Oxidation of Organic Compounds with Cerium(IV). IV. Oxidation of Benzyl and Related Alcohols[1a-d]

WALTER S. TRAHANOVSKY, L. BREWSTER YOUNG,[1c,e] AND GRACIE L. BROWN[1f]

Department of Chemistry, Iowa State University, Ames, Iowa 50010

Received May 11, 1967

Yields of products from the oxidation of benzyl and related alcohols by ceric ammonium nitrate in water or 50% aqueous acetic acid are presented. The corresponding carbonyl compound is usually obtained in a relatively pure form and in high yield. Other means of oxidizing benzyl and related alcohols to carbonyl compounds are discussed and compared to the cerium(IV) oxidation. It is concluded that cerium(IV) oxidation is often the method of choice for oxidizing benzyl and related alcohols to the corresponding aldehydes on a synthetically useful scale.

Studies of cerium(IV) oxidations of a variety of alcohols have been reported.[1a,2] Usually the carbonyl compound is the first formed product, but Schaafsma, Steinberg, and de Boer[2h] report that the oxidation of cyclopropanols with ceric sulfate leads to ring-opened products and Mosher, Clement, and Hillard[2d] report that aryl-*t*-butylcarbinols are quantitatively cleaved to benzaldehydes by cerium(IV). Only two of these reports, however, have described synthetically useful oxidations by cerium(IV) which involve the conversion of a relatively large amount of starting material to a high yield of a useful product.[1a,2i] In this paper, we report the synthetically useful conversion of benzyl and related alcohols to the corresponding carbonyl compounds by cerium(IV).[1d]

Several reagents have been used to convert benzyl and related alcohols to their corresponding carbonyl compounds on a preparative scale.[3-5] However, the use of these reagents often involves troublesome procedures or leads to poor results. The use of chromium trioxide–pyridine or *t*-butyl chromate involves a dangerous preparation of the reagent, a long reaction time, and a difficult isolation procedure.[3o] The use of dichromate in aqueous sulfuric acid, glacial acetic acid, or aqueous acetic acid often leads to further oxidation of the aldehyde.[3o] Lead tetraacetate oxidations involve careful handling of the hygroscopic oxidant.[3p] Manganese dioxide oxidations require manganese dioxide of a reactivity that is quite difficult to prepare.[3e,g,i] Permanganate oxidations can be used only in the preparation of ketones since aldehydes are further oxidized.[3h] The Oppenauer oxidation of benzyl and related alcohols has not been extensively studied, but the existing procedures are involved and inconvenient.[6] The recently developed oxidations of primary alcohols by dimethyl sulfoxide[3j,m] and dicyclohexylcarbodiimide dimethyl sulfoxide[3l,q] require the tedious isolation of the aldehyde from an excess of dimethyl sulfoxide. Oxidations by dinitrogen tetroxide, nickel peroxide, ruthenium tetroxide, or selenium dioxide involve reagents that are either too inconvenient, expensive, or toxic to use routinely.[4] Other unusual reagents have not been shown to be generally useful.[5]

In summary, it is clear that the existing methods of oxidizing benzyl and related alcohols to carbonyl compounds have disadvantages such as the use of reagents which are difficult or expensive to prepare and handle or an inconvenient procedure for isolation of product. Cerium(IV) oxidation of benzyl and related alcohols obviates these disadvantages in many cases.

Results

Ceric ammonium nitrate (0.5 *M*) in water or 50% aqueous acetic acid converts many benzyl and related alcohols to the corresponding aldehyde or ketone conveniently and in high yield. The results are summarized in Table I. The general procedure is as follows. To the alcohol is added a 0.5 *M* solution of ceric ammonium nitrate which contains 2.1 equiv of

---

(1) (a) Part III: L. Brewster Young and W. S. Trahanovsky, *J. Org. Chem.*, **32**, 2349 (1967). (b) This work was partially supported by Public Health Service Grant GM 13799-01A1 from the National Institute of General Medical Sciences, and a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society. (c) Based on work by L. B. Young in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University. (d) Preliminary communication: W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965). (e) U. S. Public Health Service Fellow, 1966–1967. (f) National Science Foundation College Teacher Research Participant, summer 1966.

(2) (a) W. H. Richardson in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 247–255, and references cited therein; (b) K. Vijayachander and S. S. Muhammad, *Bull. Chem. Soc. Japan*, **36**, 943 (1963); (c) *ibid.*, **36**, 949 (1963); (d) W. A. Mosher, W. H. Clement, and R. L. Hillard, "Selective Oxidation Processes," American Chemical Society Monograph No. 51, 1965, pp 81–88; (e) M. Ramaswamy and M. Santappa, *Current Sci.* (India), **35**, 332 (1966); (f) B. Sethuram, *ibid.*, **35**, 254 (1966); (g) M. Ramaswamy and M. Santappa, *ibid.*, **35**, 332 (1966); (h) S. E. Schaafsma, H. Steinberg, and T. J. de Boer, *Rec. Trav. Chim.*, **85**, 73 (1966); (i) R. Brossmer and D. Ziegler, *Tetrahedron Letters*, 5253 (1966); (j) H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967).

(3) (a) H. Adkins and R. C. Franklin, *J. Am. Chem. Soc.*, **63**, 2381 (1941); (b) R. R. Davies and H. H. Hodgson, *J. Soc. Chem. Ind.*, **62**, 109 (1943); (c) M. Yamashita and T. Matsumura, *J. Chem. Soc. Japan*, **64**, 506 (1943); *Chem. Abstr.*, **41**, 3753 (1947); (d) V. M. Mićović and M. L. Mihailović, *Rec. Trav. Chim.*, **71**, 970 (1952); (e) M. Harnfeist, A. Baveley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954); (f) D. L. Turner, *J. Am. Chem. Soc.*, **76**, 5175 (1954); (g) R. J. Highnet and W. C. Wildman, *ibid.*, **77**, 4399 (1955); (h) R. Stewart in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 2–68; (i) R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959); (j) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959); (k) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, **28**, 323 (1953); (l) K. E. Pfitzner and J. G. Moffat, *J. Am. Chem. Soc.*, **85**, 3027 (1963); (m) V. J. Traynelis and W. L. Hergenrother, *ibid.*, **86**, 298 (1964); (n) R. E. Partch, *Tetradron Letters*, No. 41, 3071 (1964); (o) K. B. Wiberg in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 69–184; (p) R. Criegee, *ibid.*, pp 278 ff; (q) K. E. Pfitzner and J. G. Moffat, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

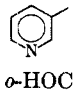
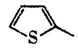
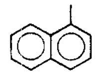
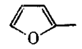
(4) (a) S. Astin, A. C. C. Newman, and H. L. Riley, *J. Chem. Soc.*, 391 (1933); (b) B. O. Field and J. Grundy, *ibid.*, 1110 (1955); (c) L. M. Berkowitz and P. N. Rylander, *J. Am. Chem. Soc.*, **80**, 6682 (1958); (d) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

(5) (a) M. Metayer and S. Roumens, *Compt. Rend.*, **225**, 1324 (1947); (b) J. Lecomte and C. Dufour, *ibid.*, **234**, 1887 (1947); (c) M. F. Hebbelynck and R. H. Martin, *Experientia*, **5**, 69 (1949); (d) L. Farkas and O. Schächter, *J. Am. Chem. Soc.*, **71**, 2827 (1949); (e) J. Blair, W. R. Logan, and G. T. Newbold, *J. Chem. Soc.*, 2443 (1956); (f) E. A. Braude, R. P. Linstead, and K. R. Wollridge, *ibid.*, 3070 (1956); (g) E. D. Bergman and I. Shahak, *ibid.*, 1418 (1959); (h) R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Commun.*, 744 (1966); (i) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Am. Chem. Soc.*, **88**, 2328 (1966).

(6) C. Djerassi in "Organic Reactions," Vol. 6, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p 222.

TABLE I

OXIDATION OF BENZYL AND RELATED ALCOHOLS TO ALDEHYDES OR KETONES BY CERIC AMMONIUM NITRATE

Alcohol, RCHOHR'		Yield[a] in H_2O, %	Yield[a] in 50% aq HOAc, %
R	R'		
1. Normal Reaction[b]			
C_6H_5	H	87[c]	94,[d] 72[c]
p-$CH_3C_6H_4$	H	86[e]	94,[d] 74[e]
o-ClC_6H_4	H	77[e], 62[c]	89,[d] 85[e]
p-BrC_6H_4	H	83[e]	93[d]
o-$O_2NC_6H_4$	H	. . .	100[d]
m-$O_2NC_6H_4$	H	94[e]	79[d]
p-$O_2NC_6H_4$	H	81[e]	92,[d] 77[e]
p-$CH_3OC_6H_4$	H	80[c]	94[d]
p-$HOCH_2C_6H_4$	H	90[e,f]	. . .
C_6H_5	C_6H_5	60[e]	57[e]
C_6H_5	CH_3	55[e]	. . .
2,4,6-$(CH_3)_3C_6H_2$	H	35[e]	89[e]
2. Special Cases[b]			
	H	75[e], 50[c]	. . .
o-$HOCH_2C_6H_4$	H	23[e,g] 42[e,h]	. . .
3. Low Yield and/or Dark Colored[b]			
m-$CH_3OC_6H_4$	H	. . .	25[e]
3,4-$(CH_3O)_2C_6H_3$	H	30[e]	. . .
	H	58[c]	. . .
	H	21[e]	28[i]
m-$(C_6H_5COO)C_6H_4$	H	. . .	18[e]
4. No Carbonyl Product[b]			
p-$CH_3SC_6H_4$	H	0[e]	0[e]
	H	0[e]	0[e]
trans-$C_6H_5CH{=}CH$	H	0[e]	0[e]
m-HOC_6H_4	H	0[e]	. . .

[a] The product was the corresponding aldehyde or ketone unless otherwise noted. [b] See Discussion. [c] Yield of distilled product. [d] Yield obtained by glpc analysis of at least two runs. [e] Yield of undistilled product, corrected for impurities by nmr. [f] Product was terephthalaldehyde. [g] Product was phthalaldehyde. [h] Product was phthalide. [i] Yield obtained by addition of a standard and nmr analysis.

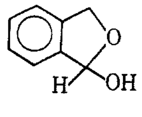
cerium(IV) for every mole of alcohol. The resulting solution or slurry is stirred and heated at 50–100° until the red-orange cerium(IV)–alcohol complex color fades to pale yellow or colorless (2–30 min). The aldehyde or ketone is isolated by extraction with ether in the usual fashion. The product obtained in this way is often greater than 95% pure.

Discussion

In general, benzyl alcohols are smoothly converted to benzaldehydes by cerium(IV) oxidation (eq 1). Isolation of the product is experimentally simpler when the reaction is carried out in water instead of 50% aqueous acetic acid. However, in certain cases, the greater solubility of the reactant in 50% aqueous acetic acid seems to result in a higher yield of desired product. For example, the oxidation of 2,4,6-trimethylbenzyl alcohol leads to 35% mesitaldehyde in water and 89% mesitaldehyde in 50% aqueous acetic acid. Thus the solvent of choice for higher molecular weight alcohols is probably 50% aqueous acetic acid.[7]

$$ArCH_2OH + 2Ce(IV) \longrightarrow ArCH{=}O + 2Ce(III) + 2H^+ \quad (1)$$

Oxidation of 1 mole of phthalyl alcohol by 4.2 moles of ceric ammonium nitrate in aqueous solution gave 42% phthalide in addition to 23% of the normal product, phthalaldehyde. High yields of phthalide have been obtained from oxidation of phthalyl alcohol by chromium trioxide–pyridine, sodium dichromate in aqueous sulfuric acid, and aqueous potassium permanganate.[3k] It was postulated that phthalide is obtained by the oxidation of the hemiacetal 1.[3k] None of these oxidations produces phthalaldehyde.[3k]



1

Conversion of 3-pyridylmethanol to 3-pyridinecarbaldehyde presented some unusual problems since the product is basic. After oxidation of the alcohol with aqueous ceric ammonium nitrate, the reaction mixture was neutralized with aqueous potassium hydroxide which produced a voluminous precipitate of cerous hydroxide. The mixture was filtered and the filtrate was extracted with chloroform. Removal of the solvent gave a 75% yield of 3-pyridinecarbaldehyde.

The alcohols studied can be divided into four classes depending on their behavior on oxidation with cerium (IV): (1) normal reaction, (2) cases that require special attention, (3) low yield of normal product and/or dark-colored material formed, (4) no normal product formed. In Table I the alcohols are divided into these four classes. From inspection of this table it can be concluded that alcohol-to-carbonyl conversion works well except in those cases where a very reactive ring system or an easily oxidized or acid-sensitive functional group is present.

In those cases where aldehyde or ketone is obtained in high yield, the convenience of the cerium(IV) oxidation seems to make it the method of choice. Ceric ammonium nitrate is an easily handled, nontoxic, nonhygroscopic solid which is readily available in pure form. Aqueous solutions >2 *M* can easily be prepared. If several reactions are to be carried out, the reagent is conveniently stored as a 1 *M* aqueous solution which is stable for months. These solutions can be standardized using ferrous ammonium sulfate as a primary standard and ferroin as indicator;[8] however, commercial grades of ceric ammonium nitrate are generally greater than 95% pure and solutions of known concentration of cerium(IV) can easily be made up by weight. Not only do cerium(IV) oxidations involve the use of a reagent that is readily available and easy to handle, but they are rapid, easy to follow, and involve easy isolation of a pure product.

Experimental Section

General.—Equipment has been previously described.[9] Melting and boiling points are uncorrected.

---

[7] We have found that aqueous acetonitrile mixtures are useful solvents for cerium(IV) oxidations. The use of acetonitrile instead of acetic acid as a cosolvent avoids the formation of acetates from reactants or products that contain hydroxy groups.

[8] G. F. Smith, G. Frank, and A. E. Kott, *Ind. Eng. Chem., Anal. Ed.*, **12**, 268 (1940).

[9] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

Materials.—Ceric ammonium nitrate was reagent grade from the G. F. Smith Chemical Co. Titration of weighed samples with 0.1 *N* ferrous ammonium sulfate using ferroin as an indicator[8] showed that the material was 97% pure and had an effective molecular weight of 563.

m-Methoxybenzyl alcohol, *p*-methoxybenzyl alcohol, *m*-hydroxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 3-pyridylmethanol, and furfuryl alcohol were Aldrich products and were used without purification. Benzyl (chlorine free), *m*-nitrobenzyl, and cinnamyl alcohols were from Eastman and were used without purification. Benzhydrol was from Matheson Coleman and Bell and was unpurified. *p*-Methylbenzyl alcohol was prepared by the saponification of *p*-methylbenzyl acetate[10] obtained from Aldrich. The product was recrystallized from heptane, mp 57.0–59.5° (lit.[11] mp 59°). 2,4,6-Trimethylbenzyl alcohol was prepared by the lithium aluminum hydride reduction of mesitaldehyde (Aldrich) and recrystallized from ligroin (bp 60–70°), mp 83–84.5° (lit.[12] mp 88–89°). *o*-Chlorobenzyl alcohol was prepared from *o*-chlorobenzyl chloride (Aldrich). A mixture of 80.5 g (0.50 mole) of the chloride, 52 g (0.53 mole) of potassium acetate, and 750 ml of 95% ethanol was refluxed for 8 hr. The mixture was filtered, 33.6 g of potassium hydroxide was added to the filtrate, and it was refluxed for 6 hr. The mixture was diluted with *ca.* 2 l. of water and extracted with chloroform. Concentration of the chloroform solution gave 30 g (42%) of *o*-chlorobenzyl alcohol. The product was recrystallized successively from ligroin, heptane, 75% aqueous ethanol, and ligroin, mp 69–70° (lit.[13] mp 69°). *p*-Bromobenzyl alcohol was prepared from *p*-bromobenzyl bromide (Aldrich) using the procedure described for the preparation of *o*-chlorobenzyl alcohol. The product was obtained in 72% yield and recrystallized from ligroin–benzene, mp 76–77.5° (lit.[14] mp 76–76.5°). *o*-Nitrobenzyl alcohol was obtained from Aldrich and recrystallized from 75% aqueous ethanol, mp 69–70° (lit.[15] mp 74°). *p*-Nitrobenzyl alcohol was prepared from *p*-nitrobenzyl bromide (Matheson Coleman and Bell) as follows. A mixture of 47.9 g (0.22 mole) of *p*-nitrobenzyl bromide, 34.4 g (0.35 mole) of potassium acetate, and 400 ml of 95% ethanol was refluxed for 3 hr. The reaction mixture was cooled to 0° by means of an ice bath and the large flat needles which precipitated were filtered and dissolved in 125 ml of hot methanol. A quantity of 60 ml of 15% sodium hydroxide solution was added. After standing for 5 min, the solution was poured into an ice–water mixture. The resulting precipitate was collected on a Büchner funnel and recrystallized from water to yield 6.4 g (16.8%) of product, mp 92.5–93° (lit.[16] mp 93°). *p*-(Methylthio)benzyl alcohol was prepared from *p*-aminobenzoic acid (Aldrich) by the method of Grice and Owen.[17] The product was recrystallized from ligroin, mp 38.2–40.5° (lit.[17] mp 37–39°). *m*-Benzoyloxybenzyl alcohol was prepared by the addition of 9.3 ml (0.081 mole) of benzoyl chloride to a solution of 10 g (0.081 mole) of *m*-hydroxybenzyl alcohol and 5.31 g (0.081 mole) of potassium hydroxide in 53 ml of water. Extraction of the resulting mixture with ether followed by removal of the ether on a rotary evaporator gave *ca.* 10 ml of a viscous brown liquid which was 95% pure as shown by its nmr spectrum. Phthalyl alcohol was prepared by the lithium aluminum hydride reduction of phthalic anhydride.[18] The product was recrystallized from ether, mp 63.5–65.5° (lit.[18] mp 64°). Terephthalyl alcohol was prepared by the lithium aluminum hydride reduction of terephthalaldehyde (Aldrich). The product was recrystallized from water, mp 117–120° (lit.[19] mp 115–116°). 2-Thiophenemethanol was prepared by the lithium aluminum hydride reduction of 2-thiophenecarbaldehyde (Aldrich) and purified by distillation, bp 65° (0.05 mm) (lit.[20] bp 97–102° (13 mm)). 1-Naphthylmethanol was prepared by the lithium aluminum hydride reduction of 1-naphthaldehyde (Aldrich). The product was recrystallized from ether, mp 59.5–60.5° (lit.[21] mp 59°).

General Procedure for Oxidation of Benzyl and Related Alcohols by Aqueous Ceric Ammonium Nitrate.—Into a 250-ml erlenmeyer flask equipped with a magnetic stirring bar was placed 0.019 mole of the alcohol and 40 ml of water. If the alcohol was a liquid at room temperature or was water soluble, 40 ml of a 1 *N* solution of ceric ammonium nitrate was added with stirring at room temperature.[22] If the alcohol was a water-insoluble solid at room temperature, the alcohol–water mixture was heated and stirred until the solid had melted and then the ceric ammonium nitrate solution was added with stirring. The mixture or solution was heated and stirred at temperatures up to 90° to complete the reaction. The initial color of the reaction mixture was usually a deep red which faded to yellow or colorless when reaction was complete. There were some exceptions to this color change, however. Reaction times and color changes observed for each alcohol are listed in Table II.

When reaction was complete, the reaction mixture was cooled and extracted three times with ether or methylene chloride. The combined organic layers were washed with a saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed by distillation on a steam bath through a 20-cm column packed with glass helices. The last traces of solvent were removed on a rotary evaporator. Purity of the weighed product was determined by nmr and is indicated in Table II. It was assumed that the only impurities were solvent and the corresponding alcohol and acetate. In some cases the product was purified by distillation.

General Procedure for Oxidation of Benzyl and Related Alcohols by Ceric Ammonium Nitrate in 50% Aqueous Acetic Acid.—Into a 250-ml erlenmeyer flask equipped with a magnetic stirring bar was placed a solution of 0.019 mole of the alcohol in 40 ml of glacial acetic acid. To this was added 40 ml of a 1 *N* solution of ceric ammonium nitrate in water. The resulting solution or mixture was heated at temperatures up to 90° to complete the reaction. Generally, the initial color of the reaction mixture was deep red and faded to yellow or colorless at the completion of the oxidation. The reaction mixture was cooled, diluted with two volumes of water, and extracted three times with ether or methylene chloride. The combined organic layers were washed with water and 1.5 *N* potassium hydroxide or saturated sodium bicarbonate. The organic layer was dried over magnesium sulfate and the solvent was removed by distillation on a steam bath through a 20-cm column packed with glass helices. The last traces of solvent were removed on a rotary evaporator. The weighed product was analyzed for purity by nmr. Reaction times, color changes, and purity of the products are listed in Table II. In some cases the product was purified by distillation.

Glpc Yields.—A quantity of 8 ml of a 0.5 *N* solution of ceric ammonium nitrate in 50% aqueous acetic acid was added to 1.9 mmoles of the benzyl alcohol and the solution was heated on a steam bath until the color changed from red to pale yellow or colorless. A quantity of 100 μl of ethyl butyrate was added as a standard and the solution was added to 25 ml of water in a separatory funnel and extracted with 25 ml of ether. The ether layer was washed with 25 ml of 1.5 *N* potassium hydroxide and dried over magnesium sulfate. The ether layer was analyzed by glpc using SF-96 or QF-1 columns at 100–225° and the ratio of aldehyde peak area–standard peak area was obtained by cutting out and weighing the peaks.

This ratio was corrected for differences in thermal conductivities and distribution ratios by adding 1.9 mmoles of the aldehyde and 100 ml of ethyl butyrate to 8 ml of a cerous ammonium nitrate solution in 50% aqueous acetic acid and treating it in the same manner as the oxidized mixture. Equation 2 was used to calculate the yield of aldehyde. A_p' and A_s' are the respective areas of the aldehyde and standard peaks from the oxidation of the alcohol. A_p and A_s are the corresponding areas obtained from the control experiment.

$$\%\ \text{aldehyde} = \frac{A_p'/A_s'}{A_p/A_s} \times 100 \qquad (2)$$

The cerous ammonium nitrate solution was prepared by adding a few drops of ethanol to the 0.5 *N* solution of ceric ammonium

---

(10) W. W. Hartman and E. J. Rahrs, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 652.

(11) H. D. Law, *J. Chem. Soc.*, **91**, 748 (1907).

(12) P. Carré, *Compt. Rend.*, **151**, 150 (1910).

(13) K. W. Rosemund and G. Jordan, *Ber.*, **58**, 162 (1925).

(14) W. H. Carothers and R. Adams, *J. Am. Chem. Soc.*, **46**, 1682 (1924).

(15) H. Lund, *Ber.*, **70**, 1520 (1937).

(16) F. Beilstein and A. Kuhlberg, *Ann.*, **147**, 339 (1868).

(17) R. Grice and L. N. Owen, *J. Chem. Soc.*, 1947 (1963).

(18) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

(19) E. Bourquelot and A. Ludwig, *Compt. Rend.*, **159**, 213 (1914).

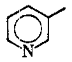
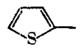
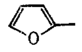
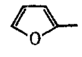
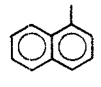
(20) W. S. Emerson and T. M. Patrick, Jr., *J. Org. Chem.*, **14**, 790 (1949).

(21) E. Bourquelot and M. Bridel, *Compt. Rend.*, **168**, 323 (1918).

(22) For oxidation of phthalyl and terephthalyl alcohols, 80 ml of water and 80 ml of 1 *N* ceric ammonium nitrate were used.

TABLE II

REACTION TIME, COLOR CHANGE, AND PRODUCT PURITY FOR OXIDATION OF BENZYL AND RELATED ALCOHOLS TO ALDEHYDES AND KETONES BY CERIC AMMONIUM NITRATE

Alcohol, RCHOHR′		Reaction time, min	Color change and product purity[a]
R	R′		
			In Water
C_6H_5	H	8	Normal;[b] crude aldehyde >95% pure; distilled aldehyde >99% pure
p-$CH_3C_6H_4$	H	8	Normal; crude aldehyde >95% pure
2,4,6-$(CH_3)_3C_6H_2$	H	2	Normal; aldehyde/alcohol = 40/60
o-ClC_6H_4	H	8	Normal; crude aldehyde 95% pure; distilled aldehyde 95% pure
p-BrC_6H_4	H	8	Normal; crude aldehyde 99% pure; mp 56.6° (lit.[c] mp 56.5–57°)
m-$O_2NC_6H_4$	H	11	Normal; crude aldehyde >95% pure
p-$O_2NC_6H_4$	H	7	Normal; crude aldehyde >95% pure; mp 100–102° (lit.[d] mp 106°)
p-$CH_3OC_6H_4$	H	5	Normal; crude aldehyde 95% pure; distilled aldehyde >95% pure
p-$CH_3SC_6H_4$	H	1	Normal; no aldehyde
m-HOC_6H_4	H	. . .	Brown tar formed on addition of ceric ammonium nitrate solution; no aldehyde formed
3,4-$(CH_3O)_2C_6H_3$	H	11	Very deep red to deep red with red-brown solid present; crude aldehyde only 50–75% pure
o-$HOCH_2C_6H_4$	H	8	Normal; major product is phthalide; several other impurities present
p-$HOCH_2C_6H_4$	H	9	Normal; crude dialdehyde >95% pure; mp 110–112° (lit.[e] mp 115–116°)
	H	9	Homogeneous deep red faded to cloudy yellow; crude aldehyde ca. 90% pure; distilled product >95% pure
	H	30	Solution turned dark on addition of ceric ammonium nitrate solution; crude product >85% pure; distilled product >95% pure aldehyde
	H	30	Solution turned dark on addition of ceric ammonium nitrate solution; crude product very impure
trans-$C_6H_5CH{=}CH$	H	3	Normal; no aldehyde formed
C_6H_5	C_6H_5	20	Normal; crude product ca. 90% pure ketone; 6.5% unreacted alcohol present
C_6H_5	CH_3	5	Normal; ketone/alcohol = 68/32
			In 50% Aqueous Acetic Acid
C_6H_5	H	12	Normal;[b] distilled aldehyde 99% pure
p-$CH_3C_6H_4$	H	11	Normal; crude aldehyde >95% pure
2,4,6-$(CH_3)_3C_6H_2$	H	1	Normal; crude aldehyde >90% pure
o-ClC_6H_4	H	12	Normal; crude aldehyde 95% pure
p-BrC_6H_4	H	10	Normal; crude aldehyde >90% pure
o-$O_2NC_6H_4$	H	10	Normal; crude aldehyde >95% pure
m-$O_2NC_6H_4$	H	25	Normal; crude aldehyde >90% pure
p-$O_2NC_6H_4$	H	10	Normal; crude aldehyde >95% pure
m-$CH_3OC_6H_4$	H	60	Deep red to medium red; crude product ca. 75% pure aldehyde
p-$CH_3OC_6H_4$	H	1	Normal; crude aldehyde >95% pure
p-$CH_3SC_6H_4$	H	1	Normal; no aldehyde
m-$(C_6H_5COO)C_6H_4$	H	5	Turned cloudy brown on addition of ceric ammonium nitrate solution, no fading; crude aldehyde very impure
	H	30	Turned dark on addition of ceric ammonium nitrate solution; no fading; no aldehyde isolated
	H	14	Turned dark on addition of ceric ammonium nitrate, no fading; crude aldehyde very impure
trans-$C_6H_5CH{=}CH$	H	3	Normal; no aldehyde isolated
C_6H_5	C_6H_5	13	Normal; crude product ca. 76% pure ketone; major impurity is starting material

[a] Product purity was determined by nmr analysis. [b] Normal color change was deep red to yellow or colorless. [c] J. Van der Lee, *Rec. Trav. Chim.*, **45**, 680 (1966). [d] O. Fisher, *Ber.*, **14**, 2525 (1881). [e] A. Weissberger and H. Bach, *ibid.*, **65**, 24 (1932).

nitrate in 50% aqueous acetic acid and heating on a steam bath until it was colorless.

Oxidation of 3-Pyridylmethanol to Nicotinaldehyde.—To a solution of 0.019 mole of 3-pyridylmethanol in 40 ml of water was added 40 ml of a 1 *N* solution of ceric ammonium nitrate in water. The deep red homogeneous solution was heated on a hot plate until the color faded to pale yellow. Near the end of the reaction a solid formed. The mixture was cooled and 1.5 *N* potassium hydroxide (*ca.* 150 ml) was added until the pH of the solution was >10 which produced a voluminous precipitate. The mixture was filtered, the residue was washed with 25 ml of chloroform, and the filtrate was extracted three times with chloroform. The combined chloroform layers were dried over magnesium sulfate and the solvent was distilled through a 20-cm column packed with glass helices. Last traces of solvent were removed on a rotary evaporator. The weighed product was analyzed for impurities by nmr. The yield of 90% pure product was 75%.

Oxidation of phthalyl alcohol with 4.2 equiv of ceric ammonium nitrate in aqueous solution led to a colorless solution which was extracted with ether. Washing of the ether layer with saturated sodium bicarbonate solution led to the formation of black solid. Removal of the solvent after drying with magnesium sulfate gave a black liquid with the composition phthalaldehyde/phthalide = 26/74. The yields indicated in Table I were obtained by stirring the ether layer vigorously with magnesium sulfate and solid sodium bicarbonate for about 1 min. Filtration and removal of the solvent gave a yellow liquid.

Registry No.—Ceric ammonium nitrate, 14320-19-5; benzyl alcohol, 100-51-6.