Mass Copolymerization.—The method for determining monomer–polymer composition curves for the five systems reported was essentially the same in each case. Solutions comprising 100 g. of total monomers were prepared by adding appropriate amounts of monomer, comonomer and benzoyl peroxide to 4-oz. French square bottles. The concentrations employed are given in Table I. Air above the monomers was swept out with nitrogen and a metal cap screwed tightly on the bottle mouth. Copolymerizations were carried out in an air oven regulated to ±1° within the polymerization temperature given in Table I. Polymerization at that temperature was continued until a slight increase in viscosity was observed or, in the case of copolymer samples high in combined nitrile, until a small amount of insoluble copolymer had precipitated from the comonomer solution. The reaction was then poured into 3000 ml. of stirred denatured ethanol (2B) at room temperature and the bottle rinsed with ethanol. In the case of vinyl acetate copolymers, hexane was used in place of ethanol throughout. The mixture was boiled to complete the coagulation and filtered. Final purification was effected by similar treatment with two fresh 1500-ml. portions of denatured ethanol. After drying in an evaporating dish for forty-eight hours in a circulating air oven at 60°, the copolymer was analyzed in duplicate for nitrogen by the micro-Dumas method. Analytical data and conversion values are summarized in Table I.

Summary

Monomer–polymer composition curves for the systems vinyl acetate–acrylonitrile, vinyl acetate–methacrylonitrile, α-methylstyrene–acrylonitrile, α-methylstyrene–methacrylonitrile and styrene–methacrylonitrile are reported. These data, along with previously published copolymerization rates, were used to check the validity of predictions based on the Price–Alfrey relationships. Excellent qualitative and good quantitative agreement was found for the systems studied.

Values for the Q and e parameters for five additional monomers are suggested, and simplified forms for copolymer equations involving any number of components are presented.

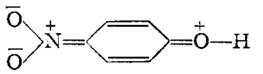
DAYTON 7, OHIO RECEIVED NOVEMBER 15, 1947

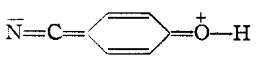
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Steric Inhibition of Resonance. III.[1] Acid Strengths of Some Nitro- and Cyanophenols

BY G. W. WHELAND, R. M. BROWNELL[2] AND E. C. MAYO

The acid strength of a phenol is greatly increased by the introduction of a nitro group para to the hydroxyl group. In most instances, in fact, the ionization constant of a *p*-nitrophenol is approximately a thousand times as large as is that of the corresponding unnitrated phenol; in other words, a para nitro group usually decreases the pK_a of a phenol by about 3 units. This greater acidity of the nitrophenol has been attributed[3,4] in part to an electrostatic interaction between the ionizable proton and the dipole moment of the nitro group; and in part also to resonance with a relatively unstable quinoid structure (such as I). Moreover, the effect produced by a para *cyano* group upon the acid strength of a phenol is qualitatively the same as (but usually rather smaller than) that produced by a para nitro group. Again, the observed increase in acid strength can be attributed[3] in part to an electrostatic interaction, since the dipole moment of the para cyano group (like that of the para nitro group) is directed so that its positive end points toward the aromatic ring, and hence toward the ionizable proton; and in part also to resonance with an unstable quinoid structure (such as II).


I


II

Although both the electrostatic and the resonance effects should therefore increase the acid strengths of the nitro- and cyanophenols, there is no *a priori* way for the estimation of either their absolute or their relative magnitudes. Data now in the literature suggest, however, that the two effects are fairly large and of comparable magnitude. Thus, calculations by Westheimer[3] have led to the conclusion that the electrostatic effect alone should decrease the pK_a of *p*-nitrophenol (with respect to that of phenol itself) by approximately 1.25 units; hence, it may be inferred that the resonance effect must be responsible for the observed further decrease of approximately 1.6 units (*cf.* Table I, below). Similarly, Westheimer's calculations show that, with *p*-cyanophenol, the electrostatic effect alone should decrease the pK_a by approximately 1.30 units; hence, it can likewise be inferred that the resonance effect must here be responsible for the observed further decrease of approximately 0.75 unit (*cf.* Table I, below).

The experiments reported in this paper were performed in order to obtain additional evidence either for or against the belief that the electrostatic and the resonance effects are about equally responsible for the relatively great acid strengths

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(1) For the second paper of this series, see Spitzer and Wheland, THIS JOURNAL, **62**, 2995 (1940).

(2) A portion of this paper is an abstract of a thesis presented by R. M. Brownell to the faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Master of Science, March, 1943. Though here published for the first time, this portion of the work has already been briefly discussed in a book by one of us (Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 185).

(3) Westheimer, THIS JOURNAL, **61**, 1977 (1939).

(4) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 205.

TABLE I

VALUES OF pK_a AT 25°

Compound	I (E. C. M.)[a]	II (R. M. B.)[a]
Phenol[b]	9.99[e]	. . .
3,5-Dimethylphenol	10.18	10.09[c]
2,6-Dimethylphenol	10.58	10.60[d]
p-Nitrophenol[b]	7.16	7.21[d]
3,5-Dimethyl-4-nitrophenol	8.25[f]	8.24[c]
2,6-Dimethyl-4-nitrophenol	7.22[d,e,f]	7.16[d,e,g]
p-Cyanophenol[b]	7.95[c]	. . .
3,5-Dimethyl-4-cyanophenol	8.21[f]	. . .
2,6-Dimethyl-4-cyanophenol	8.27[f]	. . .

[a] Since these two sets of data were obtained at quite different times, by different investigators, and hence, possibly, under somewhat different circumstances, both sets are merely recorded separately. without any attempt to average corresponding values. [b] *Cf.* Landolt–Börnstein, "Physikalisch-chemische Tabellen"; "International Critical Tables." [c] Average of four determinations. [d] Average of three determinations. [e] Average deviation, 0.02. [f] Mixtures warmed to effect solution. [g] Samples dissolved by complete neutralization with calcium hydroxide and resulting solutions back-titrated, to approximately two-thirds neutralization, with standard hydrochloric acid.

of *p*-nitro- and *p*-cyanophenols. If the resonance with the quinoid structure (such as I or II) is prevented from occurring, only the electrostatic interaction remains; hence, from the observed acid strength of the compound in question, the magnitude of the electrostatic effect alone can be directly estimated. If the resonance effect is important, such an "inhibition" of the resonance should, therefore, lead to a significant decrease in acid strength, and so to a significant increase in the value of pK_a. Now, with a *nitro*phenol, the quinoid resonance (of the type stated) is largely, if not entirely, inhibited[5] when there is a methyl group in each of the two positions ortho to the nitro group; for, under such circumstances, the nitro group cannot lie in the plane defined by the benzene ring, but must instead be twisted out of that plane by a rotation about the carbon–nitrogen bond. With a *cyano*phenol, on the other hand, the quinoid resonance can*not* be thus inhibited[1]; for, since the cyano group is linear, it cannot be twisted out of the plane of the ring by any sort of rotation.

The foregoing considerations lead to the conclusion that, if resonance is an important factor in increasing the acid strengths of the *p*-nitro- and *p*-cyanophenols, the pK_a of a *p*-nitrophenol should be appreciably increased by the introduction of two methyl groups in the positions *ortho* to the nitro group; but that that of a *p*-cyanophenol should not be greatly affected by a corresponding substitution. Since, however, methyl substituents *directly* influence the acid strengths of phenols, even in the absence of nitro or cyano groups, a complete analysis of the problem requires that the pK_a's of several phenols besides the ones mentioned be also measured.

The data obtained in this investigation are listed in Table I. As expected, methyl groups ortho to the nitro group markedly decrease the acid strength of the phenol, whereas methyl groups ortho to the cyano group have comparatively little effect. The prediction, based on the assumption that the quinoid resonance increases the acid strengths of the *p*-nitro- and *p*-cyanophenols, is therefore confirmed. Methyl groups ortho to the *hydroxyl* group slightly decrease the acid strength, presumably because of either a direct electrostatic effect or a direct resonance (hyperconjugation) effect, or of both.

From a comparison of the data given in Table I for 3,5-dimethylphenol and for 3,5-dimethyl-4-nitrophenol, it appears that the electrostatic effect of the nitro group decreases the pK_a of the latter compound by about 1.9 units. The discrepancy between this value and the one calculated by Westheimer (1.25 units) may be explained by the assumption either that the quinoid resonance in 3,5-dimethyl-4-nitrophenol is only partially inhibited, or that the methyl groups increase the electrostatic interaction between the nitro group and the proton by decreasing the effective dielectric constant of the medium.[3] That the second of these two factors (just mentioned) really exists, and is important, is suggested by the fact that the decrease in acid strength produced by methyl groups ortho to the hydroxyl group is much smaller in 2,6-dimethyl-4-nitrophenol and in 2,6-dimethyl-4-cyanophenol than it is in 2,6-dimethylphenol, even though, in neither of the first two compounds, could the methyl groups in any way affect the resonance.

Experimental

Method and Apparatus

The pK_a values reported were measured potentiometrically. A typical cell contained an aqueous solution of the desired phenol, which had been partially neutralized by standard calcium hydroxide; a Corning 015 glass electrode with an inner reference electrode[6]; and a saturated calomel electrode. The design of the calomel electrode assembly (Leeds and Northrup Company, Cat. No. 7724) was such that the liquid junction was formed through a ground glass joint at the end of the salt bridge. The cell was immersed in an oil thermostat maintained at 25 ± 0.5°. The values of the e. m. f. were measured to the nearest 0.2 mv. by means of a Leeds and Northrup vacuum tube electrometer.

The phenol concentrations in the solutions measured ranged from 0.0015 to 0.0088 *M* and were determined by the solubilities of the respective phenols, by the degrees of neutralization intended, and by the normalities of the calcium hydroxide solutions to be used. In general, the concentration of phenol was such that not less than 9 or 10 ml. of calcium hydroxide solution would be required per 100 ml. of final solution. Calcium hydroxide was

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(5) (a) Birtles and Hampson, *J. Chem. Soc.*, 10 (1937); (b) Ingham and Hampson, *ibid.*, 981 (1939); (c) Wheland and Danish, THIS JOURNAL, **62**, 1125 (1940); (d) Spitzer and Whelan, *ibid.*, **62**, 2995 (1940); (e) Westheimer and Metcalf, *ibid.*, **63**, 1339 (1941).

(6) The glass electrodes used in obtaining one set of data (II (R. M. B.), Table I) were made by Mr. John D. Farr and contained silver–silver chloride inner reference electrodes. The one used for the other set of measurements (I (E. C. M.), Table I) was a commercial product, purchased from the Central Scientific Company; the inner reference electrode was unspecified and unobservable.

chosen as the base because of the low error attending the positive ion of this substance in measurements with glass electrodes.[7] The concentrations of the calcium hydroxide solutions used varied between 0.00770 and 0.01940 N. The ionic strength of the final solution was always well under 0.01.

The glass electrode was standardized daily by measuring the e. m. f. of a cell containing a Sörensen borate-hydrochloric acid buffer with a pH of 8.25 (interpolated) at 25°.[8] The pH of each phenol solution was calculated in the usual way[9] from the corresponding e. m. f. and the appropriate value of the e. m. f. given by the buffer solution. From the pH value thus obtained, the pK_a of the phenol was computed.[10] The pK_a's were corrected for the ionic strength effect by means of the Debye-Hückel limiting law,[11] and for the hydrolysis of the salt with use of the assumption that the concentrations of hydrogen and hydroxide ion were equal to the respective activities, as determined by the measured pH.

Unless otherwise noted in Table I, each pK_a value reported is the average of at least five independent determinations, with an average deviation of not more than 0.01 pK unit. The measurements of column II (R. M. B.) were made on phenol solutions, each of which was approximately half neutralized with calcium hydroxide; those of column I (E. C. M.), on the other hand, were made on solutions which varied in degree of neutralization as widely as was permitted by the solubilities of the particular phenols concerned. If, in a measurement, there was any question whether an error had been made, the value obtained was not included in the average even if it were reasonable. Three values were rejected on statistical grounds.[12]

With the cyanophenols, it was necessary to consider the possibility that the cyano groups might be hydrolyzed during the preparation of the solutions studied. The belief that no significant hydrolysis occurred is supported by the following evidence: (1) Nitriles of comparable molecular weight are, in general, not appreciably hydrolyzed under the conditions here employed. More specifically, Thiele and Eichwede[13] have stated that 2,6-dimethyl-4-cyanophenol is not hydrolyzed when it is boiled with dilute aqueous acids or bases; and, although the hydrolysis of 3,5-dimethyl-4-cyanophenol, itself, is not mentioned in the literature, a number of comparable compounds,[14] such as 2,6-dimethylbenzonitrile[15] and 2,4,6-trimethylbenzonitrile[16] in particular, have been reported to be stable toward alkalies. Moreover, 3,5-dimethyl-4-cyanophenol was found in this present study to be apparently unaffected when it was warmed with alkaline aqueous hydrogen peroxide. (2) Calculations indicate that appreciable hydrolysis of a cyanophenol to a product of significantly different acid strength would probably be evidenced by a systematic variation, exceeding experimental deviations, in the pK_a values calculated for that compound over the range of degrees of neutralization concerned. No such systematic variations were observed. (3) The excellent agreement between individual results, which was obtained for each of the cyanophenols studied, was independent, not only of the degree of neutralization, but also of the age of a solution and of the length of time during which it was warmed. (4) The three cyanophenols investigated, when recovered from representative solutions by acidification and extraction with ethyl acetate, showed no marked change in melting point. (5) With the use of Nessler reagent, the amount of ammonia produced was shown, in typical instances, to be less than 0.5% of that corresponding to complete hydrolysis.

Materials

The temperatures reported below are uncorrected. They were taken, unless otherwise indicated, on a thermometer calibrated against one standardized by the Bureau of Standards, or on the latter itself.

Phenol.—Mallinckrodt Analytical Reagent grade was distilled; a portion of the large amount that boiled, according to a non-standardized thermometer, constantly at 177.0° was reserved for use and stored in a vacuum desiccator in the presence of phosphorus pentoxide.

3,5-Dimethylphenol.—Eastman Kodak Co. best grade was recrystallized from light petroleum ether; m. p. (R. M. B.) 62.8–63.3°, m. p. (E. C. M.) 62.5–63.0°.[17]

2,6-Dimethylphenol.—2,6-Dimethylphenol, prepared from Eastman Kodak Co. m-2-xylidine through the diazonium salt, was recrystallized from light petroleum ether; m. p. (R. M. B.), on non-standardized thermometer, 48°, m. p. (E. C. M.) 44.7–45.6°.

***p*-Nitrophenol.**—Eastman best grade was recrystallized from carbon tetrachloride; m. p. (R. M. B.) 112.6–113.0°, m. p. (E. C. M.) 113.2–113.7° and 113.0–113.5°.

3,5-Dimethyl-4-nitrophenol.—3,5-Dimethyl-4-nitrophenol, prepared by the nitration of 3,5-dimethylphenol, was isolated by the codistillation procedure used by Rassow and Schultzky[18] for p-nitrophenol. This procedure employs a high-boiling petroleum fraction; an "ink oil" obtained from the Martin Driscoll Company, Chicago, was found to have approximately the correct boiling range, *viz.*, 265–280° (760 mm.). This method was found to give much more satisfactory yields than the usual procedures for isolating the *para* isomer: m. p. (R. M. B.) 107.1–107.6°, m. p. (E. C. M.), after recrystallization from carbon tetrachloride, 107.6–108.3°.

2,6-Dimethyl-4-nitrophenol.—2,6-Dimethyl-4-nitrophenol, obtained by condensation of the sodium salt of nitromalonaldehyde with diethyl ketone, as described by Jones and Kenner,[19] was purified by several decolorizations with Norite or Nuchar and recrystallizations from various solvents, of which the most efficacious was carbon tetrachloride. Because of the evident instability of this compound at temperatures near its melting point, the melting point of any sample varied markedly with the duration of heating; the best melting points obtained for the two portions used for measurement were, respectively: m. p. (R. M. B.) 170.5–170.6°, m. p. (E. C. M.), on non-standardized thermometer, 169.6–169.7°.

***p*-Cyanophenol.**—p-Cyanophenol, prepared from p-aminophenol by a Sandmeyer reaction, was decolorized with Norite and recrystallized from carbon tetrachloride; m. p. 112.0–112.4°.

3,5-Dimethyl-4-cyanophenol.—3,5-Dimethyl-4-cyanophenol was prepared by a stepwise procedure from 3,5-dimethylphenol. The 3,5-dimethylphenol was converted, by means of a Gattermann reaction, to 2,6-dimethyl-4-hydroxybenzaldehyde and the oxime of this aldehyde was dehydrated with acetic anhydride, as described by v. Auwers and co-workers,[20] to the desired cyano-xylenol. It was found that the yield of 2,6-dimethyl-4-acetoxybenzonitrile, the intermediate involved in the dehydration

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[7] Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, chap. 7.

[8] Sörensen, *Biochem. Z.*, **21**, 131 (1909); Walbum, *ibid.*, **107**, 219 (1920).

[9] See p. 296 of ref. 7.

[10] (a) Cohn, This Journal, **49**, 173 (1927); (b) Cohn, Heyroth and Menkin, *ibid.*, **50**, 696 (1928); (c) MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1094 (1938).

[11] See ref. 10a.

[12] Pierce and Haenisch, "Quantitative Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 43.

[13] Thiele and Eichwede, *Ann.*, **311**, 363 (1900).

[14] For a general discussion of the hydrolysis of such compounds, see Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 39.

[15] Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

[16] Grignard, Bellet and Courtot, *Ann. chim.*, [9] **4**, 28 (1915); Küster and Stallberg, *Ann.*, **278**, 207 (1894).

[17] Kester (*Ind. Eng. Chem.*, **24**, 770 (1932)) states that, although melting points of 64, 64.5 and 68° have been reported, 63.2° was the highest melting point obtained in his laboratory.

[18] Rassow and Schultzky, *Angew. Chem.*, **44**, 669 (1931).

[19] Jones and Kenner, *J. Chem. Soc.*, 1842 (1931).

[20] v. Auwers, Mürbe, Saurwein, Deines and Schornstein, *Fortschr. Chem. Physik physik. Chem.*, **18**, no. 2, 5 (1924).

process, could be greatly improved through purification of this compound by vacuum distillation rather than by recrystallization from water. The crude 3,5-dimethyl-4-cyanophenol was recrystallized from benzene; it formed glistening, white scales; m. p., on non-standardized thermometer, 177.5–177.7°.

Because of reports[19,21] that 3,5-dimethyl-4-cyanophenol crystallizes from benzene in small needles and melts at about 175°, the identity of this compound was confirmed by analysis.[22]

Anal. Calcd. for C_9H_9ON: C, 73.38; H, 6.16; N, 9.52. Found: C, 73.55; H, 6.38; N, 9.46.

2,6-Dimethyl-4-cyanophenol.—2,6-Dimethyl-4-cyanophenol was prepared from mesitol by the method of Thiele and Eichwede[13] and recrystallized from medium-boiling petroleum ether; m. p. 124.0–124.4°.

Summary

1. The pK_a's of the following compounds have been determined at 25°: 3,5-dimethylphenol, 2,6-dimethylphenol, 3,5-dimethyl-4-nitrophenol, 2,6-dimethyl-4-nitrophenol, 3,5-dimethyl-4-cyanophenol, 2,6-dimethyl-4-cyanophenol.
2. The pK_a's at 25° have been redetermined for the following compounds: phenol, *p*-nitrophenol, *p*-cyanophenol.
3. The results provide evidence that the total effect produced by a para nitro or para cyano group on the acid strength of phenol is due about equally to an electrostatic interaction and to resonance.

CHICAGO, ILLINOIS RECEIVED APRIL 5, 1948

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[21] Houben and Fischer, *Ber.*, **66**, 339 (1933).

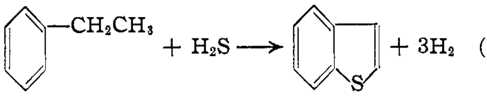
[22] The carbon–hydrogen analysis was made by Mr. James G. Burt.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Catalytic Synthesis of Thianaphthene from Ethylbenzene

BY CORWIN HANSCH AND FRED HAWTHORNE

In a recent paper, Moore and Greensfelder[1] published the procedure for a new synthesis of thianaphthene from styrene and hydrogen sulfide. While this procedure is an excellent one for the preparation of thianaphthene itself, it would not be as convenient for the preparation of substituted thianaphthenes because of the lack of availability of the proper styrenes as starting materials. Thus, it seemed that the dehydrogenation of an alkylbenzene in the presence of hydrogen sulfide might be accomplished over a single catalyst with formation of the thianaphthene in one step according to Equation I.



(I)

The present paper reports the results of such an attempt.

Experimental

All experiments were carried out in a Pyrex catalyst tube in a continuous flow system. The apparatus used was similar to that described by Hoog, Verheus and Zuiderweg.[2]

The hydrogen sulfide used in this work was commercial grade used directly from the cylinder. Eastman Kodak Co. white label ethylbenzene was distilled before using.

Catalyst Preparations. I. Chromium on Aluminum Oxide.—To a boiling solution of 36.4 g. of chromic anhydride in 400 ml. of distilled water was added 200 g. of ALORCO alumina,[3] Grade H40, Type R2200, 8–14 mesh. The mixture was dried at 100°.

II. Chromium and Nickel on Aluminum Oxide.—Chromic anhydride (7.6 g.) and 12.5 g. of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 50 cc. of water and the solution brought to boiling. To this solution was added 50 g. of activated alumina with vigorous stirring. The mixture was then dried in an oven at 100°.

For the preparation of thianaphthene, the straight chromium catalyst[4] was reduced *in situ* with a slow stream of hydrogen, for one hour at the temperature at which dehydrogenation was to be made, then a stream of hydrogen sulfide passed over the catalyst for fifteen to twenty minutes at the same temperature. Ethylbenzene was then introduced at a uniform rate. A space velocity ratio of about 9:1 of hydrogen sulfide and ethylbenzene was found to give the highest conversion. Most of the liquid products were separated in a Liebig condenser. A small amount of liquid entrained in the large volume of hydrogen sulfide and hydrogen was separated by passing the gases through a U-tube filled with glass wool and cooled in an ice-bath. Using this technique, it was possible to obtain excellent material balances in all runs. The thianaphthene was isolated by distillation and identified by a comparison of it and its picrate with that of a sample prepared by a known procedure.[5]

Discussion

Table I shows the effect of temperature and space velocity on the conversion of ethylbenzene to thianaphthene.

TABLE I

The space velocity of hydrogen sulfide in all runs was 1400 cc./cc./hr.

Catalyst	Temp., °C.	Space velocity,[a] ethylbenzene cc./cc./hr.	% Conversion to thianaphthene
I	550	160	9.3
I	575	160	18.5
I	575	260	13.2
II	575	160	17.0
II	610	245	13.2
II	625	160	18.5

[a] Calculated as cc. of vapor at S.T.P.

The above runs were made for periods of four hours. It was observed that, although the rate of dehydrogenation (as estimated by hydrogen evolution) was more rapid

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[1] THIS JOURNAL, **69**, 2008 (1947).

[2] Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 995 (1939).

[3] This type of alumina was used exclusively in the research and was supplied through the courtesy of the Aluminum Ore Company.

[4] The nickel–chromium catalysts were reduced for two hours.

[5] Hansch and Lindwall, *J. Org. Chem.*, **10**, 381 (1945).