upon evaporation left mostly as a residue the triazole hydrochloride, m.p. 148° (acetone). The hydrochloride salt was converted to the triazole by solution in a minimum amount of water and treatment with 6 *N* sodium hydroxide to give product with m.p. 93–94° (lit.[16,18] m.p. 91°, 93–94°). Total yield of product was 2.75 g. (68.3%). An analytical sample prepared by slow evaporation of an aqueous solution has m.p. 92.5–93°.

Anal. Calcd. for $C_4H_7N_3S_2$: C, 29.80; H, 4.38; N, 26.07; S, 39.77. Found: C, 29.97; H, 4.58; N, 26.22; S, 39.57.

Dimethyl Dithioimidocarbonate Hydrochloride.[25]—Addition of hydrogen chloride to about equal amounts of methyl mercaptan and methyl isothiocyanate in chloroform at 0° afforded the crystalline product (87%), m.p. 158–159° dec.

4-Amino-3-(methylthio)-Δ^2-1,2,4-triazoline-5-thione (XVI).—To a solution of 3-thiocarbohydrazide (5.31 g., 0.05 mole) in 75 ml. of water was added in small portions, over a 10-min. period, dimethyl dithioimidocarbonate hydrochloride with stirring. This reagent slowly dissolved with a steady evolution of methyl mercaptan. After 25 min., a solid began to precipitate. The thick paste which was present after 2 hr. was filtered to give 4.31 g., m.p. 174–208° (capillary). The filtrate was evaporated to dryness; the residue and product combined and recrystallized from a minimum amount of water to give 4.91 g., m.p. 186–190° (60.5%). Recrystallization again from water gave white fluffy needles, m.p. 197–197.5°.

Anal. Calcd. for $C_3H_6N_4S_2$: C, 22.21; H, 3.73; N, 34.54; S, 39.53. Found: C, 22.20; H, 4.34; N, 34.33; S, 39.43.

The benzylidene derivative (XVII) prepared at room temperature in ethanol containing a trace amount of hydrochloric acid had m.p. 205–207°.

Anal. Calcd. for $C_{10}H_{10}N_4S_2$: C, 47.99; H, 4.03; N, 22.39; S, 25.62. Found: C, 48.35; H, 4.23; N, 22.27; S, 25.58.

3-Methylthio-Δ^2-1,2,4-triazoline-5-thione (XVIII) and 3,3′-Dithiobis[5-(methylthio)-4H-1,2,4-triazole] (XIX).—XVI (4.05 g., 0.25 mmole) was dissolved in 250 ml. of water containing 60 ml. of 1 *N* hydrochloric acid and warmed to 75° to effect solution. To the solution, which was cooled rapidly to 5–10° with stirring (slush formed), a solution of sodium nitrite (1.72 g., 0.25 mmole) in 50 ml. of water was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred at 5–10° for 15 min. and then allowed to warm to room temperature. A solid was removed and the filtrate was evaporated to dryness. The residual solid was extracted with boiling 95% ethanol several times to obtain additional product. The original precipitate was then dissolved in these combined extracts, the solution filtered, and three crops of crystals collected. Fractional crystallization of these crops from absolute ethanol and then acetone permitted the separation of three compounds. These were the triazolinethione, 0.85 g. (23.2%, least soluble absolute ethanol and acetone), the disulfide, 1.13 g. (30.9%), and unchanged starting material (most soluble). A final recrystallization of the triazolinethione from water gave white plates, m.p. 248–250° (lit.[16] m.p. 254°).

Anal. Calcd. for $C_3H_5N_3S_2$: C, 24.48; H, 3.42; N, 28.55; S, 43.56. Found: C, 24.47; H, 3.23; N, 28.45; S, 43.45.

A final recrystallization of the disulfide from absolute ethanol gave white prisms, m.p. 210–211° (lit.[16] m.p. 203°).

Anal. Calcd. for $C_6H_8N_6S_4$: C, 24.64; H, 2.76; N, 28.74; S, 43.85. Found: C, 24.88; H, 3.09; N, 28.75; S, 43.98.

Attempted Preparation of IV from 1-Thiocarbamylthiocarbohydrazide.—The hydrazide[22] (11.3 g.) in 50 ml. of concentrated hydrochloric acid was heated for 40 min. at 90°. This solution after evaporation to dryness left a solid residue which was recrystallized twice from water to give tan needles, 1.1 g., m.p. 228–231° dec. Sublimation gave raised m.p. 230–232° dec., no melting point depression upon admixture with authentic 2-amino-Δ^2-1,3,4-thiadiazoline-5-thione.[26] The infrared spectra of the two samples were identical.

Anal. Calcd. for $C_2H_3N_3S_2$: C, 18.04; H, 2.27; N, 31.56; S, 48.16. Found: C, 18.39; H, 2.24; N, 30.92; S, 48.38.

1,1′-(Thiocarbonyl)bis(3-thiocarbohydrazide) (XXI).—3-Thiocarbohydrazide (50.0 g., 0.47 mole) and potassium ethyl xanthate (75.5 g., 0.47 mole) were heated in 500 ml. of 95% ethanol in a rocking autoclave at 100° for 2 hr. (instead of 5 hr.). The contents were washed out of the autoclave with water (300–500 ml.) and filtered from some gray solid. The latter was extracted with boiling water, and the extracts were combined with the original solution. The yellow solid (22.4 g.) which separated upon acidification of the reaction mixture was recrystallized from 500 ml. of hot water to give 18.0 g. (31.4%) of tan needles, m.p. 163–166°, with resolidification and remelting at 202–204° dec. Recrystallization from water three times gave a pure sample, m.p. 170–172° (203–205°).

Anal. Calcd. for $C_3H_{10}N_8S_3$: C, 14.17; H, 3.96; N, 44.07; S, 37.82. Found: C, 14.29; H, 4.18; N, 43.95; S, 37.77.

Acknowledgment.—The author is grateful to the following for their contributions: N. B. Colthup for interpreting the infrared spectra, Dr. C. A. Streuli for the nonaqueous titration data, and Dr. R. J. Magee, Dr. G. Berkelhammer, and Dr. R. W. Addor for helpful discussions.

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(25) We thank Dr. R. W. Addor of this laboratory for this preparation.

(26) L. L. Bambas, "Five-Membered Heterocyclic Compounds with Nitrogen and Sulfur or Nitrogen, Sulfur, and Oxygen," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 149-153.

Reaction of Eugenol with Synthesis Gas. Synthesis of 5,6,7,8-Tetrahydro-3-methoxy-2-naphthol

Franco Gaslini and Lucio Zion Nahum

Research Division Cartiera Vita Mayer and Company, Milano, Italy

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The reaction of eugenol with synthesis gas, in the presence of dicobalt octacarbonyl, leads to a ring closure with the formation of 5,6,7,8-tetrahydro-3-methoxy-2-naphthol. The isolation of 5,6-dihydro-3-methoxy-2-naphthol in short time experiments suggests a mechanism of ring closure with the latter as precursor. For testing purpose, 4-(3-methoxy-4-hydroxyphenyl)-1-butanol and 1(2H)-3,4-dihydro-6-methoxy-7-hydroxynaphthalenone were synthesized and treated under the same conditions.

In previous work from this laboratory,[1] it was shown that the reaction of wood or lignin with pressurized synthesis gas, in the presence of dicobalt octacarbonyl, provides good yields of phenols through an homogeneous phase catalyzed hydrogenation and/or hydroformylation of these materials.

In order to acquire some insight in the reaction occurring with wood, we have now treated eugenol and isoeugenol, as lignin model compounds, under "hydroformylation conditions."[2] Experiments with eugenol were carried out at 120–180° under a pressure of

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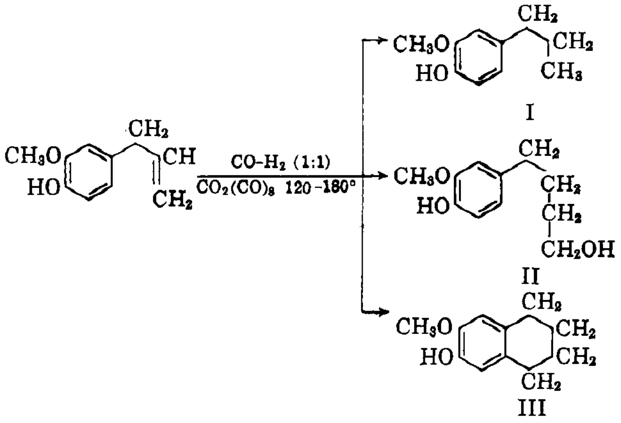
(1) F. Gaslini (to Vita Mayer and Co.), U. S. Patent 2,947,739 (Aug. 2, 1960).

(2) The term "hydroformylation conditions" has the same meaning as in I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).

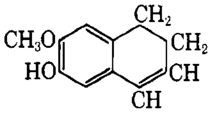
CHART A



200–400 atm. of 1:1 CO–H_2. When the reaction reached the point where gas consumption ceased (2.6–2.8 moles of gas/mole of eugenol), the products isolated were those shown in Chart A.

The yields were about 40% for 3-methoxy-4-hydroxy-1-*n*-propylbenzene (I), 30–40% for 5,6,7,8-tetrahydro-3-methoxy-2-naphthol (III), and 5% for 4-(3-methoxy-4-hydroxyphenyl)-1-butanol (II).

When the reaction was interrupted in its early stages (1.3–1.7 moles of gas/mole of eugenol), we obtained, in addition to the above-mentioned compounds, the hitherto unknown dihydronaphthol, IV, and a compound (V) which on the basis of its molecular weight and analysis could be formulated as $C_{20}H_{16}(OCH_3)_2(OH)_2$, a dimer of IV. The structure of V was not investigated further. In addition to the elemental and functional groups analysis, the identity of IV was established as follows: hydrogenation in alkaline solution with Raney alloy gave a compound melting at 81–81.5°, the infrared spectrum of which was identical with the spectrum of III. The infrared spectrum of IV reasonably indicated the existence of a double bond conjugated with the aromatic ring. In fact, we noted two bands at 3040 and 3004; a weak band at 1625 associated with a medium strong at 1585, indicating conjugation of the aromatic ring; reversed ratio of intensity between the bands at 1464 and 1445, the latter (cyclic CH_2 deformation) being stronger in III and the former in IV; and finally a medium intensity band at 750 cm.$^{-1}$, lacking in III, indicating *cis* CH=CH structure.



IV

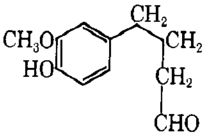
With isoeugenol, the reaction principally was straightforward hydrogenation; after 1 hr. at 140°, more than 80% of I was obtained; the remaining high boiling materials contained both phenolic and hydroxyl groups.

Discussion

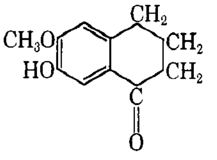
The high yields of I obtained from isoeugenol are in agreement with the well-known tendency of conjugated double bonds to undergo hydrogenation rather than hydroformylation.[3] In this connection we observed that 60% of eugenol was converted into isoeugenol when treated with dicobalt octacarbonyl and 150 atm. of pure CO at 180° for 1 hr.

The most interesting results seem to be the absence of carbonyl compounds before decobalting, the interrupted, low temperature experiments with eugenol, and the formation in high yields of compounds III and IV. The kind of ring closure leading to III and IV is rather unusual in the field of cobalt carbonyl-catalyzed reactions, since all previously reported examples involve the presence of an N or O hetero atom at the insertion point of the C unit.[4]

Since experiments with the butanol II and the dimer V, under the same conditions, gave no III or IV, the former compounds may be excluded as their precursors. Among other possible precursors, the aldehyde VI and the naphthalenone VII require consideration. Unfortunately, our attempts to prepare VI failed. VII was prepared through an eight-step synthesis and was treated under the same conditions as eugenol. A 50% yield of III was obtained, the remaining ketone being recovered unchanged. Thus it appears doubtful that VII could be an actual precursor, since carbonyl compounds were never found in the reaction products of our experiments. Incidentally, this criterion could perhaps hold also for the aldehyde VI, the complete disappearance of which would seem highly improbable in short time, low temperature reactions.[5]



VI



VII

On the other hand, the presence of the unsaturated compound IV in the early stage of the reaction strongly suggests that this ring closure occurs with the direct formation of IV, which actually gave III when hydrogenated either in "hydroformylation conditions" or in alkaline solution with Raney alloy. Following the up-to-date interpretation of the hydroformylation and related reactions,[4] we may think that cyclization occurs through some intermediates (Chart B).

Experimental

Reaction of Eugenol with Synthesis Gas. A. To Complete Absorption of Gas.—A 150-g. sample of freshly distilled eugenol, 50 ml. of benzene, and 3 g. of dicobalt octacarbonyl were charged to a stainless steel oscillating autoclave of 500-ml. capacity in which synthesis gas (1:1) then was compressed to 300 atm. The autoclave was heated at 180° and maintained at this temperature until gas absorption was complete (1 hr.). The reaction product was discharged and decobalted by heating for 2 hr. on a steam bath, followed by extraction with diluted hydrochloric acid.

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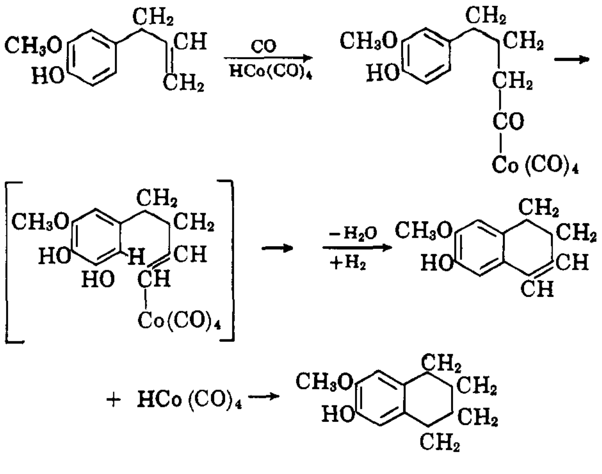
(3) I. Wender, H. W. Sternberg, and M. Orchin, "Catalysis," P. H. Emmett, Ed., Vol. V, Reinhold Publishing Corp., New York, N. Y., 1957, p. 86.

(4) H. W. Sternberg, R. Markby, and I. Wender, *Chim. Ind.* (Milan), **42**, 41 (1960).

(5) A referee asked us what is presumed to be the precursor of the butanol II. We do not at all exclude that aldehyde VI may be transitionally formed and hydrogenated in the high temperature experiments, giving butanol II. Aldehyde VI, in this enolic form, may be a possible intermediate for the ring closure to give IV; but, as carbonyl compounds are absent even before the decobalting experiments at low temperature, the point as to whether the aldehyde is formed, subsequently enolized, and finally cyclized becomes more formal than substantial.

CHART B



After evaporation of the solvent, 153 g. of a viscous oil was obtained, which was fractionated by distillation.

The first fraction (61.6 g.) boiled at 125–126° (13 mm.). Its benzoate had a melting point of 72.6–73° and did not depress the melting point of the benzoyl derivative of an authentic sample of 3-methoxy-4-hydroxy-1-propylbenzene, obtained by catalytic hydrogenation of eugenol.[6]

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.55; H, 7.03.

The second fraction distilled at 158–160° (13 mm.) giving 60 g. of a white crystalline compound which, after crystallization from *n*-heptane, was identified as 5,6,7,8-tetrahydro-3-methoxy-2-naphthol (III), m.p. 81.5–82°, lit.[7] m.p. 81–82°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; OCH_3, 17.39. Found: C, 74.12; H, 7.92; OCH_3, 17.47.

III, methylated with dimethyl sulfate, yielded 5,6,7,8-tetrahydro-3,4-dimethoxynaphthalene, m.p. 56.4–56.8°. It did not depress the melting point of an authentic sample prepared by Clemmensen reduction of 1(2H)-3,4-dihydro-6,7-dimethoxynaphthalenone.[8]

New derivatives of III are the benzoate, m.p. 109.5–110.3° (from ethanol), and 1-naphthylurethane, m.p. 145–145.5° (from ligroin).

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; OCH_3, 10.98. Found: C, 75.97; H, 6.41; OCH_3, 11.03.

Anal. Calcd. for $C_{22}H_{21}O_3N$: C, 76.06; H, 6.09; N, 4.03. Found: C, 76.15; H, 6.30; N, 4.10.

The third fraction, distilling at 150–160° (2.5 mm.), yielded 18 g. of a viscous liquid containing about 50% of 4-(3-methoxy-4-hydroxyphenyl)-1-butanol, which was identified through its bis-*p*-nitrobenzoate, melting at 124–126°; the melting point was not depressed on admixture with a sample obtained by synthesis.

B. Low Temperature, Controlled Absorption of Gas.—An 80-g. sample of eugenol, 100 ml. of benzene, 1.5 g. of dicobalt octacarbonyl, and 200 atm. of synthesis gas were charged in the autoclave and heated at 120°. When 1.7 moles of gas/mole of eugenol was absorbed, the reaction was stopped by cooling the autoclave. The reaction product was decobalted as previously described and distilled under a pressure of 2.5 mm., giving 22 g. of a fraction boiling at 145–150°, solid at room temperature. After repeated crystallizations from aqueous ethanol, colorless plates were obtained melting at 108–109°, which were identified as 5,6-dihydro-3-methoxy-2-naphthol (IV).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86; OCH_3, 17.58; OH, 9.65. Found: C, 75.04; H, 6.92; OCH_3, 17.55; OH, 9.63.

The hydroxyl group was determined by acetylation with acetic anhydride.

When the same reaction was allowed to proceed until gas absorption was 1.3 moles/mole of eugenol, a nondistillable brownish residue was obtained which was suspended in diethyl ether and filtered. A white compound (V), slightly soluble in ether, insoluble in *n*-heptane, was isolated which, after crystallization from benzene, melted at 197–198°. The yield was 10–15% of the reaction product.

Anal. Calcd. for $C_{20}H_{16}(OCH_3)_2(OH)_2$: C, 74.97; H, 6.86; O, 18.16; OCH_3, 17.67; OH, 9.64. Found: C, 74.87; H, 6.92; O, 18.16; OCH_3, 17.44; OH, 9.72.

The hydroxyl group was determined by acetylation with acetic anhydride. The molecular weight, determined by cryoscopy in benzene, was 300 (calcd. for $C_{22}H_{24}O_4$: 352.4).

Derivatives of V were benzoate, m.p. 223–224° (from ethanol); methyl ether, m.p. 131.5–132° (from aqueous ethanol); and acetate, m.p. 159.5–160° (from aqueous ethanol).

Hydrogenation of IV with Raney Alloy.—A 1-g. sample of Raney alloy was added in small portions to 0.65 g. of IV, dissolved in 40 ml. of 5% aqueous sodium hydroxide. The reaction product was filtered, and the filtrate was poured into dilute hydrochloric acid. The precipitate was filtered and crystallized from aqueous ethanol to give 0.51 g. of pure product, melting at 81–82°. It did not depress the melting point of a sample of III.

Hydrogenation of IV with Synthesis Gas.—A 5.75-g. sample of IV in 50 ml. of benzene was treated with synthesis gas at 180° under the same conditions as in A. After decobalting and evaporation of the solvent, a residue was obtained which was crystallized from aqueous ethanol, after boiling with charcoal, giving 1.51 g. melting at 82–83°. After recrystallization from *n*-heptane, it had m.p. 81–81.7° and did not depress the melting point of III.

3-(3-Methoxy-4-hydroxyphenyl)propanoic Acid (VIII).—A solution of 41 g. of ferulic acid in 1600 ml. of 8% sodium hydroxide was treated with stirring with 40 g. of Raney alloy in 1-g. amounts over 30 min. After stirring an additional 30 min., the mixture was filtered and the filtrate was poured with stirring into a mixture of ice and excess hydrochloric acid. The solution was extracted with ether and the ether was dried and distilled, giving 40 g. of a residue which, after crystallization from water, gave pure VIII, melting at 91–91.5°, lit.[9] m.p. 90–91°.

4-(3-Methoxy-4-hydroxyphenyl)butanoic Acid (X).—A 20-g. sample of VIII was dissolved in sodium hydroxide and acetylated with acetic anhydride. The product was crystallized from water giving 17.5 g. of crystals, melting at 97.5–98.5°, lit. m.p.[9] 93–94°.

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92; acid equiv. wt., 238.2. Found: C, 60.60; H, 5.82; acid equiv. wt., 238.2.

A 40-g. sample of the acetate was refluxed with 240 ml. of redistilled thionyl chloride during 30 min. The excess thionyl chloride was distilled then at the water pump at room temperature. To the residue, 50 ml. of dry benzene was added and then evaporated *in vacuo*, and this procedure was repeated. The crystalline residue (41 g.) was dissolved in 50 ml. of absolute ether and added dropwise to a stirred solution of diazomethane at 0–5°, prepared from 110 g. of nitrosomethylurea in 1200 ml. of ether. After one night at room temperature, the solution was filtered and the ether was removed under reduced pressure, giving 46 g. of crude diazo ketone. The crystalline diazo ketone was dissolved in 650 ml. of anhydrous ethanol and, to the stirred solution, at 70°, a slurry of 3 g. of silver oxide in 50 ml. of ethanol was added in small amounts over 3 hr. The mixture was refluxed several hours; when no more unchanged diazo ketone could be detected, the mixture was filtered and evaporated. Distillation yielded 26 g. of ethyl 4-(3-methoxy-4-acetoxyphenyl) butanoate (IX), boiling at 168–170° (2 mm.). By saponification with 10% aqueous potassium hydroxide, followed by crystallization from water, 20 g. of pure X was obtained, melting at 120.5–121.5°, lit.[10] m.p. 114–116°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 63.04; H, 6.67.

4-(3-Methoxy-4-hydroxyphenyl)-1-butanol (II).—A solution of 22 g. of IX was added dropwise, over a period of 3 hr. to a suspension of 10 g. of lithium aluminum hydride in 1200 ml. of anhydrous ether. Upon completion of the addition, the mixture was stirred an additional hour, treated with 300 ml. of water, and acidified with 2 *N* sulfuric acid. The ether layer was removed and the aqueous layer was extracted with ether. The combined ether solutions were dried and evaporated. The residue was distilled. A crystalline fraction (15 g.), boiling at 163–170° (2 mm.), was obtained. After crystallization from carbon tetrachloride, pure II was obtained, melting at 58–58.7°.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22; OH, 17.33. Found: C, 67.36; H, 8.10; OH, 17.25.

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[6] D. E. Levin and A. Lovy, *J. Am. Chem. Soc.*, **55**, 1955 (1933).

[7] T. Momose and S. Goya, *Chem. Pharm. Bull.* (Tokyo), **7**, 849 (1959).

[8] T. Momose, H. Hoya, Y. Ohkura, and M. Iwasaki, *ibid.*, **2**, 119 (1954).

[9] I. A. Pearl, *J. Org. Chem.*, **24**, 736 (1959).

[10] H. L. Holmes and L. W. Trevoy, *Can. J. Research*, **22B**, 109 (1944).

1(2H)-3,4-Dihydro-6-methoxy-7-hydroxynaphthalenone (VII).—A 20-g. sample of X dissolved in aqueous alkali was acetylated with acetic anhydride, giving 19 g. of the acetyl derivative (XI) which, after crystallization from water, melted at 65.5–66.5°.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.72; H, 6.30.

To a cooled stirred solution of 20 g. of XI in 130 ml. of dry benzene at 0°, was added 20 g. of phosphorus pentachloride in portions. The mixture was warmed to room temperature to complete the reaction and then cooled until benzene began to solidify. At this point, a solution of 20 g. of anhydrous stannic chloride in 20 ml. of dry benzene was added with stirring. After standing for 3 hr. at 0°, the mixture was hydrolyzed by the addition of ice followed by 60 ml. of concentrated hydrochloric acid. A 120-ml. portion of ether was added and the mixture was shaken until complete solution occurred. The organic layer was then washed with 5% hydrochloric acid, 5% sodium hydroxide, and water. After evaporation of the ether, 11 g. of residue, melting at 118–120°, was obtained. This residue was saponified with 10% potassium hydroxide, whereupon 8 g. of VII, melting at 150.2–150.9° after crystallization from water, was obtained.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29; OCH_3, 16.14. Found: C, 68.46; H, 6.16; OCH_3, 16.0.

By methylation with dimethyl sulfate, 1(2H)-3,4-dihydro-6,7-dimethoxynaphthalenone was obtained, m.p. 98–98.5° (from *n*-heptane), lit.[11] m.p. 99°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; OCH_3, 30.06. Found: C, 69.61; H, 6.54; OCH_3, 30.01.

The semicarbazone had m.p. 226.5–227° (from ethanol).

Anal. Calcd. for $C_{13}H_{17}N_3O_3$: N, 15.96. Found: N, 15.81.

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(11) K. N. Campbell, A. Scharge, and B. K. Campbell, *J. Org. Chem.*, **15**, 1135 (1950).

The Synthesis of 7-Alkylamino-1-naphthols

DANIEL L. ROSS AND JULIA J. CHANG

Research Laboratories, Polaroid Corporation, Cambridge 39, Massachusetts

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1,7-Dihydroxynaphthalene, when heated with aqueous solutions of methylamine, ethylamine, isopropylamine, and dimethylamine, gave good yields of the corresponding 7-alkylamino-1-naphthols uncontaminated with the other position isomer. The selectivity of the reaction is explained in terms of steric effects.

In the course of searching for new couplers for the preparation of azo dyes, it became desirable to develop a synthesis of 7-alkylamino-1-naphthols. The method described for the primary amine, alkali fusion of 7-aminonaphthalene-1-sulfonic acid,[1a,b] was not suitable for the substituted derivatives. Although the precursors, the 7-alkylaminonaphthalene-1-sulfonic acids, were easily prepared by the Bucherer reaction with 2-naphthol-8-sulfonic acid, alkali fusion of the N-methyl compound was accompanied by at least 50% demethylation and gave a mixture of 7-methylamino-1-naphthol (**8a**) and 7-amino-1-naphthol, while fusion of the N-isopropyl compound resulted in extensive degradation of the molecule. The Bucherer reaction using various primary aliphatic amines with 1,7-dihydroxynaphthalene, under a wide variety of conditions, gave only mixtures of both possible monosubstitution products, 1,7-diamine, and recovered starting material.

An early report[2] that 1,7-dihydroxy-2-naphthoic acid gave 7-amino-1-naphthol when heated at 180° with concentrated ammonia solution led us to investigate the reaction of aliphatic amines with 1,7-dihydroxynaphthalene in the absence of the bisulfite usually used in the Bucherer reaction.

Uncatalyzed reactions of amines with naphthols have been previously reported.[3] For example, N-methyl-β-naphthylamine was obtained in 80% yield on heating β-naphthol with aqueous methylamine at 200–220° for 7 hr.[4] Depending on the reaction temperature, either 3-amino-2-naphthol or 2,3-naphthalenediamine could be obtained from 2,3-dihydroxynaphthalene,[5] while the corresponding diamines were formed when 1,5-,[6] 1,8-,[6] and 2,7-dihydroxynaphthalenes[7] were heated to 250–300° with aqueous ammonia. Similar conditions were used to prepare α- and β-naphthylamine from the corresponding naphthols.[8] However, there is but a single example reported in which a simple dihydroxynaphthalene, containing both an α- and a β-hydroxy group, has been treated under these conditions. When 1,3-dihydroxynaphthalene was heated with ammonia at 130–140°, 3-amino-1-naphthol (preferential replacement of the β-hydroxy group) and some diamine were obtained.[9] Treatment with aniline gave 3-anilino-1-naphthol.

In the present work, when aqueous methylamine was heated with 1,7-dihydroxynaphthalene, a single aminonaphthol was produced. Reasonable yields of 7-methylamino-1-napthol (**8a**) were obtained over a considerable range of temperature (130–180°) and molar ratios of amine to dihydroxynaphthalene. In addition, it was only when forcing conditions were used (180°, four equivalents of methylamine) that any significant amount of 1,7-diamine was formed. There was no detectable amount of the other isomer, 8-methylamino-2-naphthol, present. Ethylamine, isopropylamine, and dimethylamine also reacted, at increasingly higher temperatures, to give the corresponding 7-amino-1-naphthols uncontaminated by the other possible position isomers and with no significant formation of diamines. In a single experiment, using aqueous ammonia at 130°, only starting material was recovered. Similarly, none of the desired product was obtained when *t*-butylamine was used.

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