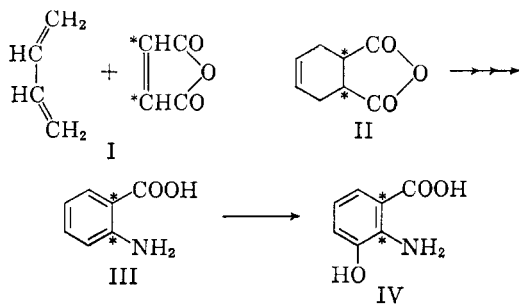
Aromatization of II by the method of Newman[3] gave 70–80% yields of 1,2-C^{14}-labeled phthalic anhydride, which on reaction with concentrated ammonium hydroxide yielded 1,2-C^{14}-labeled phthalimide[4] in 95% yield. Reaction of the latter with potassium hypobromite[5] produced 1,2-C^{14}-labeled anthranilic acid (III) in 70–75% yields after a different and simpler isolation procedure than that reported.[5] Finally, persulfate oxidation of III[6] afforded 10–15% yields of the 3-hydroxy derivative (IV) which was separated by ion exchange chromatography and further purified by recrystallization as the hydrochloride. 5-Hydroxyanthranilic acid was a concomitant product of this oxidation reaction.



Experimental

Melting points, taken in a capillary, are corrected.

Ring (1,2)-C^{14}-Labeled Anthranilic Acid (III).—To 1.0 g. of maleic anhydride (cold), 8.4 mg. of maleic anhydride, C^{14}-labeled at the Π-bond carbons (I, 0.5 mc.) and 2 ml. of benzene cooled to 0° was added 2 ml. of butadiene cooled in a Dry Ice–acetone bath. The mixture was stoppered tightly and kept at room temperature for 20 hr., then excess butadiene was expelled on the steam bath. The resultant solution (benzene dilution may be necessary) was filtered and diluted with an equal volume of ligroin (b.p. 30–60°). After cooling to −15°, 1.38 g. (91%) of 1,2-C^{14}-labeled-1,2,3,6-*cis*-tetrahydrophthalic anhydride (II), m.p. 98–100° was obtained.[2]

A refluxing solution of 1.3 g. of II and 2.6 ml. of glacial acetic acid was treated during 30–40 min. (stirring), with 1.1 ml. of bromine in 2.9 ml. of acetic acid. The solution was refluxed for 18 hr., and the solvent was evaporated (bath temperature 60–70°) with a water pump aspirator. The residue was kept (stirring) at 200–210° (oil bath temperature) for 7–9 hr. The dark residue was transferred to a sublimation tube with benzene, the benzene was removed with water pump evacuation, and the residue was dried *in vacuo* over potassium hydroxide to remove hydrogen bromide. Sublimation gave 1.03 g. (79%) of 1,2-C^{14}-labeled phthalic anhydride, m.p. 129–131°.[7] Further purification is usually unnecessary. Benzene–ligroin (b.p. 30–60°) may be used for recrystallization.

To 1.0 g. of the above phthalic anhydride in a small test tube was added carefully 1.0 ml. of 12 *M* ammonium hydroxide and the mixture was dried over a free flame during 5–10 min. The residual melt was heated to 270–280° during 5–10 min. where it was kept for a few more minutes. The material was sublimed at 150°/0.5 mm. to give 0.93 g. (93%) of **1,2-C^{14}-labeled phthalimide,** m.p. 229–232°.[4]

This phthalimide (0.93 g.) was added to an ice-cold solution of 0.34 ml. of bromine in 15.4 ml. of 2 *N* potassium hydroxide. The suspension was stirred to solution (10 min.) while cooling in an ice bath. Then 0.9 g. of potassium hydroxide pellets was added and the mixture again stirred to solution while cooling. The clear solution was stirred at room temperature for 8–10 min. and warmed to 80° during 5 min. Upon cooling in an ice bath and adding 1.8 ml. of acetic acid, crude III separated and was extracted with ether. After removal of the solvent and acetic acid, *in vacuo*, the material was sublimed (105°/0.5 mm.) to give 0.65 g. (77%) of III which melted at 144–146°.[5]

1,2,C^{14}-Labeled 3-Hydroxyanthranilic Acid (IV).[8]—A stirred solution of 0.65 g. of III, 140 ml. of 2 *N* potassium hydroxide and 32 ml. of water was treated during 4 hr. with 2.6 g. of potassium persulfate in 50 ml. of water. Hydrochloric acid (40 ml. of 12 *M*) was added, the dark solution was heated on the steam bath for 30 min., and the solution was evaporated to dryness at the water pump. The residue was extracted with 30 ml. of hot absolute ethanol in five portions. The combined, filtered extracts were evaporated to dryness *in vacuo*, leaving a residue (0.5 g.) which was dissolved in 10 ml. of water and chromatographed on a column (10 × 1 cm.) of Dowex 1-acetate. The column was washed with water, then eluted with a gradient of acetic acid with 50 ml. of water in the mixing bottle into which was added 6 *N* acetic acid; 10-ml. fractions were collected. 5-Hydroxyanthranilic acid (identified by paper chromatography and fluorescence)[9] was recovered from fractions 4 and 5 and 3-hydroxyanthranilic acid (IV)[9] in fractions 8–15. These were pooled and distilled in a flash evaporator. The residue was dissolved in water and the solvent again evaporated to remove acetic acid. Recrystallization from absolute alcohol by addition of a little ether gave 50 mg. of 1,2-C^{14}-labeled-3-hydroxyanthranilic acid (V) hydrochloride, m.p. 226–227° dec., identified by comparison with authentic material, by paper chromatography and by fluorescence.[9] The filtrate was evaporated to dryness. To the residue was added 50 mg. of 3-hydroxyanthranilic acid. Recrystallization gave 60 mg. more material, m.p. 227–228° with sufficient specific activity, for metabolic studies.

(3) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1542 (1941).

(4) W. A. Noyes and P. K. Porter, *Org. Syntheses*, Coll. Vol. I, 457 (1941).

(5) M. M. S. Hoogewerf and W. A. Van Dorp, *Rec. trav. chim.*, **10**, 5 (1891).

(6) E. Boyland and P. Sims, *J. Chem. Soc.*, 980 (1954).

(7) I. Heilbron, *Dictionary of Organic Compounds*, **4**, 193 (1953).

(8) J. F. Nyc and H. K. Mitchell, *J. Am. Chem. Soc.*, **70**, 1847 (1948).

(9) E. Boyland, P. Sims, and D. C. Williams, *Biochem. J.*, **62**, 546 (1956).

The Steric Course of the Acid-Promoted Addition of Acetic Acid to Norcarane

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Although the unsaturation of cyclopropane and its derivatives has long been known, investigations of the steric course of addition to cyclopropane derivatives appear to be lacking. This report describes preliminary findings of our investigation of the acid-promoted opening of the cyclopropane ring of norcarane and deals primarily with the steric course of the addition reaction.

Norcarane was treated with glacial acetic acid in the presence of *p*-toluenesulfonic acid at 46.5° for eighty-eight hours. An infrared spectrum of the crude product mixture showed the following pertinent bands: carbonyl at 5.76 μ, acetate ester at 8.07 μ and double bond at 6.11 μ. Analysis by gas chromatography showed the product mixture to contain 57% hydrocarbon and 43% acetate. Further analysis by gas chromatography indicated the hydrocarbon fraction was made up of 3- and/or 4-methylcyclohexene (63–66%), 1-methylcyclohexene (26–25%), and cycloheptene (11–8%); no trace of unreacted norcarane could be found.

Saponification of the crude product mixture gave material which proved to be a mixture of cycloalkanols. The infrared spectrum showed the following pertinent bands: hydroxyl at 2.74–2.95 μ, methyl group at 6.90 and 7.30 μ, and bands at 9.37 μ, 9.50 μ, and 9.65 μ. The last three bands are especially characteristic of *trans*-2-methylcyclohexanol and are clearly distinguishable from the bands in the same region which are characteristic of the *cis* isomer.[1] Gas chromatograms of the mixture of cycloalkanols showed the presence of at least five components. Components present in minor amounts were 1) 1-methylcyclohexanol; 2) *cis*-2-methylcyclohexanol, integrated peak area along with 1-methylcyclohexanol—4%; 3) *trans*-3- and/or *trans*-4-methylcyclohexanol—1% and 4) cycloheptanol—15%. The major peak represented 79% of the mixture and was identical in retention time with *trans*-2-, *cis*-3-, or *cis*-4-methylcyclohexanol. Since it was not possible to achieve resolution of these cycloalkanols, the mixture of cycloalkanols was oxidized to a mixture of ketones and these were examined. Chromic acid oxidation of the mixture of cycloalkanols gave material whose infrared spectrum showed an unsymmetrical carbonyl band at 5.85 μ and weak absorption at 2.70–2.95 μ. A gas chromatogram of this material showed the following peaks: 1) 1-methylcyclohexanol—3%; 2) 2-methylcyclohexanone—76%; 3) 3-methylcyclohexanone—5%; 4) 4-methylcyclohexanone—less than 1%; 5) cycloheptanone—15%. The close agreement of the amount of 2-methylcyclohexanone in the mixture of cycloalkanones with the integrated area of the predominant cycloalkanol peak in the mixture of cycloalkanols clearly indicates that this cycloalkanol is largely *trans*-2-methylcyclohexanol.

trans-2-Methylcyclohexanol was also isolated as its 3,5-dinitrobenzoate from the mixture of 3,5-dinitrobenzoates by elution chromatography.

Dependence of the ring opening on the presence of strong acid was demonstrated by the result that only norcarane was recovered from a mixture of glacial acetic acid and norcarane after one week at 46.5°.

Results have been obtained which indicate that formation of *trans*-2-methylcyclohexyl acetate is largely kinetically controlled. A mixture containing 59% *cis*-2-methylcyclohexyl acetate and 41% *trans*-2-methylcyclohexyl acetate was treated with sulfuric acid in glacial acetic acid at 50° for five hundred hours. The product included a hydrocarbon fraction (16%), which consisted largely of 1-methylcyclohexene and 3- and/or 4-methylcyclohexene (less than 1%), and an acetate fraction, 84%, which on saponification afforded a mixture of cycloalkanols made up of 14% 1-methylcyclohexanol, 27% *cis*-2-methylcyclohexanol, and 59% *trans*-2-methylcyclohexanol. These results show that only 46% of the initial *cis*-2-methylcyclohexyl acetate was transformed to other products in five hundred hours. Since the *trans* isomer in the mixture of cycloalkyl acetates from ring opening is present to the extent of 79% after only eighty-eight hours, the *trans* isomer is being formed more rapidly than it could be formed by the isomerization of the less stable *cis*-2-methylcyclohexyl acetate under comparable conditions.

Although addition of acetic acid to 3-methylcyclohexene may account for some of the *trans*-2-methylcyclohexyl acetate, certainly this is not the path by which the preponderant amount of this material is formed. Addition to 3-methylcyclohexene could reasonably be expected to give nearly equal amounts of 2- and 3-methylcyclohexyl acetates, however equal amounts of the two methylcyclohexyl acetates are not afforded in the ring opening reaction.

The nearly exclusive formation of *trans*-2-methylcyclohexyl acetate among the methylcyclohexyl acetates demonstrates that addition of acetic acid to norcarane under the conditions employed proceeds in a stereospecific manner. Final interpretation of all aspects of the ring opening reaction, including olefin formation, ring enlargement, and stereochemistry of addition, awaits the results of experimental work now in progress.

Experimental

Norcarane.—Norcarane was prepared by the method of Simmons and Smith.[2] Purification was effected by double distillation through a Todd column, b.p. 115.8–115.9°. Gas-liquid chromatographic analysis of the purified norcarane showed it contained approximately 2% of an impurity which appeared as a shoulder on the low retention time side of the norcarane peak. Brief treatment of the purified norcarane in ether solution with cold dilute permanganate resulted only in consumption of norcarane with no effect whatsoever on reducing the amount of impurity. Therefore the impurity was considered to be inert material which would not give rise to spurious results in the ring opening reactions of norcarane.

Acid-Promoted Addition of Acetic Acid.—A sealed glass tube containing 1.84 g. of norcarane and 25 ml. of 0.0745 M *p*-toluenesulfonic acid in glacial acetic acid was placed in a constant temperature bath at 46.5°. After 88 hr., the tube was withdrawn, cooled and its contents added to 50 ml. of water and 50 ml. of ether. The aqueous layer was ex-

(1) E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

(2) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

tracted three times with 30-ml. portions of ether. The combined ether extracts were washed three times with 30-ml. portions of water, three times with 30-ml. portions of 5% sodium bicarbonate, and finally with saturated salt solution. The ether solution was dried over anhyrous magnesium sulfate. The ether was removed by distillation through a 12-in. Vigreux column. The remaining oil, 2.71 g., was subjected immediately to gas-liquid chromatographic analysis using a 4-ft. diethylene glycol adipate on Celite column at 81°. The column had been calibrated using known amounts of 3-methylcyclohexene and a mixture of *cis*- and *trans*-2-methylcyclohexyl acetates. The chromatogram showed that the product mixture was made up of 27% acetate, 36% hydrocarbon, and 37% residual ether, which amounts to 43% acetate and 57% hydrocarbon excluding residual ether. Gas-liquid chromatographic analysis of the product mixture using an 11-ft. 4% squalane on firebrick column at 80.8°, flow rate 49 ml./min. showed in addition to residual ether, three peaks at 9.8 min. (63%), 12.5 min. (26%), and 14.2 min. (11%); retention times in the order given were identical with retention times of 3-[3] or 4-methylcyclohexene[4] (authentic samples not separable), 1-methylcyclohexene,[4] and cycloheptene.[5] The norcarane peak at 16.8 min. was absent. A chromatogram obtained using a 11.5-ft 15% Silicone 550 on firebrick column at 81.0°, flow rate 54.5 ml./min. showed three peaks at 7.8 min. (66%), 10.0 min. (25%), 11.8 min. (8%); again retention times, in the order given, were identical with 3- or 4-methylcyclohexene (authentic samples not separable), 1-methylcyclohexene and cycloheptene. The norcarane peak at 13.0 min. was lacking.

In the infrared spectrum, the mixture of cycloalkyl acetates and cycloalkenes showed the following bands; 5.76, 6.11, 6.90, 7.30, 8.07, 10.13 (strong), 10.27 μ.

Saponification.—The mixture of cycloalkyl acetates, 2.33 g., and 5 g. of potassium hydroxide in 25 ml. of water were stirred rapidly at about 35° for 6 hr. The aqueous phase was saturated with sodium chloride and 20 ml. of ether was added. The aqueous layer was extracted three times with 15-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. Distillation of the ether through a 12-in. Vigreux column and subsequent vacuum distillation of the remaining oil afforded 552 mg. of cycloalkanols, b.p. 72–80° (20 mm.). Pertinent bands in the infrared spectrum were found at 2.74, 2.95, 5.77 (trace), 6.82, 6.83, 7.30, 9.37, 9.50, 9.65, 9.71 (weak), and 10.96 μ (weak). Gas-liquid chromatographic analysis using a 11-ft., 17% glycerol on Celite column at 100°, flow rate 52.6 ml./min., showed five peaks at 7.2 and 8.0 min. (4%), 11.0 min. (79%), 15.5 min. (about 1%), 27 min. (15%); the retention times in the order given were identical with 1-methylcyclohexanol, *cis*-2-methylcyclohexanol,, *trans*-2- or *cis*-3- or *cis*-4-methylcyclohexanol[1] (authentic samples not separable), *trans*-3- or *trans*-4-methylcyclohexanol[1] (authentic samples not separable), and cycloheptanol.[4] No trace of cyclohexylcarbinol[6] at 20.5 min. could be found. Gas-liquid chromatographic analysis using a 13-ft .,5% erythritol on "Celite" column at 86.6°, flow rate 46.8 ml./min. gave four peaks, at 9 min., 11 min., 20 min., and 30 min.; in the order given, these four peaks correspond to the retention times of 1-methylcyclohexanol and *cis*-2-methylcyclohexanol (authentic samples not separable), *trans*-2-methylcyclohexanol, *trans*-3- and *trans*-4- methylcyclohexanol (authentic samples not separable), and cycloheptanol. No trace of cyclohexylcarbinol at 22 min. could be found. A synthetic mixture of 45 mg. of 3-methylcyclohexanol (29% *cis*) and 103 mg. of 2-methylcyclohexanol (88% *trans*) gave only one peak in the immediate region of 11.0–13.0 min. A synthetic mixture containing equal quantities by volume of *cis*-3-methylcyclohexanol and *trans*-2-methylcyclohexanol afforded two peaks at 11.0 and 13.0 min.

Oxidation of Cycloalkanols.—The mixture of cycloalkanols was oxidized by the method of Brown and Garg.[7] To 440 mg. of cycloalkanol (3.85 mmoles) in 7 ml. of ether was added 386 mg. of sodium dichromate dihydrate (1.30 mmoles) in 0.3 ml. of 96% sulfuric acid and 2.0 ml. of water. The chromic acid solution was added slowly over a period of 15 min. with a rapid stirring and in such a manner that the temperature did not exceed 28°. The two phase system was stirred for an additional 2 hr. After work-up by the usual method, the remaining oil was distilled to give 295 mg. of cycloalkanones b.p. 49–55° (10 mm.). Pertinent bands in the infrared were found at 2.75, 2.90, 5.85 (unsymmetrical), 6.90, and 7.30 μ. Gas-liquid chromatographic analysis used an 8′ Carbowax 20M column at 141°; the flow rate was 61.2 ml./min. Peaks were found at 19 min. (1-methylcyclohexanol, 3%), 21 min. (2-methylcyclohexanone,[4] 76%), 23.5 min. (3-methylcyclohexanone[8] 5%), 25 min. (4-methylcyclohexanone,[6] less than 1%), and 35.5 min. (cycloheptanone,[8] 15%). Identification of each peak was made by adding a known amount of authentic sample to a known amount of the mixture of cycloalkanones. In each case addition of authentic sample resulted only in enlarging the peak in question and produced no new peaks.

Preparation and Separation of 3,5-Dinitrobenzoates.—A mixture of cycloalkanols originating from norcarane was produced by the method similar to that described above. Treatment of 446 mg. of cycloalkanols with freshly prepared 3,5-dinitrobenzoyl chloride in anhydrous pyridine gave 821 mg. of the crude 3,5-dinitrobenzoates, m.p. 82–100°. Chromatography of 59.4 mg. of the crude 3,5-dinitrobenzoate mixture on a silicic acid–Celite–rhodamine 6G column,[9] 30 cm. × 12 mm., resulted in incomplete separation of the major component, *trans*-2-methylcyclohexyl 3,5-dinitrobenzoate. The column was eluted with 0.5% ether-*n*-hexane. Results of the chromatography are summarized below. Mixture of fractions 1, 2, or 3 with authentic *trans*-2-methylcyclohexyl 3,5-dinitrobenzoate (m.p. 116.5–117.5°) showed no depression in melting points. Isolation of the next most abundant component, cycloheptyl 3,5-dinitrobenzoate, was not realized. Rechromatography of combined fractions 11–25 effected no separation.

Fractions	Combined Weight in Mg.	M.P. Range of Fractions
1–3	12.8 (22%)	(116.0–117.5)–(113–116°)
4–5	9.0	(107–114)–(103–113°)
6–10	12.4	(99–114)–(66–82°)
11–25	22.2	(57–65)–(56–64)

Acid Treatment of 2-Methylcyclohexyl Acetate.—A mixture of *cis*- (59%) and *trans*-2-methylcyclohexanol (41%, analysis by gas-liquid chromatography) was converted to a mixture of acetates by warming with freshly distilled acetic anhydride. A sealed glass tube containing 3.0 g. of this mixture of acetates and 10 drops of 96% sulfuric acid in 50 ml. of glacial acetic acid remained in a constant temperature bath at 50° for 500 hr. Work-up of the contents of the tube in a manner similar to that employed in the norcarane ring opening furnished 2.23 g. of oil. Gas-liquid chromatographic analysis using a diethylene glycol adipate on Celite column showed the material to consist of 84% acetate and 16% hydrocarbon and in addition some residual ether; gas-liquid chromatographic analysis using a 4% squalene on fire brick column showed that the hydrocarbon content consisted of less than 1% 3- or 4-methylcyclohexene and the remainder 1-methylcyclohexene. Saponification

(3) A. Berlande, *Compt. rend.*, **213**, 437 (1941).

(4) Purchased from the Aldrich Chemical Co. and distilled.

(5) Purchased from the Columbia Organic Chemical Co. and distilled.

(6) Purchased from Eastman Organic Chemicals and distilled.

(7) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(8) Prepared from cycloheptanol by oxidation according to Brown and Garg.[7]

(9) J. W. White, Jr., and E. C. Dryden, *Anal. Chem.*, **20**, 853 (1945).

of the 2.15 g. of the crude mixture of acetate was accomplished by employing 5 g. of potassium hydroxide in 25 ml. of water. Work-up and distillation yielded 483 mg. b.p. 72–80° (21 mm.). The infrared showed bands at 2.82, 2.95, 6.85, 6.90 in addition to several bands in the 9.0–11.0-μ region. Gas-liquid chromatography on a 5% erythritol on Celite column produced three peaks identical with 1-methylcyclohexanol (14%), *cis*-2-methylcyclohexanol (27%), and *trans*-2-methylcyclohexanol (59%).

Norcarane and Acetic Acid.—A sealed tube containing 1.9 g. of norcarane and 10 ml. of glacial acetic acid remained in a constant temperature bath for 1 week at 46.5°. Work-up in the usual manner furnished an oil which by gas-liquid chromatographic analysis on an 11-ft. 4% squalene on firebrick column showed only the presence of norcarane.

Gas-Liquid Chromatographic Analyses and Infrared Spectra.—A Baird double beam infrared spectrophotometer was employed to determine the infrared spectra. The gas-liquid chromatographic analyses were carried out with an instrument constructed in these laboratories. The instrument contained a Gow-Mac thermal conductivity cell. Helium was employed as the mobile phase.

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A Dihydroresorcinol Derivative[1]

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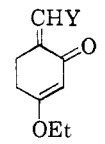
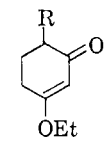
As a result of our need for 6-hydroxymethylene-3-ethoxycyclohex-2-enone (Ia) the formylation of the dihydroresorcinol derivative, 3-ethoxycyclohex-2-enone(IIa), was investigated. Reaction between the latter, ethyl formate, and sodium ethoxide in benzene yielded a single, crystalline $C_9H_{12}O_3$ compound. Its spectral properties, its alcohol solution giving a positive ferric chloride test, and its conversion to a copper chelate revealed the product to be a readily enolizable substance. It could be transformed into an enol acetate with acetic anhydride and pyridine and into an enol ether by base-induced reaction with isopropyl iodide. While *a priori* the formyl group could have entered the dihydroresorcinol nucleus at C-2,-4, or -6, the preliminary evidence favored C-6 as its site of attachment. Nevertheless, a search for more rigorous data was undertaken.

Catalytic hydrogenation of the formylation product yielded a dihydro derivative whose ultraviolet spectrum was identical with that of dihydroresorcinol ethyl ether(IIa). Thus the formyl (or hydroxymethylene) group had been reduced to



Ia. Y = OH
b. Y = O—*i*-Pro
c. Y = OAc
d. Y = H

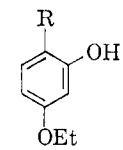


IIa. R = H
b. R = CH_2OH
c. R = CH_2OAc

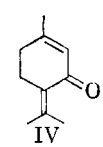
a hydroxymethyl function whose position was limited to C-4 or -6 (IIb), since at C-2 it would have been expected to alter the nuclear chromophore.

Catalytic hydrogenation of the enol acetate of the formylation product yielded a mixture from which a crystalline $C_9H_{12}O_2$ compound was isolated. Its spectral properties showed it to be an aromatic substance. On the assumption of its being 4-ethoxy-2-hydroxytoluene(IIIa) this compound was synthesized. Diazoethane treatment of β-resorcylaldehyde yielded 4-ethoxysalicylaldehyde(IIIb). Reduction of the latter with zinc and acetic acid afforded the cresol IIIa, identical in all respects with the product of hydrogenation of the enol acetate of the formylation product. These results establish firmly the C-6 attachment of the carboxaldehyde (or hydroxymethylene) function in the initial formylation product. They further suggest that the latter's enol ether, enol acetate, and dihydro derivative are represented by Ib, Ic, and IIb, respectively.

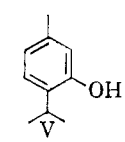
IIIa. R = CH_3
b R = CHO
c. R = CN



The unusual transformation of Ic into IIIa under hydrogenation conditions proceeds most probably *via* Id, produced either by direct hydrogenolysis of Ic or by the latter's hydrogenation to IIc and catalyst-induced β-elimination of acetate to Id.[3] The extraordinary isomerization of an alkylidenecyclohexenone(Id) into a phenol(IIIa) finds precedence in the recent conversion of piperitenone(IV) into thymol(V) under hydrogenation conditions.[4]



IV



V

As an alternate route from the aldehyde IIIb to the cresol IIIa, the Wolff-Kishner reduction of the former's semicarbazone had been examined briefly. This reaction yielded a mixture of prod-

(1) Financial support for this work by Ciba Pharmaceutical Products Inc., Summit, N. J., hereby is gratefully acknowledged.

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(3) *Cf.* E. Wenkert, A. K. Bose, and T. L. Reid, *J. Am. Chem. Soc.*, **75**, 5514 (1953).

(4) E. D. Bergmann and P. Bracha, *J. Org. Chem.*, **24**, 994 (1959).