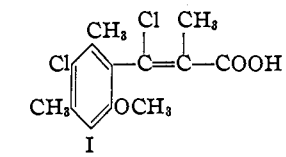
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

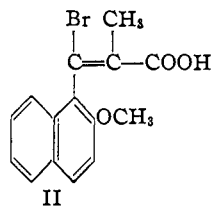
Restricted Rotation in Aryl Olefins. VI. Substituted β-(2,7-Dimethoxy-1-naphthyl)-α-methylacrylic Acids[1]

BY ROGER ADAMS, M. W. MILLER, F. C. MCGREW AND A. W. ANDERSON

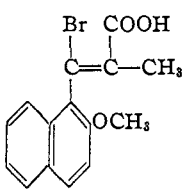
Failure to resolve the aryl olefins II, III, IV and V was reported in the preceding paper.[1] Compound I, on the other hand, was resolved[2] and an active form had a half-life period of 173 minutes in *n*-butanol at 44°. The difference between I and



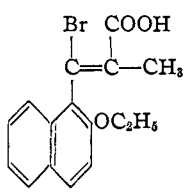
I



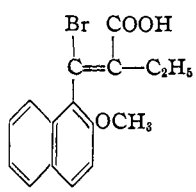
II



III

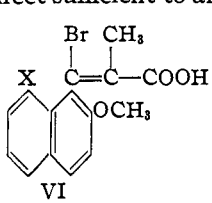


IV

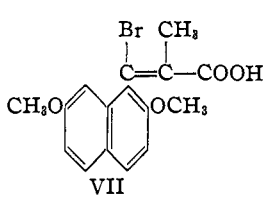


V

the other molecules lies primarily in the replacement of the methyl group in the 2-position of the benzene nucleus by the —CH= of an aromatic residue, thus allowing free rotation and resulting in non-resolvability of the molecules. The present investigation was undertaken to obtain molecules of the type shown in VI which resemble II, III, IV and V in all respects except for the additional group in the 8-position. Such a group should increase the interference and might result in a steric effect sufficient to allow resolution.

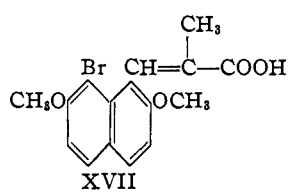


VI

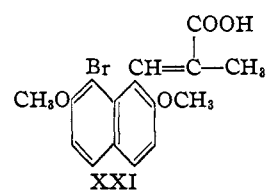


VII

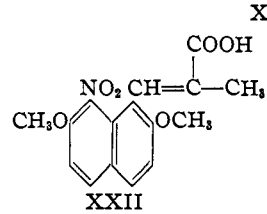
The synthetic problem of preparing such molecules was not simple. The approach selected was that involving the preparation of a compound (VII) by the general procedure used in the previous paper.[1] It contains a methoxyl group in the 7-position which should activate substitution in the 8-position and thus allow the formation of a molecule of the desired type (VI) after the substituent groups in the 1- and 2-positions have been introduced. Unfortunately, complications prevented the attainment of the proposed objective. The compounds actually obtained and studied are shown in formulas XVII, XXI and XXII. The syntheses of these compounds and the factors which interfered with the preparation of the substances particularly desired are described below.



XVII



XXI



XXII

2,7-Dihydroxynaphthaldehyde (VIII) was methylated to 7-methoxy-2-hydroxynaphthaldehyde (IX) which by means of the Perkin synthesis, using propionic anhydride and potassium propionate, was converted to 2-methyl-9-methoxy-4,3-β-naphthopyrone (X). This last product was formed also by another route; treatment of the 2,7-dihydroxynaphthaldehyde with propionic anhydride and potassium propionate led to the 2-methyl-9-propionoxy-4,3-β-naphthopyrone (XI) which was saponified readily to 2-methyl-9-hydroxy-4,3-β-naphthopyrone (XII), and then methylated to give compound X.

Upon nitration, the 2-methyl-9-methoxy-4,3-β-naphthopyrone (X) gave a mononitro product, 2-methyl-10-nitro-9-methoxy-4,3-β-naphthopyrone (XIII), and upon bromination, 2-methyl-10-bromo-9-methoxy-4,3-β-naphthopyrone (XIV). The position of the bromine atom was established as in the ring by direct bromination of 7-methoxy-2-hydroxynaphthaldehyde to 7-methoxy-8-bromo-2-hydroxynaphthaldehyde (XV) and conversion of this product by a Perkin synthesis to compound XIV.

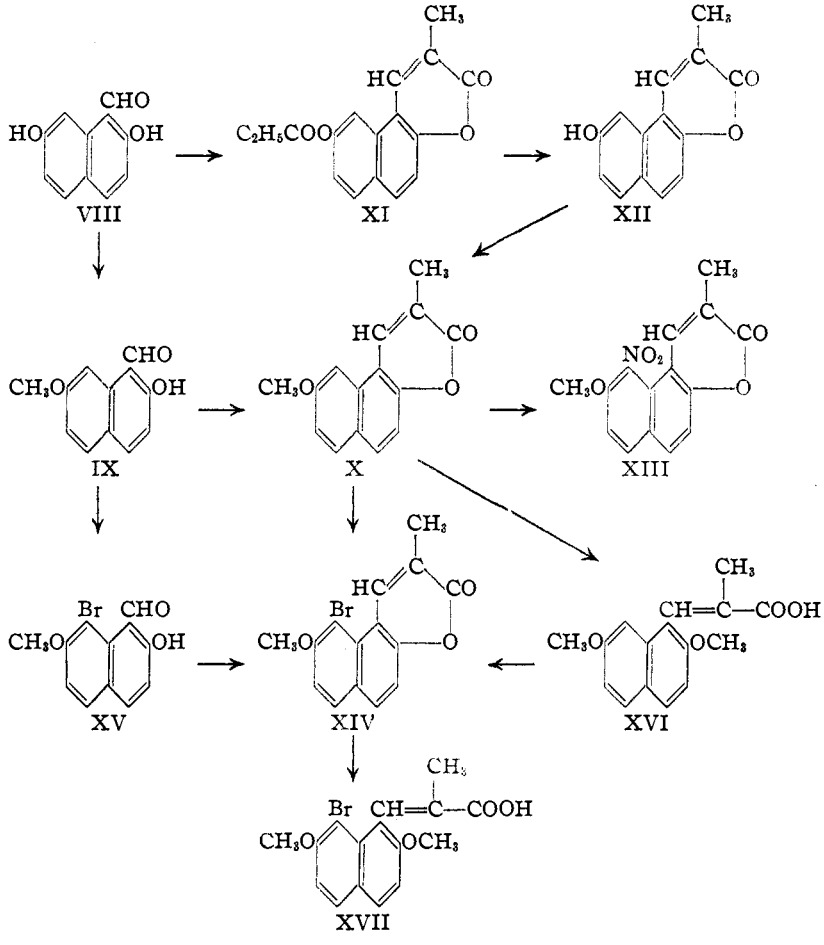
The 2-methyl-9-methoxy-4,3-β-naphthopyrone

(1) For previous paper, see Adams, Binder and McGrew, THIS JOURNAL, **64**, 1791 (1942).

(2) Adams and Binder, *ibid.*, **63**, 2773 (1941).

(X) was hydrolyzed and methylated to β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid (XVI). Upon attempted bromination of compound XVI, however, compound XIV was produced, demethylation and pyrone formation taking place simultaneously. On the other hand, the bromination product, β-(2,7-dimethoxy-8-bromonaphthyl)-α-methylacrylic acid (XVII) resulted upon hydrolysis and methylation of the corresponding pyrone (XIV).

CHART I



2,7-Dihydroxynaphthalene was methylated to 2,7-dimethoxynaphthalene (XVIII) into which an aldehyde group was introduced to give 2,7-dimethoxynaphthaldehyde (XIX). A Perkin synthesis with potassium propionate and propionic anhydride converted this aldehyde to β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid (XX). In contrast to compound XVI, this isomer (XX) brominates without demethylation and is converted to β-(2,7-dimethoxy-β-bromonaphthyl)-α-methylacrylic acid (XXI). Similarly, nitration gives the analogous nitro compound, β-(2,7-dimethoxy-8-nitronaphthyl)-α-methylacrylic acid (XXII).

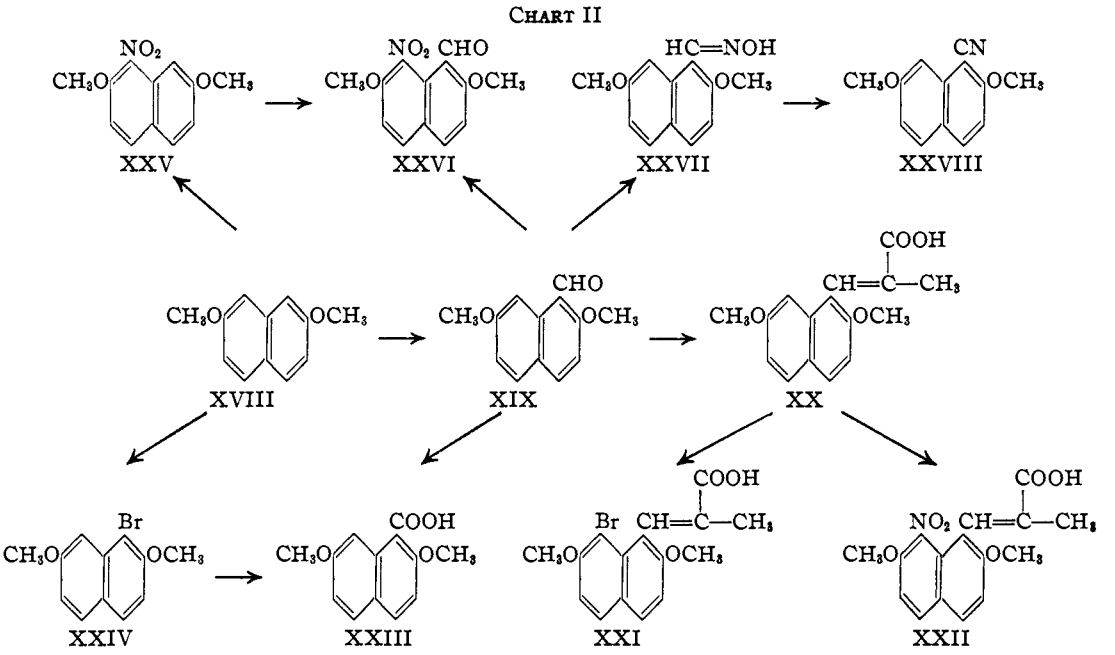
The position of the aldehyde group in 2,7-dimethoxynaphthaldehyde (XIX) was established by oxidation of the molecule to 2,7-dimethoxynaphthoic acid (XXIII). This same acid was obtained by bromination of 2,7-dimethoxynaphthalene (XVIII) to 2,7-dimethoxybromonaphthalene (XXIV) and replacement of the halogen by a carboxyl group through the corresponding lithium derivative and carbonation. Nitration of 2,7-dimethoxynaphthalene gave 2,7-dimethoxy-8-nitronaphthalene (XXV), into which an aldehyde group was introduced to form 2,7-dimethoxy-8-nitronaphthaldehyde (XXVI). This latter product was prepared also by direct nitration of 2,7-dimethoxynaphthaldehyde.

The 2,7-dimethoxynaphthaldehyde (XIX) formed an oxime (XXVII) which dehydrated to the nitrile (XXVIII). This nitrile proved very resistant to hydrolysis.

The configuration of compound XVI is assigned on the basis of its formation from the pyrone; the brominated product (XVII) probably has a similar structure. The carboxyl is *cis* to the 2-methoxyl group. The compounds XX and XXI are stereoisomeric with XVI and XVII prepared from 2,7-dimethoxynaphthaldehyde and consequently are written with the carboxyl group *trans* to the 2-methoxyl group. This conforms to the results previously reported on analogous compounds derived from β-methoxynaphthaldehyde.[1] Compounds XX and XXI are more soluble in organic solvents than their geometric isomers (XVI and XVII). By ultraviolet irradiation compound XVI is converted to its isomer (XX).

The position taken by the bromine atom in the bromination of compound X was shown to be in

CHART II



the naphthalene nucleus. Similarly, the bromine probably entered the 8-position in bromination of compound XX, although this was not proved. Compound XXI could not be brominated further which confirms the probability that the 8-position is substituted and indicates the steric influence of an 8-substituent upon the reactivity of the aliphatic double bond. Compound XVII, in which the position of the bromine atom is established, also could not be brominated. In an attempt to prove the nitro group to be in the 8-position in compound XXII, an effort was made to synthesize structure XXII by conversion of the nitroaldehyde (XXVI) to the acrylic acid; the Perkin condensation did not take place under the conditions usually used for effecting such a synthesis.

The acids XVII, XXI, and XXII were converted into alkaloidal salts and resolution attempted. Only a single salt was obtained in each instance and decomposition resulted in inactive acids. A study of Stuart models of these acids leads to the prediction that restricted rotation should exist in these molecules in spite of the presence of a hydrogen atom on the carbon atom attached to the ring, a condition which previously has been shown always to result in molecules with no restricted rotation.[3] The unreliability of accurate deductions from Stuart models is illustrated again.

(3) Maxwell and Adams, THIS JOURNAL, **52**, 2959 (1930).

Experimental

2,7-Dihydroxynaphthaldehyde (VIII).—A mixture of 20 g. of 2,7-dihydroxynaphthalene, 22 g. of anhydrous zinc cyanide and 200 cc. of dry ether was cooled with ice. Agitation was started and a brisk stream of dry hydrogen chloride was bubbled through until the yellow aldimine hydrochloride was precipitated completely. This usually took about an hour. The yellow precipitate was dissolved in 500 cc. of 30% ethanol and heated on a steam cone. During the hydrolysis, the excess ether distilled and the remaining solution was treated with Norite and filtered. On cooling the filtrate, it became semi-solid with greenish yellow crystals of the aldehyde; yield, 18 g. This product was pure enough for subsequent use. It can be recrystallized from 30% ethanol; yellow crystals; m. p. 159–160° (cor.). Morgan and Vining[4] report m. p. 159.5–160.5° when crystallized from benzene.

7-Methoxy-2-hydroxynaphthaldehyde (IX).—A solution of 10 g. of 2,7-dihydroxynaphthaldehyde in 100 cc. of water containing 6 g. of potassium hydroxide was stirred and 10 g. of dimethyl sulfate added over a period of two hours. The reaction mixture was filtered and the filtrate acidified with dilute sulfuric acid. The precipitate thus obtained was purified by crystallization from ethanol; white crystals, m. p. 128–129° (cor.); yield 6.2 g. (60%).

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.95. Found: C, 71.30; H, 5.30.

2-Methyl-9-methoxy-4,3-β-naphthopyrone (X).—A mixture of 2 g. of 7-methoxy-2-hydroxynaphthaldehyde, 2 g. of fused potassium propionate and 10 cc. of propionic anhydride was refluxed for six hours at 175–180°. After cooling, the excess anhydride was decomposed with 10% aqueous potassium hydroxide, the solid filtered by suction and recrystallized from ethanol; long silky needles, m. p.

(4) Morgan and Vining, *J. Chem. Soc.*, **119**, 177 (1921).

186.5–187.5°. The substance showed a blue fluorescence in ethanol solution.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.04. Found: C, 74.94; H, 4.93.

2-Methyl-9-propionoxy-4,3-β-naphthopyrone (XI).—A mixture of 10 g. of 2,7-dihydroxynaphthaldehyde, 10 g. of freshly fused potassium propionate and 20 g. of propionic anhydride was refluxed for twenty-four hours. After cooling, the excess of propionic anhydride was decomposed with 10% aqueous sodium hydroxide and the pink precipitate filtered, washed well with water and dried. It was purified by crystallization from ethanol; slightly pinkish crystals, m. p. 161–162° (cor.); yield, 8.5–9 g. (60%).

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.35; H, 5.02. Found: C, 72.32; H, 5.12.

2-Methyl-9-hydroxy-4,3-β-naphthopyrone (XII).—A mixture of 25 g. of 2-methyl-9-propionoxy-4,3-β-naphthopyrone and 200 cc. of 25% aqueous potassium hydroxide was refluxed for three hours. The solution was filtered while still hot and the filtrate upon cooling deposited a yellow precipitate of the potassium salt. The salt was not isolated but the mixture was acidified with 50% sulfuric acid and a purplish, gelatinous precipitate formed. It was purified by a crystallization from ethanol followed by solution in aqueous potassium hydroxide, refluxing the solution with Norite, precipitation with acid and finally crystallization again from ethanol; white needles, m. p. 263–266° (bloc Maquenne); yield, 18 g. (80%).

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.47. Found: C, 74.22; H, 4.62.

2-Methyl-9-methoxy-4,3-β-naphthopyrone (X).—To a mixture of 20 g. of 2-methyl-9-hydroxy-4,3-β-naphthopyrone and 100 cc. of dioxane, which was mechanically stirred until complete solution had taken place, was added 24 g. of pure dimethyl sulfate. Over a period of five to six hours, 150 cc. of 1% aqueous potassium hydroxide was allowed to run in. Colorless platelets of the product separated as the reaction proceeded. The compound was purified by recrystallization from ethanol; long silky needles, identical with the product prepared directly from 7-methoxy-2-hydroxynaphthaldehyde.

A third procedure was by direct conversion of the propionoxy compound to the methyl ether by the general method of Nierenstein.[5]

A solution of 0.5 g. of 2-methyl-9-propionoxy-4,3-β-naphthopyrone and 1 cc. of piperidine in 20 cc. of dioxane was treated with an ether solution of diazomethane and the mixture allowed to stand at room temperature for about three weeks. Upon evaporation nearly to dryness and addition of water a solid precipitated. This was purified by crystallization from ethanol. Unchanged material was first recovered. The more soluble portion proved to be the 9-methoxy derivative; yield, 0.1 g. The balance of the pyrone was recovered.

2-Methyl-10-nitro-9-methoxy-4,3-β-naphthopyrone (XIII).—To a suspension of 0.5 g. of 2-methyl-9-methoxy-4,3-β-naphthopyrone in 8 cc. of glacial acetic acid was added 1 cc. of nitric acid (sp. gr. 1.42). After shaking thoroughly, the reaction mixture was allowed to stand for one hour. The colorless crystals of the pyrone dissolved and yellow crystals separated. They were purified from ethanol, m. p. 276–278° (cor.); yield, 0.3 g. (50%).

Anal. Calcd. for $C_{15}H_{11}O_5N$: N, 4.90. Found: N, 4.74.

2-Methyl-10-bromo-9-methoxy-4,3-β-naphthopyrone (XIV).—To a solution of 10 g. of 2-methyl-9-methoxy-4,3-β-naphthopyrone in 150 cc. of chloroform was added 6.66 g. of bromine in 50 cc. of chloroform. The mixture was then placed in an icebox overnight. The hydrogen bromide was removed by a stream of air bubbled through the solution, then the chloroform was distilled. The red solid residue was washed with ethanol, then with dilute aqueous potassium hydroxide, and finally with water. It was purified by recrystallization from ethanol; white needles m. p. 218–219° (cor.); yield, 12 g. (91%).

Anal. Calcd. for $C_{15}H_{11}O_3Br$: C, 56.50; H, 3.45. Found: C, 56.11; H, 3.49.

The same product was made from 8-bromo-7-methoxy-2-hydroxynaphthaldehyde (XV) described below. A mixture of 0.25 g. of the bromoaldehyde, 0.25 g. of potassium propionate and 2 g. of propionic anhydride was allowed to react according to the procedure used for similar compounds previously described. It proved to be identical with the compound prepared by bromination of the bromine-free pyrone.

A third method for synthesis of this compound was also found. To a solution of 0.25 g. of the less-soluble β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid (XVI), described below, in 25 cc. of carbon tetrachloride was added 0.117 g. of bromine dissolved in 5 cc. of carbon tetrachloride. The residue after evaporation of the solvent was alkali-insoluble and crystallized as colorless needles from ethanol, m. p. 218–219° (cor.).

7-Methoxy-8-bromo-2-hydroxynaphthaldehyde (XV).—To a solution of 5 g. of 7-methoxy-2-hydroxynaphthaldehyde in 200 cc. of carbon tetrachloride was dropped in slowly with stirring 4.25 g. of bromine in 25 cc. of carbon tetrachloride. After stirring for one hour the solution was washed with aqueous sodium bisulfite. The carbon tetrachloride was distilled until the solution was clear and then evaporated completely with a stream of air. The product was recrystallized from methanol; flaky yellow crystals, m. p. 97–99° (cor.); yield 4 g. (57%).

Anal. Calcd. for $C_{12}H_9O_3Br$: C, 51.27; H, 3.23 Found: C, 50.63; H, 3.18.

Less-soluble β-(2,7-Dimethoxynaphthyl)-α-methylacrylic Acid (XVI).—A mixture of 5 g. of 2-methyl-9-methoxy-4,3-β-naphthopyrone (X) and 5 g. of potassium hydroxide dissolved in 75 cc. of absolute ethanol was heated for about twenty minutes until complete solution had taken place. On cooling, long yellow needles of the potassium salt crystallized and were filtered. The potassium salt thus obtained was dissolved in 200 cc. of 5% aqueous potassium hydroxide. Over a period of four days with constant stirring at room temperature, 25 g. of dimethyl sulfate was added. If the dimethyl sulfate was added too rapidly, the unmethylated lactone precipitated. After complete addition, the red solution containing a small amount of precipitate was made acid to congo red with dilute sulfuric acid, then basic with 20% aqueous potassium hydroxide.

(5) Nierenstein, THIS JOURNAL, **52**, 4012 (1930).

The precipitate (about 2.3 g.) of unchanged lactone and methyl ether methyl ester separated and was filtered. The filtrate was acidified with dilute sulfuric acid whereupon there formed a gummy precipitate of the compound with only the phenolic group methylated. The mixture of lactone and methyl ether methyl ester was refluxed for one hour with 50 cc. of 20% aqueous potassium hydroxide, acidified and finally again made alkaline. This procedure served to give a precipitate of pyrone, the filtrate containing the potassium salt of the ether acid. Upon acidification of the filtrate, the ether acid was obtained and combined with the same material obtained in the earlier part of the procedure. It was purified by crystallization from ethanol; white needles, m. p. 158–159° (cor.); yield, 2.5 g. (44%).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88; neut. equiv., 272. Found: C, 70.64; H, 6.08; neut. equiv., 272.

Less-soluble β-(2,7-Dimethoxy-8-bromonaphthyl)-α-methylacrylic Acid (XVII).—The same procedure as used in other hydrolyses and methylations was employed with 2-methyl - 10 - bromo - 9 - methoxy - 4,3 - β - naphthopyrone (XIV). From 14.5 g. of bromopyrone was obtained 12 g. of crude product which after several recrystallizations from ethanol followed by crystallization from a mixture of chloroform and petroleum ether (b. p. 60–110°) was pure; white crystals, m. p. 166° (cor.) with decomposition; yield, 7.5 g. (47.5%).

Anal. Calcd. for $C_{16}H_{15}O_4Br$: C, 54.69; H, 4.27. Found: C, 54.67; H, 4.49.

Attempted Resolution of Compound XVII.—From 7 g. of β - (2,7 - dimethoxy - 8 - bromonaphthyl) - α - methylacrylic acid and 6.5 g. of quinine in 200 cc. of ethyl acetate was deposited 7.3 g. of salt on cooling. This and subsequent fractions and also the recrystallized salts all had the same rotation. No mutarotation was observed in the salt solutions and decomposition of the salts resulted in an inactive acid; m. p. of salt, 98–99° (cor.).

Anal. Calcd. for $C_{16}H_{15}O_4Br \cdot C_{20}H_{24}O_2N_2$: C, 64.00; H, 5.81. Found: C, 63.78; H, 5.99. *Rotation.* 0.0501 g. made up to 25 cc. with ethyl acetate at 28° gave α_D −0.26°; *l*, 2; $[\alpha]^{28}D$ −64.8°.

2,7-Dimethoxynaphthaldehyde (XIX).—To a solution of 10 g. of 2,7-dihydroxynaphthaldehyde (VIII) in 100 cc. of 10% aqueous potassium hydroxide was added slowly, with stirring, 10 cc. of dimethyl sulfate. The greenish gummy precipitate that formed was redissolved by addition to the reaction mixture of 25 cc. of 30% aqueous potassium hydroxide. This was followed by a slow addition of dimethyl sulfate until the solution was acid. The solid was filtered and washed with dilute aqueous sodium hydroxide, then purified by crystallization from methanol; colorless needles, m. p. 99–100° (cor.); yield, 8 g. (69%). Acidification of the alkaline wash waters gave 1 g. of crude 7-methoxy-2-hydroxynaphthaldehyde.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.84; H, 5.45.

The product was made also by dissolving the 2,7-dihydroxynaphthaldehyde in toluene, adding solid potassium carbonate and then dimethyl sulfate, or by the zinc cyanide–hydrogen chloride method for 2,7-dimethoxynaphthalene (XVIII).

The semicarbazone, prepared in ethanol, formed colorless needles from cellosolve; m. p. 247° (bloc Maquenne).

Anal. Calcd. for $C_{14}H_{15}O_3N_3$: C, 61.51; H, 5.54; N, 15.38. Found: C, 61.13; H, 5.39; N, 15.18.

More-soluble β-(2,7-Dimethoxynaphthyl)-α-methylacrylic Acid (XX).—A mixture of 20 g. of dry crude 2,7-dimethoxynaphthaldehyde, 20 g. of fused potassium propionate and 80 cc. of propionic anhydride was refluxed at 170° for ten hours. Then a solution of 62 g. of potassium hydroxide in 200 cc. of water was added and the mixture heated until all but a small amount of tar dissolved. It was treated with Norite then acidified to congo red. The product was purified by crystallization from ethanol; colorless needles, m. p. 153° (cor.); yield, 12 g. (48%).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88. Found: C, 70.65; H, 6.00.

A mixed melting point of this isomer with the less-soluble gave a depression. This more-soluble geometric isomer was also formed by irradiation of the less-soluble acid (IX) with ultraviolet light.

In a 50-cc. quartz flask was placed a solution of 0.4 g. of the acrylic acid (XVI) in 40 cc. of ethanol. This solution was irradiated with ultraviolet light for sixty hours, then evaporated to dryness. The solid obtained was dissolved in dilute alkali, filtered and recovered by acidification. The compound was purified by several crystallizations from dilute ethanol; white, feathery needles; m. p. 152–153° (cor.). A mixed melting point with the parent compound was depressed to 127–129° while a mixed melting point with the more-soluble acid prepared from 2,7-dimethoxynaphthaldehyde gave no depression.

More-soluble β-(2,7-Dimethoxy-8-bromonaphthyl)-α-methylacrylic Acid (XXI).—A mixture of 8.6 g. of β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid (XX) in 150 cc. of chloroform and 20.6 cc. of solution of 25 g. of bromine in 100 cc. of chloroform was allowed to stand in the dark for sixty-five hours. The chloroform was evaporated with a stream of air and the residue purified from ethanol using Norite, then from acetic acid; colorless needles, m. p. 190° (cor.); yield, 5 g. (45%).

Anal. Calcd. for $C_{16}H_{15}O_4Br$: C, 54.69; H, 4.27; Br, 22.82. Found: C, 54.80; H, 4.34; Br, 23.28.

Attempted Resolution of Compound XXI.—From 5.4 g. of β-(2,7-dimethoxy-8-bromonaphthyl)-α-methylacrylic acid and 5.1 g. of quinine, dissolved in 200 cc. of ethanol, was obtained upon cooling 4.35 g. of salt. More salt was obtained by concentrating the solution, but the rotations on each fraction and also on the salts obtained by recrystallization of these fractions were essentially the same. No mutarotation was observed in the salt and decomposition of the salt resulted in an inactive acid; m. p. of salt 183–184° (cor.).

Anal. Calcd. for $C_{16}H_{15}O_4Br \cdot C_{20}H_{24}O_2N_2$: C, 64.00; H, 5.81. Found: C, 63.51; H, 5.96. *Rotation.* 0.0501 g. made up to 25 cc. with ethanol at 28° gave α_D −0.31°; *l*, 2; $[\alpha]^{28}D$ −77.4°.

From 62 g. of acid and 8.3 g. of brucine in 100 cc. of ethyl acetate was deposited 7.0 g. of salt on cooling. Subsequent fractions and all the salts obtained by recrystallization had identical rotations. No mutarotation was observed in the salt and decomposition of it resulted in an

inactive acid; m. p. of salt, 208–210° (cor.) with decomposition.

Anal. Calcd. for $C_{16}H_{15}O_4Br \cdot C_{23}H_{26}O_4N_2$: C, 62.81; H, 5.54. Found: C, 62.49; H, 5.42. *Rotation.* 0.0500 g. made up to 25 cc. with ethyl acetate at 28° gave α_D −0.21°; *l*, 2; $[\alpha]^{28}D$ −52.5°.

β-(2,7-Dimethoxy-8-nitronaphthyl)-α-methylacrylic Acid (XXII).—A suspension of 2 g. of more-soluble β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid (**XX**) in 20 cc. of glacial acetic acid was stirred rapidly and 2 cc. of concentrated nitric acid (sp. gr. 1.42) was dropped in slowly. After twenty minutes the starting material had been replaced by orange crystals. The mixture was cooled to 15° and filtered. The product was washed with water, extracted with boiling ethanol to remove color and then crystallized from acetic acid; yellow microcrystals; m. p. 197–198°; yield, 1.2 g. (50%).

Anal. Calcd. for $C_{16}H_{15}O_6N$: N, 4.42. Found: N, 4.86.

Attempted Resolution of Compound XXII.—This compound was converted to its quinine salt by mixing equivalent amounts of acid and base in an equal mixture of dioxane and ethanol. Five fractions were isolated by evaporation of the solvent and filtration at intervals. All five fractions gave essentially the same melting point and rotation and upon decomposition at 0° with 2 *N* hydrochloric acid only an optically inactive product was isolated; white crystals; m. p. 156°.

Anal. Calcd. for $C_{36}H_{39}O_8N_3$: N, 6.55. Found: N, 6.26. *Rotation.* 0.1482 g. made up to 10 cc. with pyridine at 0° gave α_D −0.508°; *l*, 1; $[\alpha]^0D$ −34.3°.

2,7-Dimethoxynaphthoic Acid (XXIII).—A mixture of 5 g. of 2,7-dimethoxynaphthaldehyde and a solution of 2.5 g. of potassium permanganate and 0.5 g. of sodium carbonate in 100 cc. of water was stirred for one hour at room temperature until the permanganate decolorized. The manganese dioxide was filtered and the alkaline filtrate on acidification gave the product. It was purified by crystallization from dilute ethanol; colorless needles, m. p. 112–113° (cor.); yield, poor.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.30; H, 5.18; neut. equiv., 232. Found: C, 67.50; H, 5.39; neut. equiv., 230.

The same compound was prepared from 2,7-dimethoxybromonaphthalene described below. To 0.200 g. of lithium in 50 cc. of dry ether was added 2.8 g. of butyl chloride and the reaction was stirred for one hour. A solution of 5 g. of 2,7-dimethoxybromonaphthalene in 40 cc. of dry ether was then added and the stirring continued for thirty minutes. The ether solution was cooled to 0° and carbonated with dry-ice chips. After warming to room temperature the addition compound was decomposed with iced hydrochloric acid and extracted several times with ether. The ether layer was extracted with dilute sodium hydroxide, the alkaline layer then acidified and the product filtered. It was purified by recrystallization from dilute ethanol; white needles, m. p. 112–113° (cor.); yield, 2.9 g. (68%). A mixed melting point of this compound with that obtained by the oxidation gave no depression.

2,7-Dimethoxybromonaphthalene (XXIV).—A solution of 10 g. of 2,7-dimethoxynaphthalene in 50 cc. of chloroform was brominated by slowly dropping in a solution of 8.5 g. of bromine in 20 cc. of chloroform. The reaction mixture was washed with water and evaporated to dryness. The pinkish residue was recrystallized from methanol; colorless crystals, m. p. 88–89° (cor.); yield, 13 g. (91%).

Anal. Calcd. for $C_{12}H_{11}O_2Br$: C, 53.92; H, 4.12; Br, 29.97. Found: C, 53.82; H, 4.07; Br, 30.29.

2,7-Dimethoxy-8-nitronaphthaldehyde (XXVI).—Into a suspension of 1 g. of 2,7-dimethoxynaphthaldehyde in 10 cc. of glacial acetic acid was dropped slowly with vigorous stirring 0.5 cc. of nitric acid (sp. gr. 1.42). After two hours the solution was poured into water. The precipitate was purified from acetic acid; yellowish crystals, m. p. 190° (cor.); yield, 0.8 g. (65%).

Anal. Calcd. for $C_{13}H_{11}O_5N$: C, 59.75; H, 4.25; N, 5.36. Found: C, 59.55; H, 4.17; N, 5.49.

A second method[6] involved the introduction of an aldehyde group into the 2,7-dimethoxy-8-nitronaphthalene (**XXV**). Into a mixture of 16.8 g. of 2,7-dimethoxy-8-nitronaphthalene (**XXV**), 29.5 g. of zinc cyanide and 84 g. of benzene, dry hydrogen chloride was passed for one hour. Then 25 g. of powdered anhydrous aluminum chloride was added and hydrogen chloride passed in for six hours. The mixture was decomposed by refluxing with dilute hydrochloric acid, cooled and filtered. The product was dried and extracted with boiling toluene to remove the product from tar. From the toluene crystals formed. They were further purified from ethanol; tan needles, m. p. 190° (cor.); yield, 4.7 g. (25%).

This product could not be made to condense in the Perkin reaction with potassium propionate and propionic anhydride.

2,7-Dimethoxynaphthaldoxime (XXVII).—A mixture of 0.5 g. of hydroxylamine hydrochloride in 3 cc. of water, 1.5 g. of 2,7-dimethoxynaphthaldehyde in 15 cc. of dioxane and 5 cc. of water, and 0.6 g. of sodium acetate was heated for twenty minutes on a steam-bath. After cooling, a precipitate formed. It was purified from ethanol; colorless prisms, m. p. 181–182° (cor.); yield, 1.5 g. (93%). The product was insoluble in aqueous alkali.

Anal. Calcd. for $C_{13}H_{13}O_3N$: N, 6.06. Found: N, 6.21.

2,7-Dimethoxynaphthonitrile (XXVIII).—A mixture of 1 g. of 2,7-dimethoxynaphthaldoxime and 5 cc. of acetic anhydride was refluxed for one hour. After addition of about 30 cc. of water, crystals appeared. These were purified from ethanol; colorless needles, m. p. 129° (cor.); yield, 0.9 g. (98%).

Anal. Calcd. for $C_{13}H_{11}O_2N$: N, 6.57. Found: N, 6.51.

No method was found for hydrolysis of the nitrile to the corresponding acid.

Summary

1. The following α-naphthylacrylic acids have been prepared: β-(2,7-dimethoxy-8-bromonaphthyl)-α-methylacrylic acids (both geometric isomers), and β-(2,7-dimethoxy-8-nitronaphthyl)-α-methylacrylic acid. None of these three compounds could be resolved.

(6) Weber, *Ber.*, **14**, 2206 (1881).

2. 7-Methoxy-2-hydroxynaphthaldehyde is converted by a Perkin synthesis to 2-methyl-9-methoxy-4,3-β-naphthopyrone. This compound brominates or nitrates in the 10-position. The resulting bromopyrone is hydrolyzed and methylated to β-(2,7-dimethoxy-8-bromonaphthyl)-α-methylacrylic acid. The unbrominated pyrone is also hydrolyzed and methylated and yields β-(2,7-dimethoxynaphthyl)-α-methylacrylic acid. Upon bromination of this acid, the halogen enters the 10-position, simultaneous hydrolysis of the methoxyl group occurs and pyrone formation results. The mode of preparation of the acrylic acid and the bromoacrylic acid leads to the conclusion that the carboxyl is *cis* to the 2-methoxyl group of the naphthalene nucleus.

3. These acids are both less soluble than the corresponding geometric isomers made directly by the appropriate Perkin reaction on 2,7-dimethoxynaphthaldehyde and bromination. No tendency to pyrone formation appears in this last reaction. The less-soluble acrylic acid is converted to the more soluble by irradiation with ultraviolet light.

URBANA, ILLINOIS RECEIVED APRIL 21, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Higher Hydrocarbons.[1] II. Five 11-Substituted Heneicosanes

BY F. C. WHITMORE, J. N. COSBY, W. S. SLOATMAN AND D. G. CLARKE

In the first paper[2] of this series the methods of preparation and the properties for seven alkyl substituted docosanes were given. A brief survey was made of the literature relating to the preparation of hydrocarbons containing more than twenty carbon atoms.

Whereas the first paper covered only isoparaffins, this paper reports on a variety of mixed type compounds. In this group of compounds the paraffin chain remains constant, but different type substituents are located in the 11-position. Changes of this type have considerably greater influence on the properties than moving a side chain or varying the molecular weight.[2]

Lubricating oil fractions in a given molecular weight range show large variations in properties. From the extensive studies[3] of Research Project No. 6 of the American Petroleum Institute these differences in the properties of the various lubricant fractions can only be due to differences in the hydrocarbon type. Therefore, this and future papers will describe series of hydrocarbons in which there are variations in hydrocarbon type. Generalizations on the properties and comparison with those in the literature will be published later.

Special emphasis has been placed on obtaining pure compounds. The requirements of purity and the methods of obtaining and determining the purity have been discussed in the earlier paper.[2]

The synthesis of these compounds involved the addition of an excess of *n*-decylmagnesium bromide to the following esters: ethyl caproate, methyl 2-ethylbutyrate, ethyl cyclopentanecarboxylate, and methyl benzoate. The resulting tertiary carbinols were dehydrated over copper sulfate in an atmosphere of nitrogen. The purified olefins were hydrogenated in a high pressure bomb over various nickel catalysts.

Only one intermediate, ethyl cyclopentanecarboxylate, presented any serious problem. Methods for its preparation in the literature did not seem promising. The method used in this work was the little used reaction[4] involving the addition of cyclopentylmagnesium bromide to an excess of ethyl carbonate.

With 11-phenyl-11-heneicosanol only one olefin can be obtained on dehydration. Therefore this was isolated and purified as usual. However it is probably an inseparable mixture of the *cis*- and *trans*-isomers.

The selective hydrogenation of the olefinic double bond in the presence of the phenyl group as in the case of 11-phenylheneicosane required special study. It was found possible to carry out this hydrogenation if the olefin was first very carefully purified by distillation and passage through silica gel. The hydrogenation was then carried out at room temperature over very active Raney nickel at a pressure of 1500 to 1800 lb. per sq. in.

Table I is a summary of the important properties of these hydrocarbons. The methods used

(1) American Petroleum Institute Research Project No. 42.

(2) Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942).

(3) Mair, Willingham and Streiff, *Ind. Eng. Chem.*, **30**, 1256 (1938).

(4) Loder and Whitmore, THIS JOURNAL, **57**, 2727 (1935).