations mentioned earlier.[3c] From a study of the ease with which the benzoates of isomeric hydroxy-5,6,7,8-tetrahydroacetonaphthones underwent the Baker–Venkataraman transformation, O'Farrell, *et al.*,[5] recently concluded that the 1,2-bond of 5,6,7,8-tetrahydronaphthalene has a higher bond order than the 2,3-bond. Similar work also led these authors to conclude that the 4,5-bond in indan is of higher order than the 5,6-bond. However, these results are qualitative in character, and they do not differentiate between contributions to the bond orders by "ordinary" substituent effects and by Mills–Nixon bond fixation.

Very few physical measurements have been performed on tetrahydronaphthalene with a view toward establishing the bond structure of its aromatic ring. The dipole moment measurements on 2,3-dibromo-5,6,7,8-tetrahydronaphthalene[6] have not been interpreted satisfactorily. However, Arnold and Evans[7] have shown that the acidities of 6-nitro-3,4-xylenol, 6-nitro-5-indanol and 3-nitro-5,6,7,8-tetrahydro-2-naphthol are virtually the same. Hence, the aromatic bonds in question in all three compounds must have nearly identical double-bond character, thus precluding any appreciable Mills–Nixon bond fixation.

Discussion

Synthetic Work.—Of the tetrahydronaphthalene derivatives (III–VI) required for this work, all of the monosubstituted compounds (III and IV) are known. However, IVa and IVb were prepared from 5,6,7,8-tetrahydro-1-naphthoyl chloride by

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[1] Parts of the work reported herein were presented at the International Symposium on Hydrogen Bonding, Ljubljana, Yugoslavia, July 29–August 2, 1957, and at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 8–13, 1957.

[2] Department of Chemistry, Fordham University, New York 58, N. Y.

[3] (a) I. M. Hunsberger, THIS JOURNAL, **72**, 5626 (1950); (b) I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, *ibid.*, **74**, 4839 (1952); (c) I. M. Hunsberger, D. Lednicer, H. S. Gutowsky, D. L. Bunker and P. Taussig, *ibid.*, **77**, 2466 (1955).

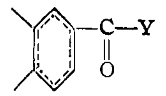
[4] G. M. Badger, *Quart. Revs.* (*London*), **5**, 147 (1951).

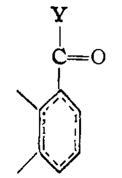
[5] M. P. O'Farrell, D. M. S. Wheeler, M. M. Wheeler and T. S. Wheeler, *J. Chem. Soc.*, 3986 (1955).

[6] N. V. Sidgwick and H. D. Springall, *ibid.*, 1532 (1936).

[7] R. T. Arnold and R. L. Evans, THIS JOURNAL, **62**, 556 (1940).

Rosenmund reduction and by reaction with dimethylcadmium, respectively, rather than by previously published methods.


III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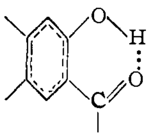
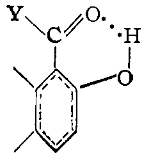
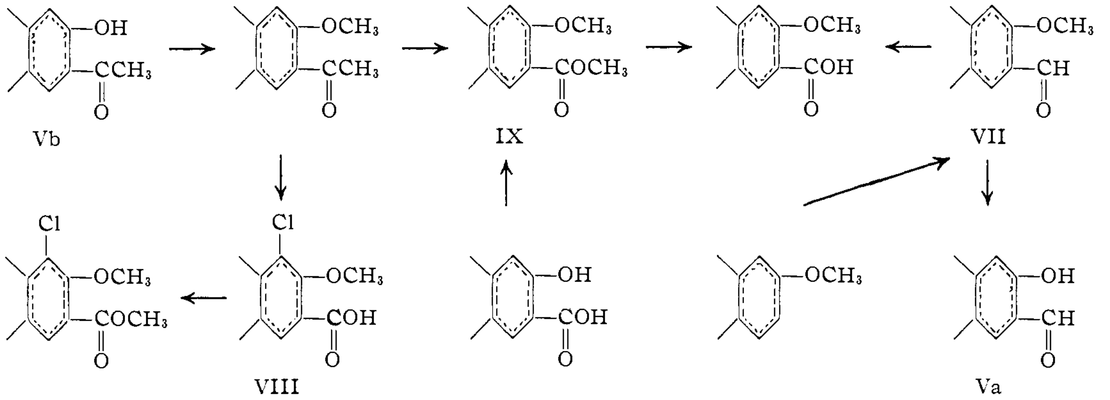
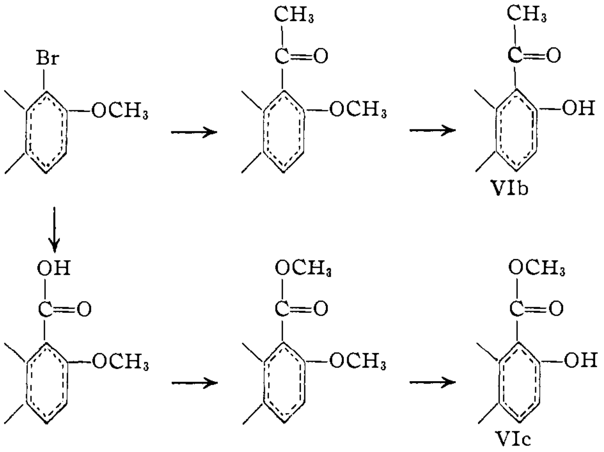

V


VI

a,Y = -H; b,Y = -CH$_3$; c,Y = -OCH$_3$

Of the disubstituted tetrahydronaphthalenes V and VI, only VIc is a new compound, but Va was prepared by a new process. Furthermore, we had completed our synthesis of Vb before the appearance of the almost identical preparation of O'Farrell, *et al.*[5] The hydroxyketone VIb was prepared by the general method of O'Farrell, *et al.*,[5] but our synthesis proceeded in much higher yield. Some unique results also have been obtained by subjecting 3-methoxy-5,6,7,8-tetrahydro-2-acetonaphthone to the haloform reaction.





The starting materials required for preparing the 2,3-disubstituted tetrahydronaphthalenes were 5,6,7,8-tetrahydro-2-naphthol (obtainable from tetrahydronaphthalene) and methyl 3-hydroxy-2-naphthoate, which was reduced to the known tetrahydro ester Vc and the latter saponified to the known tetrahydro acid.

A methoxyaldehyde, m.p. 52–53°, of unassigned structure is reported in the patent literature[8] as the product from the reaction of 2-methoxy-5,6,7,8-tetrahydronaphthalene with N-methylformanilide and phosphorus oxychloride. This reaction in our hands gave a 50% yield of methoxyaldehyde (VII), m.p. 51.6–52°, which was oxidized with potassium permanganate in acetone solution to 3-methoxy-5,6,7,8-tetrahydro-2-naphthoic acid. The structure of the latter was established by mixture m.p. with an authentic sample prepared[9] by converting 3-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid to the methyl ester of the methoxyacid followed by saponification. Hence, the two methoxyaldehydes appear to be identical, and VII has the structure shown. Thus, the aldehyde group enters the less hindered position *ortho* to the methoxyl, as was observed[3c] for the corresponding *o*-xylene and indan derivatives. The known hydroxyaldehyde (Va) was prepared by demethylation of VII. Fries rearrangement of the acetate of 5,6,7,8-tetrahydro-2-naphthol produced a 53% yield of recrystallized Vb, which very closely agrees with the yield reported by O'Farrell, *et al.*[5] On subjecting the methyl ether of Vb to the haloform reaction, the expected methoxy acid never was obtained. If the reaction was conducted at 55° in an aqueous medium, a chlorinated methoxyacid, almost certainly having structure VIII, was obtained. However, if the reaction was performed by adding a solution of the methoxyketone in methanol to the hypochlorite at 11° and letting the stirred mixture warm up to room temperature over 5 hr., the methyl ester IX of the methoxyacid separated from the reaction mixture. Although only a low yield of IX was obtained, more thorough investigation probably would increase the yield. It is interesting to note that ester IX was not obtained from any of the several reactions performed at the higher temperature even if methanol was present; instead, low yields of the chlorinated methoxy acid VIII

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(8) I. G. Farbenind, A.-G., French Patent 648,069, Feb. 1, 1928; *C. A.*, **23**, 2446 (1929).

(9) R. T. Arnold, H. E. Zaugg and J. Sprung, THIS JOURNAL, **63**, 1314 (1941).

were obtained. If the ester forms first under these conditions, it is saponified quickly.

Isolation of a chlorinated acid from a haloform reaction has been reported by Arnold, *et al.*,[10] who acidified the reaction mixture before decomposition of the excess hypochlorite. (Even though we decomposed the excess hypochlorite before acidification, the unchlorinated acid was not obtained.) These authors[10] also obtained an ester as the product of the haloform reaction. It seems likely that conditions for performing the haloform reaction can be found which will make the one-step conversion of a methyl ketone to the ester of the corresponding acid a general reaction.[11]

Incidentally, the conversion of Vb to the known methoxyester IX is a proof of structure for Vb independent of that of O'Farrell, *et al.*[5]

The starting material for the 1,2-disubstituted tetrahydronaphthalenes was 5,6,7,8-tetrahydro-2-naphthol. This compound was converted in low yield to the known VIa[9] by the Reimer–Tiemann reaction. VIb and VIc both were prepared from 1 - bromo - 2 - methoxy - 5,6,7,8 - tetrahydronaphthalene. Although VIb was prepared according to the method of O'Farrell, *et al.*,[5] we obtained a much higher yield, particularly in the preparation of 2-methoxy-5,6,7,8-tetrahydro-1-acetonaphthone by reaction of acetyl chloride with the cadmium derivative of the bromoether. In our hands the starting bromoether could not be obtained pure except by a tedious process of distillation and recrystallization. However, only very pure material was used, and this may have been responsible for the higher yields. Esterification of the known 2-methoxy-5,6,7,8-tetrahydro-1-naphthoic acid with diazomethane followed by selective demethylation to VIc proceeded smoothly and in high yield. These processes represent excellent synthetic approaches to these vicinally substituted compounds.

Infrared Work.—Table I records the frequencies of the carbonyl absorption of compounds III–VI in 0.02 molal carbon tetrachloride solutions, along with the $\Delta\nu$(C=O) values for V and VI.

TABLE I

FREQUENCIES (IN CM.$^{-1}$) OF THE CARBONYL ABSORPTION BANDS AND $\Delta\nu$(C=O) VALUES (IN CM.$^{-1}$) FOR THE TETRAHYDRONAPHTHALENE DERIVATIVES IN 0.02 *M* CARBON TETRACHLORIDE SOLUTIONS

Compound	C=O band	$\Delta\nu$ (C=O)
5,6,7,8-Tetrahydro-2-naphthaldehyde (IIIa)	1706	
5,6,7,8-Tetrahydro-2-acetonaphthone (IIIb)	1688	
Methyl 5,6,7,8-tetrahydro-2-naphthoate (IIIc)	1725	
5,6,7,8-Tetrahydro-1-naphthaldehyde (IVa)	1699	
5,6,7,8-Tetrahydro-1-acetonaphthone (IVb)	1685	
Methyl 5,6,7,8-tetrahydro-1-naphthoate (IVc)	1725	
3-Hydroxy-5,6,7,8-tetrahydro-2-naphthaldehyde (Va)	1660	46
3-Hydroxy-5,6,7,8-tetrahydro-2-acetonaphthone (Vb)	1649	39
Methyl 3-hydroxy-5,6,7,8-tetrahydro-2-naphthoate (Vc)	1680	45
2-Hydroxy-5,6,7,8-tetrahydro-1-naphthaldehyde (VIa)	1649	50
2-Hydroxy-5,6,7,8-tetrahydro-1-acetonaphthone (VIb)	1631	54
Methyl 2-hydroxy-5,6,7,8-tetrahydro-1-naphthoate (VIc)	1665	60

Table II compares the $\Delta\nu$(C=O) values of V and VI with those determined earlier[3c] for the corresponding derivatives of indan and *o*-xylene.

TABLE II

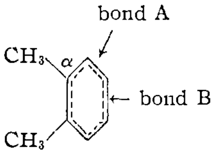
AVERAGE $\Delta\nu$(C=O) VALUES (CM.$^{-1}$)

Bond A[a]	Indan[3c]	*o*-Xylene[3c]	Tetrahydronaphthalene
OH, CHO	48	50	50
OH, $COCH_3$	51	49	54
OH, $COOCH_3$	51	54	60
Average[b]	50	51	55
Bond B[a]			
OH, CHO	43	37	46
OH, $COCH_3$	40	41	39
OH, $COOCH_3$	49	49	45
Average[b]	44	42	43
Average difference[c]	6	9	12

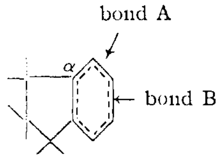
[a] Refer to formulas X, XI and XII. [b] Average values are used in the discussion for the reason given earlier.[3c] [c] Average $\Delta\nu$(C=O) for bond A minus average $\Delta\nu$(C=O) for bond B.

The $\Delta\nu$(C=O) values for the *o*-xylenes should afford an approximate separation of any "substituent" effect of the methylene groups in indan and tetrahydronaphthalene from any Mills–Nixon bond fixation. The average $\Delta\nu$(C=O) values for bond B in *o*-xylene, indan and tetrahydronaphthalene are very nearly identical (42, 44 and 43 cm.$^{-1}$, respectively), while the values for bond A are consistently larger (51, 50 and 55 cm.$^{-1}$, respectively) and cover a wider range.

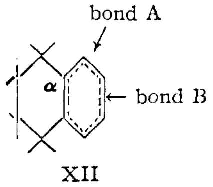
Although these results cannot be interpreted quite as easily as those for benzene,[3a] naphthalene[3a] and phenanthrene,[3b] it is clear that in *o*-xylene, indan and tetrahydronaphthalene corresponding bonds have close to the same double-bond character. For the latter three hydrocarbons, it is significant that $\Delta\nu$(C=O) values for bond B do not differ from the $\Delta\nu$(C=O) value for the benzene bond (43 cm.$^{-1}$) by more than experimental error, ±1 cm.$^{-1}$. This is strong evidence that in all three hydrocarbons bond B has 50 ± 1% double-bond character.



X



XI



XII

The $\Delta\nu$(C=O) values for bond A offer some difficulty in interpretation. They are larger than those for bond B by amounts considerably greater than the experimental error. The differences

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(10) R. T. Arnold, R. Buckles and J. Stoltenberg, THIS JOURNAL, **66**, 208 (1944).

(11) I. M. H. is indebted to Dr. R. T. Arnold for a stimulating discussion of this subject.

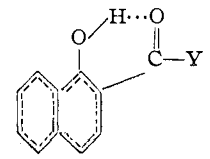
might result from either of two causes or perhaps even from a combination of the two: (a) substituent and bond fixation effects which increase the double-bond character of bond A without affecting bond B, (b) some mechanism which shifts the position of the carbonyl absorption in compounds of type VI without affecting the double-bond character of either bond A or bond B and without affecting the carbonyl absorption in compounds of type V.

As to the first of these possibilities, one must assume that the $\Delta\nu$(C=O) value of 51 cm.$^{-1}$ for bond A in *o*-xylene measures the "normal substituent effects" of the methyl groups in *o*-xylene and closely approximates those of the methylene groups in indan and tetrahydronaphthalene. Then the different values, 50 and 55 cm.$^{-1}$, for indan and tetrahydronaphthalene could be interpreted as a bond fixation effect of -1 and $+5$ cm.$^{-1}$, respectively. These frequency differences would correspond to -1 and $+5\%$ double-bond character, assuming that 50% double-bond character produces the average $\Delta\nu$(C=O) of 43 cm.$^{-1}$ found for benzene and bond B in the three hydrocarbons. The different signs of the apparent fixation of bond A in indan and tetrahydronaphthalene, according to this approach, agree with the Mills–Nixon model. However, as discussed in detail earlier, the small effect in indan is within experimental error[3c]; moreover, if valence is to be conserved, there should be a reciprocal fixation of bond B, but none is observed even in tetrahydronaphthalene in spite of the relatively large apparent $\Delta\nu$(C=O) value for bond A. These reasons lead us to believe factor (a) is of no more than minor importance.

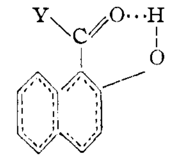
As stated in (b), there may be a mechanism which increases the $\Delta\nu$ (C=O) value for bond A without affecting the double-bond character of either bond A or bond B. In fact, the preferred interpretation of our results is obtained by assuming that the bulk of the methyl groups in *o*-xylene and of the methylene groups in indan and tetrahydronaphthalene displaces the carbonyl oxygen atom in compounds like VI so that it is somewhat closer to the hydrogen of the hydroxyl group than is the case in compounds like V.[12] Such an effect, for which we propose the name "Steric Facilitation of Chelation," would make the hydrogen bond stronger[13] in type VI than in type V compounds and would make the $\Delta\nu$ (C=O) value for bond A larger than that for bond B in all three hydrocarbons without affecting the double-bond character of bond A or bond B. We cannot be certain of course that the larger $\Delta\nu$(C=O) values for bond A are entirely attributable to this steric effect, but certainly the steric effect is the main factor. It seems difficult to believe that electrical effects could differ appreciably in compounds as similar, for example, as V and VI.

Arnold[14] and later Verkade[15] have concluded that the steric effect of a methylene group in tetrahydronaphthalene is larger than that of a methylene group in indan. Hence, it would be expected that the difference between the average $\Delta\nu$(C=O) values for bonds A and B is greater for tetrahydronaphthalene (12 cm.$^{-1}$) than for indan (6 cm.$^{-1}$). In other words, if angle α is smaller in tetrahydronaphthalene than in indan (see formulas XII and XI) and if steric facilitation of chelation is operative, one would expect that tetrahydronaphthalene derivatives of type VI would exhibit stronger chelation than their indan analogs. Although Arnold[14] and Verkade[15] both have concluded that the steric effect of a methyl group in *o*-xylene is larger than that of any methylene group, the difference in average $\Delta\nu$(C=O) values for bonds A and B in *o*-xylene (9 cm.$^{-1}$) is intermediate between the corresponding differences for indan and tetrahydronaphthalene. Hence, our results indicate that the steric effect of a methyl group in *o*-xylene is intermediate between that of a methylene group in indan and of the same group in tetrahydronaphthalene.[16] This difference may be caused by unequal electronic effects of the groups in question, such as hyperconjugation of the methyl and methylene groups with the aromatic ring. It should be emphasized that our conclusions rest on infrared spectral data, while those of Arnold[14] and Verkade[15] rest largely on ultraviolet and chemical data. Manifestations of steric effects may not be the same in excited and unexcited states of a given molecule.

The concept of steric facilitation of chelation appears to permit a refinement in our earlier interpretations of the bond structure of naphthalene[3a] and phenanthrene.[3b] Thus, the average $\Delta\nu$(C=O) value for compounds of type XIII was 54 cm.$^{-1}$ as compared to 59 cm.$^{-1}$ for compounds of type XIV.



XIII



XIV

Y = $-$H, $-CH_3$ and $-OCH_3$

Although this difference was neglected in our earlier work, it seems likely that the *peri*-CH would exert a greater steric effect on a carbonyl-containing substituent in the 1-position (formula XIV) than on a hydroxyl group in the 1-position (formula XIII) and that the steric effect of the *peri*-CH in naphthalene should be less than that of a methylene group in indan. If this interpretation is accepted, these compounds apparently are the first to be discovered in which *steric crowding increases the strength of an intramolecular hydrogen bond.*

From an examination of the ester carbonyl absorption bands of methyl crotonate and of the enol form of methyl acetoacetate, a $\Delta\nu$(C=O) value of 71 cm.$^{-1}$ was obtained for the C=C bond of propylene.[3b] This value was slightly less than the 75 cm.$^{-1}$ value obtained for both XVb and XVc.

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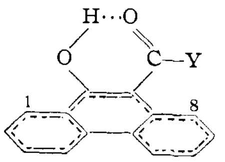
[12] This suggestion was made independently by Dr. Douglas J. Hennessy, and the authors are indebted to him for many helpful discussions of it and of other questions.

[13] L. Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 327–334.

[14] S. W. Fenton, A. E. DeWald and R. T. Arnold, THIS JOURNAL, **77**, 979 (1955), and preceding papers in the series.

[15] R. Van Helden, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **73**, 39 (1954), and preceding papers in the series.

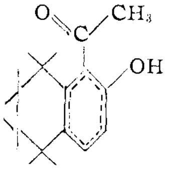
[16] Verkade, *et al.* (ref. 15), have found that the steric effect of a *single* methyl group is considerably less than that of two adjacent methyl groups; these authors state that the magnitude of the former effect is intermediate between that of the methylene groups of indan and tetrahydronaphthalene.



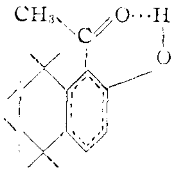
XVa, Y = H
XVb, Y = CH_3
XVc, Y = OCH_3

One might have expected the $\Delta\nu$(C=O) value for propylene to be considerably larger than for phenanthrene since the C=C bond of propylene very likely has greater double-bond character than the 9,10-bond of phenanthrene. Part of this apparent anomaly would be resolved on the assumption that the steric effect of the 1- and 8-CH groups of phenanthrene crowds the two chelated groups at the 9- and 10-positions closer than they otherwise would be, thereby strengthening the hydrogen bond. Such a steric effect gains credence from the fact that XVa, containing the smaller aldehyde group, showed a $\Delta\nu$(C=O) value of only 61 cm.$^{-1}$. Moreover, in Table II the $\Delta\nu$(C=O) values for bond A are consistently larger for the ketones and esters than for the aldehydes, again in accord with the relative steric effects of the substituents.

O'Farrell, *et al.*,[5] have suggested that the preferred conformation of 2-hydroxy-5,6,7,8-tetrahydro-1-acetonaphthone is that (XVI) which is unfavorable for chelation. Nonetheless, in carbon tetrachloride solution we find a large $\Delta\nu$(C=O) of 54 cm.$^{-1}$ for this compound, showing that it exists in the chelated form (XVII). The arguments of O'Farrell, *et al.*,[5] are based on the relative hindrance exerted by the adjacent methylene group on the carbonyl (in XVI) as compared to the methyl group (in XVII). Apparently these workers give insufficient weight to the stabilizing effects of the strong hydrogen bond produced by the conjugated chelation in XVII. Moreover, the effects of the latter could complicate the interpretation of their ultraviolet spectra. It is noteworthy that the infrared spectrum of the hydroxyketone does suggest an equilibrium between XVI and XVII. In addition to the strong absorption band of the chelated form at 1631 cm.$^{-1}$, a weak absorption band was found at 1690 cm.$^{-1}$. This is close to the carbonyl absorption, at 1685 cm.$^{-1}$, in the parent compound IVb without the hydroxyl group and could very well arise from a small percentage of the non-chelated form. The infrared spectra of the hydroxyester VIc are very similar in this regard. Thus, methyl 2-hydroxy-5,6,7,8-tetrahydro-1-naphthoate (VIc) has a weak absorption band at 1733 cm.$^{-1}$ in addition to the strong band at 1665 cm.$^{-1}$ attributable to the chelated form. The 1733 cm.$^{-1}$ band is close to the ester carbonyl absorption at 1725 cm.$^{-1}$ in the parent compound IVc without the hydroxyl, again suggesting the presence of a small percentage of the non-chelated form. In any event, the analysis by O'Farrell, *et al.*, supports the assumption that the carbonyl oxygen would be brought closer to the hydroxyl hydrogen by the steric effects in the chelated form XVII.



XVI



XVII

In addition to the steric effects proposed here to explain the larger $\Delta\nu$(C=O) value for bond A, these values may be partially attributable to some substituent effects of an electronic nature, such as those treated by Berthier and Pullman[17] in their theoretical analysis of the Mills–Nixon effect. Even though the steric and electronic effects cannot be separated in the present study, comparison of the results for indan and tetrahydronaphthalene with those for benzene and *o*-xylene show that the Mills–Nixon bond fixation is very small and could, at most, be significant only in the 1,2-bond (bond A) of tetrahydronaphthalene.

Work in progress in these laboratories is designed to supply further tests of the validity of the concept of steric facilitation of chelation.

Experimental[18]

5,6,7,8-Tetrahydro-2-acetonaphthone[19] was distilled three times, b.p. 137° at 10 mm.,[20] lit. b.p. 132.5–134.5° at 3.5–4 mm.[19] The methyl ester of 5,6,7,8-tetrahydro-2-naphthoic acid[19,21] was distilled twice, b.p. 137—138° at 4 mm.,[20] n^{19}_D 1.5449, lit. b.p. 149–150° at 4–4.5 mm.[19] **5,6,7,8-Tetrahydro-2-naphthaldehyde**, prepared by Rosenmund reduction[19] of the acid chloride[22] in boiling tetrahydronaphthalene, was distilled twice under nitrogen, b.p. 123–124° at 4 mm.[20]; lit. b.p.'s: 116–119° at 3 mm.,[19] 150° at 13 mm.[22] and 138° at 14 mm.[23]

Catalytic reduction of 1-naphthoic acid according to published procedures[24] and also at 50° and 2500 lb./in.^{2} gave only unchanged starting material. Hydrogenation of methyl 1-naphthoate[25] gave a mixture of products which on saponification yielded only a small quantity of pure 5,6,7,8-tetrahydro-1-naphthoic acid. The desired acid (m.p. 149.5–151.5°) finally was obtained from 5,6,7,8-tetrahydro-1-naphthylamine.[14] **Methyl 5,6,7,8-tetrahydro-1-naphthoate** was distilled twice, b.p. 158.5–159° at 15.5 mm.,[20] n^{26}_D 1.5437; lit.[26] values: b.p. 93.5–96.5° at 0.5–1.0 mm., n^{25}_D 1.5431. Rosenmund reduction[27] of 5,6,7,8-tetrahydro-1-naphthoyl chloride[28] required 2 hr. in boiling tetrahydronaphthalene and gave, *via* the bisulfite adduct, a 25% yield of distilled **5,6,7,8-tetrahydro-1-naphthaldehyde** as a colorless oil, b.p. 151–152.5° at 19 mm., n^{25}_D 1.5740, lit.[23] b.p. 131–133° at 12 mm.; after redistillation under nitrogen the b.p. was 143–143.5° at 17 mm.[20]; **semicarbazone**, m.p. 186.5–188° (from 90% ethanol), lit.[23] m.p. 187°.

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(17) G. Berthier and A. Pullman, *Bull. soc. chim. France*, [5] **17,** 88 (1950).

(18) All m.p.'s and b.p.'s are uncorrected unless specified otherwise. Nearly all of the distillations were performed in a modified Claisen flask with a short vacuum-jacketed column. Unless designated otherwise, all elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All neutral equivalent determinations were performed in our laboratories.

(19) M. S. Newman and H. V. Zahm, THIS JOURNAL, **65**, 1097 (1943).

(20) Spectral sample.

(21) M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

(22) C. L. Hewett, *J. Chem. Soc.*, 1286 (1938).

(23) J. v. Braun, *Ber.*, **55**, 1700 (1922).

(24) W. G. Dauben, C. F. Hiskey and A. H. Markhart, THIS JOURNAL, **73,** 1393 (1951); J. Cason and D. D. Phillips, *J. Org. Chem.*, **17,** 298 (1952).

(25) H. Adkins and E. E. Burgoyne, THIS JOURNAL, **71**, 3528 (1949).

(26) M. S. Newman and T. S. Bye, *ibid.*, **74**, 905 (1952).

(27) For the general procedure consult E. Mosettig in "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 369–370.

(28) S. I. Sergievskaya and E. G. Nikhamkina, *J. Gen. Chem.* (*U.S.S.R.*), **15,** 940 (1945); *C. A.*, **40,** 6453 (1946).

5,6,7,8-Tetrahydro-1-acetonaphthone.—Methylmagnesium bromide, prepared (nitrogen atmosphere) from 5.11 g. (0.210 g. atom) of magnesium in 150 ml. of dry ether, was treated during 0.5 hr. with 18.5 g. (0.101 mole) of anhydrous cadmium chloride. After 1 hr. of reflux, the ether was replaced by 150 ml. of dry benzene. A solution of 5.0 g. (0.026 mole) of 5,6,7,8-tetrahydro-1-naphthoyl chloride[28] in 120 ml. of dry benzene was added over 45 minutes, and the mixture was refluxed for 2 hr. On working up the product as described elsewhere in this paper 2.1 g. (47%) of colorless oil, b.p. 152–155° at 19 mm., $n^{25.5}_{\mathrm{D}}$ 1.5550, was obtained; lit.[26] values: b.p. 95.5–99° at 0.5–1 mm., n^{20}_{D} 1.5550. Redistillation gave the spectral sample, b.p. 156.5° at 20 mm., $n^{25.5}_{\mathrm{D}}$ 1.5550; **semicarbazone**, m.p. 221–224° (from nitromethane), lit.[26] m.p. 221.5–223.5°.

2-Hydroxy-5,6,7,8-tetrahydro-1-naphthaldehyde.—The Reimer–Tiemann reaction[9] on 10 g. (0.068 mole) of 5,6,7,8-tetrahydro-2-naphthol[29,30] gave 1.0 g. of a mixture of hydroxyaldehydes, m.p. 79–92° (from aqueous alcohol). Three more recrystallizations afforded 0.25 g. (2.1%) of 2-hydroxy-5,6,7,8-tetrahydro-1-naphthaldehyde, m.p. 86.8–87.8°[20]; lit.[9] m.p. 86–87°. The neutral product,[31] m.p. 167–170°, also was obtained in low yield from the mother liquors.

1-Bromo-2-methoxy-5,6,7,8-tetrahydronaphthalene.—5,6,7,8-Tetrahydro-2-naphthol[29,30] was brominated[29] many times under a variety of conditions. Invariably the brominated product melted over a wide range, presumably because the desired bromonaphthol was contaminated with unbrominated phenol. Vacuum distillation failed to achieve a separation, and tedious fractional crystallization from acetic acid and methanol was required to obtain pure 1-bromo-5,6,7,8-tetrahydro-2-naphthol as tiny white needles, m.p. 75.5–77°, lit.[29] m.p. 74.5°. If the crude bromination product was methylated[32] in acetone solution according to the procedure described elsewhere in this paper, careful vacuum distillation achieved a fairly good separation of what apparently was brominated ether from unbrominated ether. Nevertheless, here again repeated distillation and fractional recrystallization from methanol were required to produce the pure bromoether as transparent blades, m.p. 40–40.5°,[33] lit.[9] m.p. 38–39°. Some bromoether also was obtained by brominating 2-methoxy-5,6,7,8-tetrahydronaphthalene in acetic acid.[34] The bromoether always crystallized very slowly unless its solution in methanol was "seeded." Although several large quantities of very pure bromoether were prepared, we were unable to eliminate the very tedious purification. Best results were obtained by methylating the impure bromophenol and concentrating purification efforts on the methylated product.

2-Methoxy-5,6,7,8-tetrahydro-1-acetonaphthone.[34]—A Grignard reagent was prepared (nitrogen atmosphere) in 55 ml. of ether from 1.33 g. (0.0547 g. atom) of magnesium, 9.87 g. (0.0410 mole) of pure 1-bromo-2-methoxy-5,6,7,8-tetrahydronaphthalene[5,9] and trace amounts of iodine and ethyl bromide. The nearly clear solution was stirred under reflux for about 1.5 hr., during which time the Grignard reagent suddenly precipitated and did not redissolve on adding 105 ml. of ether. After rapid addition of 4.95 g. (0.0270 mole) of dry cadmium chloride the mixture was stirred 2 hr. under reflux until a negative Gilman test was obtained. The ether was replaced by 180 ml. of dry benzene and the volume was adjusted to about 80 ml. by distillation. Acetyl chloride (3.89 g., 0.050 mole) in 60 ml. of benzene was added over 0.5 hr., and the resulting brown-red suspension was refluxed for 4 hr. The mixture was poured into ice-water and stirred with dilute sulfuric acid. The yellow benzene layer was separated and the aqueous layer extracted twice with ether. The combined extracts were washed with water, sodium hydroxide and water. Evaporation of the dried extract gave 7.24 g. (87%)[35] of the crude ketone as an oily yellow solid. One recrystallization from a small amount of methanol produced 2.74 g. of needles, m.p. 81.5–85°. A second recrystallization afforded 1.60 g. of feathery white needles, m.p. 84.5–85° (drops at 80.5°),[33] lit.[5] m.p. 81–82°.

2-Hydroxy-5,6,7,8-tetrahydro-1-acetonaphthone.[34]—The pure methoxyketone (1.75 g., 0.00858 mole) and 13 g. of aluminum chloride (Fisher reagent) were heated for 4 hr. in 40 ml. of dry benzene, the temperature being raised gradually from 45° to reflux. Gas evolution started at 50°, and refluxing occurred during the last 45 min. The very dark mixture was decomposed with ice and dilute hydrochloric acid. The orange-brown benzene layer was separated, the aqueous layer was extracted twice with ether, and the combined extracts were shaken twice with 2% sodium hydroxide. Acidification of the alkaline layer yielded 0.92 g. (56%)[36] of crude hydroxyketone, m.p. 110–115° (drops at 95°). One recrystallization from petroleum ether (b.p. 30–60°) produced 0.70 g. of transparent rods, m.p. 111.5–115.5° (drops at 105°). A second recrystallization afforded transparent rods[20] which melted sharply at 111–112°[33] and quickly resolidified to prisms, m.p. 115–116°. This polymorphism apparently was not observed by O'Farrell, *et al.*,[5] who recorded m.p. 112–113°.

Methyl 2-Methoxy-5,6,7,8-tetrahydro-1-naphthoate.—2-Methoxy-5,6,7,8-tetrahydro-1-naphthoic acid[9] (1.04 g., 0.00505 mole) was esterified with diazomethane to yield 1.07 g. (96%) of methyl ester, m.p. 42.5–46°. Several recrystallizations from aqueous methanol and from petroleum ether (b.p. 60–75°) produced transparent plates, m.p. 44.5–46°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.25; H, 7.20.

Methyl 2-Hydroxy-5,6,7,8-tetrahydro-1-naphthoate.—A solution of 1.07 g. (0.00486 mole) of the methoxyester in 105 ml. of dry, thiophene-free benzene containing 9 g. of aluminum chloride (Fisher reagent) was placed in a bath preheated to 57°. During 45 min. the bath temperature was raised to 82°, and the mixture then was refluxed for 0.5 hr. Gas evolution started at 63° and increased as the temperature was raised. The benzene became very dark during the first 0.5 hour of heating. The reaction mixture was worked up as described elsewhere in this report to yield an alkali-soluble oil (phenolic odor) which crystallized in the refrigerator to yield 0.87 g. (87%) of crude hydroxyester, m.p. 36–41.5° (drops at 30°).[33] Three recrystallizations from small amounts of methanol afforded transparent plates,[20] m.p. 42–43°, showing a light green color in methanol with ferric chloride.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 69.89; H, 6.84. Found: C, 70.09; H, 6.92.

3-Methoxy-5,6,7,8-tetrahydro-2-naphthaldehyde.[37]—A mixture of 25.4 g. (0.188 mole) of N-methylformanilide and 31.4 g. (0.206 mole) of phosphorus oxychloride was let to stand 0.5 hr. and then heated with 14.6 g. (0.090 mole) of 2-methoxy-5,6,7,8-tetrahydronaphthalene (b.p. 134–137° at 15 mm.) for 4.5 hr.[38] in a bath at 60–65°. Decomposition with ice and dilute hydrochloric acid gave a reddish-tan solid which was recrystallized from petroleum ether (b.p. 60–75°) to yield 5.95 g. of aldehyde, m.p. 51–52.5°, plus another 2.56 g., m.p. 48.5–51.5°, the total yield being 8.51 g. (50%). The analytical sample, m.p. 51.6–52°, was obtained by recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.71; H, 7.42. Found: C, 75.91; H, 7.33.

3-Hydroxy-5,6,7,8-tetrahydro-2-naphthaldehyde.[37]—To 2.0 g. (0.011 mole) of the methoxyaldehyde in 15 ml. of boiling glacial acetic acid 4 ml. of 48% hydrobromic acid was added during 5 min. The dark red mixture was refluxed until carbonization began (40 min.), then diluted to 200 ml. with water, and extracted 3 times with ether. The combined ether layers were extracted with 2 portions of 5% sodium hydroxide and the latter acidified to yield 0.40 g. (22%) of light tan solid, m.p. 52–55°. Two recrystallizations afforded the pure aldehyde,[20] m.p. 55.2–56.4° (lit.[9] m.p. 56–57°), deep blue color with ferric chloride in ethanol.

Evaporation of the ether layer containing neutral material yielded a dark solid which on recrystallization from aqueous

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(29) G. Schroeter, Svanoe, H. Einbeck, H. Geller and E. Riebensahm, *Ann.*, **426**, 83 (1922).

(30) Aldrich Chemical Co., Milwaukee, Wisc.

(31) R. Woodward, THIS JOURNAL, **62**, 1208 (1940).

(32) Compare with R. T. Arnold, *et al.* (ref. 9), and with M. P. O'Farrell, *et al.* (ref. 5).

(33) M.p. taken on a Köfler hot-stage.

(34) Compare O'Farrell, *et al.* (ref. 5).

(35) O'Farrell, *et al.* (ref. 5), reported an 18% yield of what apparently was the crude ketone. Our higher yield may have resulted from using a purer sample of the methoxy bromide.

(36) O'Farrell, *et al.* (ref. 5), listed no yield in their preparation.

(37) Consult the procedure (ref. 3c) used earlier for preparing similar compounds.

(38) Heating for 2.5 hr. gave a lower yield.

ethanol left 0.80 g. (40%) of unreacted methoxyaldehyde, m.p. 50–55°, no color with ferric chloride in ethanol.

3-Methoxy-5,6,7,8-tetrahydro-2-naphthoic Acid.—To 0.45 g. (0.0024 mole) of the methoxyaldehyde in 25 ml. of acetone (A.C.S.) 0.24 g. (0.0020 mole) of magnesium sulfate in 25 ml. of water was added. Potassium permanganate (0.62 g.) in 22 ml. of water was introduced dropwise at 50° during 1 hr. The filtered mixture was acidified to give 0.32 g. (65%) of tan powder, m.p. 108–112°. Recrystallization from aqueous methanol afforded white crystals, m.p. 116–117°; no depression on mixing with authentic methoxyacid prepared[9] from 3-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid *via* the methyl ester of the methoxyacid.

Anal. Calcd. for $C_{12}H_{14}O_3$: neut. equiv., 206. Found: neut. equiv., 209.

Preparations without the magnesium sulfate gave lower yields as did those in which aqueous suspensions of the aldehyde were used. When the aldehyde was heated for 40 min. at 55–85° with silver oxide[39] 70% of the starting material was recovered unchanged.

3-Hydroxy-5,6,7,8-tetrahydro-2-acetonaphthone.[5]—On mixing 32.1 g. (0.240 mole) of aluminum chloride (Fisher reagent) with 35.0 g. (0.184 mole) of 5,6,7,8-tetrahydro-2-naphthyl acetate[29] (b.p. 155–159° at 15 mm.) a vigorous reaction occurred immediately, and hydrogen chloride was evolved rapidly. The tan solid obtained on decomposition of the cooled mixture with ice and hydrochloric acid was recrystallized from methanol to yield 20.7 g. (59.1%) of pale yellow crystals. Another recrystallization produced 18.6 g. (53.1%)[40] of hydroxyketone as 4 fractions, the first two (9.4 g.) melting at 72–73° and the last two (9.2 g.) at 70.5–72.5°; a blue-green color was obtained in alcohol with ferric chloride.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 75.77; H, 7.42. Found: C, 75.97; H, 7.51.

The sodium salt of this hydroxyketone is quite insoluble even in dilute alkali, but is readily soluble in water. The methanol liquors from the crude ketone contained a heavy oil (5.2 g.) from which some tetrahydronaphthol was isolated.

3-Methoxy-5,6,7,8-tetrahydro-2-acetonaphthone.[37]—To a stirred solution of 25.2 g. of potassium hydroxide in 15 ml. of water, 16.8 g. (0.088 mole) of the hydroxyketone and 25.2 g. of dimethyl sulfate in 160 ml. of acetone were added during 65 min. Water (70 ml.) was added and the mixture heated (steam-bath) for 75 min., poured into water, and extracted with ether. Distillation of the dried extract gave 15.5 g. (86.1%) of oily yellow crystals which were recrystallized from petroleum ether (b.p. 60–75°) to produce 13.4 g. of pure methoxyketone, m.p. 41.5–42.5°, plus an additional 0.58 g., m.p. 40–41.5° (total yield 13.9 g., 77.4%), from the mother liquor.

Anal.[41] Calcd. for $C_{13}H_{16}O_2$: C, 76.42; H, 7.84. Found: C, 76.71; H, 8.05.

Preparations involving the alternate and portionwise addition of 20% potassium hydroxide and methyl sulfate were less satisfactory. The use of methyl sulfate with aqueous alkali and of methyl sulfate with sodium methoxide[42] proved to be unsatisfactory, the former because of insolubility of the sodium salt of the phenol.

4-Chloro-3-methoxy-5,6,7,8-tetrahydro-2-naphthoic Acid.—To 1.0 g. (0.0049 mole) of 3-methoxy-5,6,7,8-tetrahydro-2-acetonaphthone was added 45 ml. of potassium hypochlorite solution[21] (*ca.* 0.06 mole of hypochlorite) at 55°. The cloudy mixture was heated at 65–70° for 1.5 hr., during which time chloroform was evolved. The mixture was cooled to 50° and excess hypochlorite removed by addition of 2.4 g. of sodium bisulfite in 10 ml. of water. An exothermic reaction occurred. The oily crystals obtained on acidification were triturated with petroleum ether (b.p. 35–60°) to give 0.6 g. of solid, m.p. 131–141°. Two recrystallizations from aqueous ethanol afforded 0.40 g. (33%) of white crystals, m.p. 152–154°. The analytical sample, m.p. 154–156°, was obtained by another recrystallization from ethanol.

Anal. Calcd. for $C_{12}H_{13}O_3Cl$: C, 59.87; H, 5.44; Cl, 14.73; mol. wt., 241; neut. equiv., 241. Found: C, 60.13; H, 5.27; Cl, 14.05; mol. wt. (Rast), 237; neut. equiv., 235.[43]

This reaction was performed under a variety of conditions, but in most cases only a very low yield of chlorinated acid was obtained. The yield was erratic even in preparations performed under the same conditions.

Methyl 4-Chloro-3-methoxy-5,6,7,8-tetrahydro-2-naphthoate.—Methylation of 1.34 g. (0.0056 mole) of the chloro acid with diazomethane afforded 0.74 g. (52%) of ester as a yellow oil. The analytical sample, m.p. 43.6–44.0°, was prepared by four recrystallizations from petroleum ether (b.p. 30–65°).

Anal. Calcd. for $C_{13}H_{15}O_3Cl$: C, 61.29; H, 5.93. Found: C, 60.82, 60.62; H, 6.18, 5.66.

Methyl 3-Methoxy-5,6,7,8-tetrahydro-2-naphthoate.—To 300 ml. of potassium hypochlorite solution[21] (*ca.* 0.46 mole of hypochlorite) at 11° was added, with stirring, 2.0 g. (0.0098 mole) of 3-methoxy-5,6,7,8-tetrahydro-2-acetonaphthone in 60 ml. of methanol. The mixture was stirred for 5 hr., during which time the temperature rose to 30°. Filtration produced 0.92 g. of light yellow crystals, recrystallization of which from methanol afforded 0.34 g. of white crystals, m.p. 99.5–101.5°, plus an additional 0.06 g., m.p. 97–99°, from the mother liquor, the total yield being 0.40 g. (19%). The larger fraction was recrystallized twice to yield the analytical sample, m.p. 100.5–101.5°; no depression in m.p. was observed on mixing with authentic methyl 3-methoxy-5,6,7,8-tetrahydro-2-naphthoate prepared[9] from authentic 3-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27; O, 21.82. Found: C, 71.52; H, 7.25; O, 20.96.

Methyl 3-Hydroxy-5,6,7,8-tetrahydro-2-naphthoate.—Methyl 3-hydroxy-2-naphthoate was reduced incompletely over Raney nickel at 50° and 50 lb./in.^{2} The desired tetrahydro ester finally was obtained by the method used earlier for the ethyl ester.[9] Thus, a solution of 20.2 g. (0.100 mole) of methyl 3-hydroxy-2-naphthoate in 50 ml. of methanol containing a small amount of W-7 Raney nickel[44] was shaken with hydrogen for 2 hr. at 150° and 1100 lb./in.^{2}. The filtered mixture, on cooling, gave 7.0 g. (34%) of colorless crystals, m.p. 39.2–41.4°. Three recrystallizations from methanol afforded the spectral sample, m.p. 40–41°, lit.[29] m.p. 42°.

3-Hydroxy-5,6,7,8-tetrahydro-2-naphthoic Acid.—3-Hydroxy-2-naphthoic acid was not reduced in absolute alcohol over W-7 Raney nickel at 65° and a hydrogen pressure of 50 lb./in.^{2} or at 150° and 1100 lb./in.^{2}. Reduction with aluminum–nickel alloy in alkaline solution[45] was attempted many times using a variety of conditions on purified 3-hydroxy-2-naphthoic acid, but an impure product always was obtained. Of the many purification methods which were attempted, none produced anything more than an extremely low yield of the tetrahydro acid.

Saponification of methyl 3-hydroxy-5,6,7,8-tetrahydro-2-naphthoate afforded an 84% yield of hydroxyacid, m.p. 180.5–182°, lit.[9] m.p. 180–182°; the **acetate** melted at 150–152° (from ethyl acetate), lit.[29] m.p. 142–143°.

Infrared Work.—Spectra were obtained as described previously.[3c]

Acknowledgments.—The authors take pleasure in thanking the Research Corporation for grants to I. M. H. supporting this work. Special thanks also are due to Messrs. Donald Worth and James B. Smith for performing some of the synthetic work, to Mr. Arthur Rosenthal for preparing the Raney nickel, and to Messrs. Robert L. Rutledge and James J. Brader for assistance with some of the infrared measurements.

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(39) I. A. Pearl, *Org. Syntheses*, **30**, 101 (1950).

(40) O'Farrell, *et al.* (ref. 5), reported a 55% yield of recrystallized ketone.

(41) Analysis by Dr. C. Tiedcke, Teaneck, N. J.

(42) D. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 198.

(43) Determined potentiometrically in our laboratories.

(44) H. R. Billica and H. Adkins, *Org. Syntheses*, **29**, 24 (1949).

(45) B. Whitman, O. Wintersteiner and E. Schwenk, *J. Biol. Chem.*, **118**, 792 (1937); D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942); D. Papa, E. Schwenk and H. Breiger, *ibid.*, **14**, 366 (1949).