**15d**: colorless powder; mp >300 °C; IR (KBr) 3500, 3430, 3060, 2980, 1645, 1480, 1240, 1140, 875, 850, 840, 820, 780, 715 cm$^{-1}$; $^1$H NMR (Me$_2$SO-$d_6$) $\delta$ 1.28 (9 H, s), 2.27 (6 H, s), 2.59 (3 H, s), 5.90 (2 H, s), 7.27 (2 H, s), 7.94 (2 H, d, $J$ = 7 Hz, H$_b$), 8.75 (2 H, d, $J$ = 7 Hz). Anal. Calcd for $C_{19}H_{26}NCl\cdot{}^1/_3H_2O$: C, 73.64; H, 8.67; N, 4.52. Found: C, 73.96; H, 8.47; N, 4.52.

**Registry No. 2a**, 76497-10-4; **2b**, 76447-50-2; **3a**, 78919-65-0; **3b**, 78919-66-1; **3c**, 78919-67-2; **3d**, 78939-65-8; **3e**, 78919-68-3; **3f**, 78919-69-4; **3g**, 78919-70-7; **3h**, 78919-71-8; **3i**, 78919-72-9; **3j**, 78919-73-0; **4a**, 78919-74-1; **4b**, 78919-75-2; **5a**, 78919-76-3; **5b**, 78919-77-4; **6a**, 78919-78-5; **6b**, 78919-79-6; **8a**, 78919-80-9; **8b**, 78919-81-0; **8c**, 78919-82-1; **8d**, 78919-83-2; **8e**, 78919-84-3; **8f**, 78919-85-4; **8g**, 78919-86-5; **8h**, 78939-66-9; **10**, 19387-83-8; **11a**, 78919-87-6; **11b**, 78919-88-7; **11c**, 78919-89-8; **11d**, 78919-90-1; **11e**, 78919-91-2; **12**, 19387-84-9; **13**, 50849-03-1; **14**, 78919-92-3; **15a**, 78919-93-4; **15b**, 78919-94-5; **15c**, 78919-95-6; **15d**, 78919-96-7; methanol, 67-56-1; ethanol, 64-17-5; butanol, 71-36-3; 2-propenol, 107-18-6; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 5,13-di-*tert*-butyl-8,16-diethyl[2.2]metacyclophane, 76447-78-4; 5,13-di-*tert*-butyl-8,16-dipropyl[2.2]metacyclophane, 76447-79-5; 5,13-di-*tert*-butyl-8,16-dibutyl[2.2]metacyclophane, 76466-37-0; 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane, 67691-35-4.

# Notes

## Manganic Oxidation of 3-Substituted Toluenes

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The oxidation of toluenes that contain an electron-releasing group in the meta position to benzyl esters and benzaldehydes is of interest because such compounds, particularly the 3-phenoxy derivatives, are useful intermediates for the preparation of pyrethroid insecticides.[1,2] The direct oxidation of 3-phenoxytoluene (**1e**) with Co(OAc)$_2$/O$_2$ or Co(OAc)$_2$/O$_2$/aldehyde has been reported to give 3-phenoxybenzyl alcohol (or acetate) and 3-phenoxybenzaldehyde in yields of 21% and 29%, respectively, whereas amounts of byproducts were formed (25–50%, respectively).

The two-step oxidation of 3-phenoxytoluene to 3-phenoxybenzaldehyde, involving free-radical-initiated bromination of the methyl group followed by hydrolysis, has been reported.[3] However, bromination of the toluene on a large scale produces significant aryl bromide byproducts. This problem has been overcome by use of *N*-bromosuccinimide as the brominating agent, giving a 77% yield of 3-phenoxybenzaldehyde[3a]. For large-scale industrial preparations, one-step oxidations by metal salts are preferred. We report here studies of the oxidation of meta-substituted toluenes **1a–f** with manganic (Mn$^{III}$) salts.

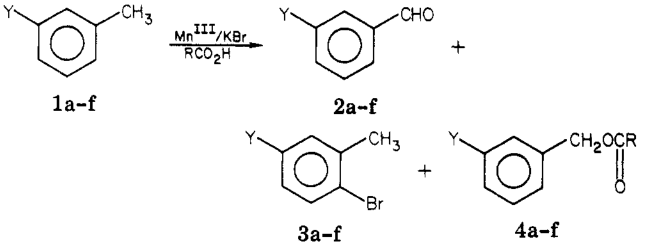
Manganic salts in acetic acid alone[4,5], or with addition of a strong acid[6], are among the most effective reagents for oxidation of 4-halogeno- and 4-alkoxytoluenes. Addition of KBr has been reported to give improved yields[7,8]. We have obtained very low yields (<7%) in using these reagents on the much less reactive meta compounds **1a–f**, presumably because of thermal decomposition of Mn$^{III}$[7] and reduction of Mn$^{III}$ to Mn$^{II}$ by AcOH and Br$^-$; accumulation of Mn$^{II}$ in such reactions has been shown to inhibit them.[9,10]

Table I. Oxidation of Substituted Toluenes (Molar Percentages)

| 1 | Y | transformed | 2a–f | 3a–f | 4a–f |
|---|---|---|---|---|---|
| a | 3-Br | 58 | 9 | 5 | 85 |
| b | 3-Cl | 74 | 8 | 8 | 80 |
| c | 3-CH$_3$O | 87 | 4 | 57 | 35 |
| d | 3-C$_2$H$_5$O | 69 | 3 | 56 | 38 |
| e | 3-C$_6$H$_5$O | 99 | 4 | 53 | 26 |
| f | 3-CH$_3$CO$_2$ | 59 | 0 | 38 | 27 |

### Results

We have found that the inhibiting effect of Mn$^{II}$ can be avoided by carrying out the oxidation with KMnO$_4$ in the presence of an aliphatic acid, its anhydride, and a halide such as KBr. KMnO$_4$ forms the Mn$^{III}$ carboxylate in situ in a modification of a reported procedure.[4] KMnO$_4$ decarboxyles carboxylic acids and gives Mn(O$_2$CR)$_3$, RCO$_2$K, and H$_2$O, as shown by UV–visible spectra.



The addition of KMnO$_4$ is carried out in portions in order to reoxidize Mn$^{II}$ to Mn$^{III}$ and prevent accumulation of the former. This procedure requires only one-fifth the amount of Mn that must be used with Mn(OAc)$_3$ as the

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0022-3263/81/1946-4562$01.25/0

Table II. Influence of the Halide Ion upon the Oxidation of 1e[a,b]

| | KCl | KBr | BTEA[c] | $Et_4NBr$ | $CuBr_2$ | $CuCl_2$ | $MnBr_2$ | $MnCl_2$ |
|---|---|---|---|---|---|---|---|---|
| % transformed | 46 | 99 | 0 | 70 | 99 | 31 | 99 | 6 |
| % **2e** | 8 | 4 | 0 | 4 | 0 | 0 | 0 | 27 |
| % **3e** or **5e** | 32[d] | 53 | 0 | 84 | 81 | 74[d] | 90 | 34[d] |
| % **4e** (R = $CH_3$) | 0 | 26 | 0 | 6 | 0 | 0 | 0 | 11 |

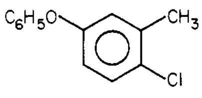
[a] Results are given in molar percentages [100 g of $KMnO_4$/mol of **1e** was used in all experiments except with KCl (400 g) and $CuCl_2$ (31 g)]. [b] Without halide or with NaF, no transformation occurs. [c] BTEA = benzyltriethylammonium chloride. [d] 2-Chloro-5-phenoxytoluene (**5e**) is formed.

Table III. Oxidation of 1e in Various Solvents

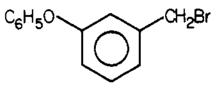
| | solvent | | | |
|---|---|---|---|---|
| | $HCO_2H$ | $CH_3CO_2H$ | $C_2H_5CO_2H$ | $n$-$C_3H_7CO_2H$ |
| % transformed | 39 | 99 | 43 | 25 |
| % 2e | 0 | 4 | 18 | 15 |
| % 3e | 100 | 53 | 1 | 0 |
| % 4e | 0 | 26 | 81 | 77 |
| solubility in KBr, $M$/1 | 2.2 | $65 \times 10^{-3}$ | $6.6 \times 10^{-3}$ | |
| $T$, °C | 101 | 117 | 141 | |

reagent. The water formed in the reaction is taken up by the acid anhydride.

Results of applying this oxidation system to **1a–f** are summarized in Table I. The methyl group of **1c–f**, in which the meta substituent is attached to the ring through oxygen, is less susceptible to oxidation than that of the halotoluenes **1a,b**, and ring bromination is favored with the former. Table II shows that KBr was more effective than KCl in forming the desired products; no reaction occurred without halide or with NaF. The more soluble halides ($CuBr_2$, $Et_4NBr$, $MnBr_2$, and $CuCl_2$) yielded almost exclusively **3e** or **5e**. When $CuBr_2$ was replaced by Cu(OAc)$_2$ no reaction occurred, indicating that $Cu^{2+}$ was not the oxidizing agent.



**5e**



**6e**

Table III shows the effect of the aliphatic acid solvent on the types and amounts of products. It appears that methyl oxidation is favored over ring bromination as the solubility of KBr in the acid decreases.

Figure 1 shows the formation of various products during the course of the portionwise addition of $KMnO_4$ in the oxidation of **1e** in AcOH, as determined by VPC after each addition. Compounds **3e** and **4e** were formed in an aproximately constant ratio until 80% of the $KMnO_4$ had been added, when the formation of **4e** leveled off. Similar results were obtained with propionic acid as the solvent.

## Discussion

3-Phenoxybenzyl bromide (**6e**) was identified in the reaction mixture by mass spectroscopy. Its formation was followed by VPC during the oxidation. It appears to be an intermediate in the reaction and is solvolyzed by $RCO_2K$.

An electron-transfert mechanism[4,5] seems improbable because no reaction occured in the absence of KBr. The reaction appears to involve oxidation of $Br^-$ to $Br^\cdot$. When **1e** (0.1 mol) was oxidized in the presence of $CH_3NO_2$ (0.1 mol), the conversion of **1e** dropped from 99% to 4%. Under our conditions $CH_3NO_2$ acts as a radical trap[11,12] since a small amount of it seems to be in the "acinitro" form (salified or not). This is shown by the strong decrease of the 270-nm band of an acetic solution of $CH_3NO_2$ ($n \rightarrow \pi^*$ of $NO_2$) when $CH_3CO_2K$ was added and by the increased rate of deuteration of $CH_3NO_2$ in $CH_3CO_2D$ when AcOK was added. (The concentration of this trapping species is probably lower than 1% and could not be measured by RMN nor by Raman spectroscopy). During the general oxidation procedure, AcOK is provided by the reaction of $KMnO_4$.

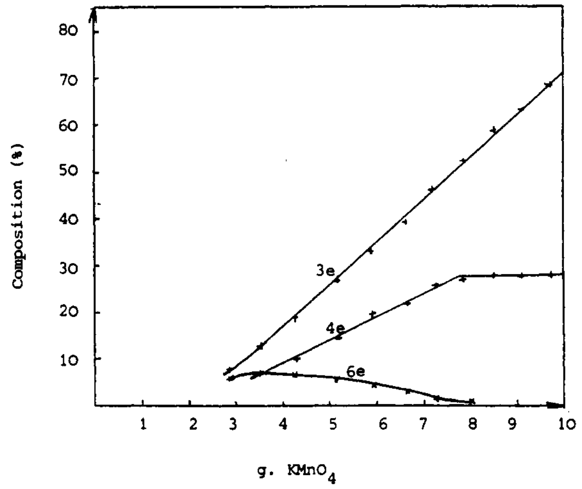
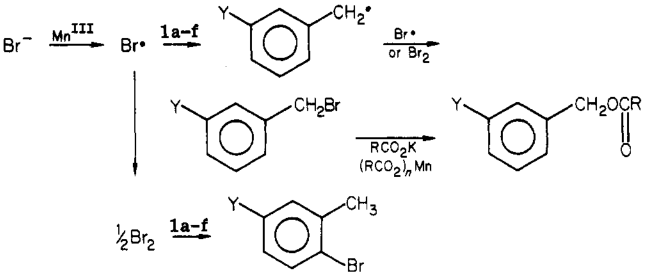


**Figure 1.** Distribution of the products during the oxidation of **1e** in AcOH.

Scheme I



In the absence of substrate, $Br^\cdot$ combines with $Br_2$ as indicated by UV–visible spectra. Compounds **3c–e** are also formed by the action of $Br_2$ on **1c–e** in AcOH. We found that, in the oxidation of **1e**, $Br_2$ could be trapped by anisole, which is ring-brominated faster than **1e**[13]. This procedure limited the formation of **3e** without affecting

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the yields of the other products.

The pathway shown in Sheme I seems to account for the results of these experiments.

## Use in Synthesis

The procedure outlined in this paper provides a useful one-step method for oxidation of meta-substituted toluenes. Thus, **1e** was oxidized to a combined yield of the benzaldehyde **2e** and the benzyl ester **4e** of 43% when propionic acid was used as solvent. Addition of anisole to the reaction can also suppress the formation of ring-brominated byproducts in AcOH solution. Use of $KMnO_4$ obviates the need for preparation of $Mn^{III}$ salts as well as reducing the amount of manganese required.

## Experimental Section

Microanalyses were performed by the CNRS. The UV spectra were recorded on a Perkin-Elmer 137UV, IR spectra on a Beckman IR 4210, $^{1}H$ NMR spectra on an Hitachi Perkin-Elmer 24-B, and $^{13}C$ NMR spectra on a Brucker WP 60 with shifts given in $\delta$ and $Me_4Si$ used as a reference. Mass spectra were recorded on a Girdel VPC-coupled quadrupole Riber Mag spectrometer. VPC analyses were performed on a Girdel 30 instrument using glass columns containing 5% $OV_1$ (silicone rubber) on Chromosorb W (Interchim supplier).

**Manganic acetate and propionate** were prepared according to the literature.[14]

**3-(Phenoxy-$d_5$)toluene** was prepared by Ullman reaction of bromobenzene-$d_5$ with *m*-cresol and was converted to **2-bromo-5-(phenoxy-$d_5$)toluene** by bromination with $CuBr_2$ in AcOH following the general oxidation procedure.

**General Oxidation Procedure.** A mixture of 0.1 mol of **1a–f**, 0.2 mol of the halide, 90 mL of the carboxylic acid, and 10 mL of the corresponding acid anhydride was heated to reflux temperature. $KMnO_4$ (10 g, 0.063 mol) was then added in 1-g portions, the color being allowed to disappear before each new addition. The reaction mixture was cooled and poured into 100 mL of water, acidified wit HCl, and extracted continuously for 16 h with ether. The solvents were evaporated, and the residue was distilled in one fraction. Yields were determined by CPV analysis using authentic samples as internal standards. Products were isolated by fractional distillation.

**5-Subtituted 2-Bromotoluenes (3).** These compounds were prepared by a modification of the preceding procedure with AcOH as the solvent and 0.065 mol of $CuBr_2$ or 0.075 mol of $MnBr_2$ as the halide.

**Product Data.** The reaction products were identified by mass spectra which were compared to the spectra of authentic samples[15] when possible. Data are reported below for compounds (**3d**, **3e**, and **4e** for R = $C_2H_5$ or $C_3H_7$) which were not found in the literature.

**2-Bromo-5-ethoxytoluene (3d)**: bp 129 °C (10 mm); $n_D^{20}$ 1.5461; $^{1}H$ NMR $\delta$ 1.25 (t, 3 H), 2.20 (s, 3 H), 3.76 (q, 2 H), 6.10–7.30, (m, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 138.8 ($C^1$), 115.3 ($C^2$), 132.9 ($C^3$), 113.6 ($C^4$), 158.4 ($C^5$), 117.3 ($C^6$), 23.0, 14.8, 63.5 (values in agreement with those calculated by using increments[16]); mass spectrum, *m/e* (relative intensity) 216 (75), 214 (74), 188 (100), 186 (98), 107 (83), 78 (56), 77 (76). Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15; Br, 37.15; 0, 7.44. Found: C, 50.02; H, 5.18; Br, 37.17; 0, 7.43.

**2-Bromo-5-phenoxytoluene (3e)**: bp 114–116 °C (0.15 mm); $n_D^{20}$ 1.6022; $^{1}H$ NMR ($CCl_4$) $\delta$ 2.35 (s, 3 H), 6.40–7.50 (m, 8 H); $^{13}C$ NMR [on 2-bromo-5-(phenoxy-$d_5$)toluene in order to check the position of Br on the ring] $\delta$ 140.2 ($C^1$), 119.2 ($C^2$), 134.1 ($C^3$), 118.7 ($C^4$), 157.5 ($C^5$), 122.1 ($C^6$) (values in agreement with those calculated using increments[17]); mass spectrum *m/e* (relative intensity), 264 (95), 262 (100), 89 (70), 77 (95), 51 (54). for 2-bromo-5-(phenoxy-$d_5$)toluene, *m/e* (relative intensity) 269 (96), 267 (100), 94 (30), 93 (37), 90 (29), 89 (56), 82 (62), 78 (35), 77 (25), 54 (42). Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21; Br, 30.37; O, 6.08. Found: C, 58.72; H, 4.20; Br, 30.49; 0, 6.74.

**3-Phenoxybenzyl Propionate and Butyrate (4e). Propionate (4e, R = $C_2H_5$)**: bp 123 °C (0.02 mm); $n_D^{20}$ 1.5463; IR 1735 (C=O), 1180 $cm^{-1}$ (CO); $^{1}H$ NMR ($CCl_4$) $\delta$ 1.08 (t, 3 H), 2.30 (q, 2 H), 4.88 (s, 2 H), 6.60–7.40 (m, 9 H); mass spectrum, *m/e* (relative intensity) 256 (14, 200 (100), 149 (32), 89 (41), 77 (41), 57 (40). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; O, 18.73. Found; C, 74.82; H, 6.50; O, 18.98.

**Butyrate (4e, R = $C_3H_7$)**: bp 141 °C (0.3 mm); $n_D^{20}$ 1.5439; IR 1735 (C=O), 1175 $cm^{-1}$ (CO); $^{1}H$ NMR ($CCl_4$) $\delta$ 0.89 (t, 3 H), 1.16–1.97 (m, 2 H), 2.20 (t, 2 H), 4.86 (s, 2 H), 6.60–7.40 (m, 9 H); mass spectrum, *m/e* (relative intensity) 270 (10), 200 (100), 183 (18), 89 (27), 77 (31), 71 (21). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; O, 17.76. Found; C, 75.57; H, 6.75; O, 17.26.

**Solvolysis of 6e.** Compound **6e** was prepared by following a reported procedure[3]. A solution of **6e** (20 mmol) in 20 mL of propionic acid and 2 mL of propionic anhydride was heated to reflux, and 6 % of the **6e** was hydrolyzed in 2.5 h. When 60 mmol of NaOAc was added to **6e** AcOH, and $Ac_2O$ in the same proportions and under conditions as above, **4e** (85%) was obtained in a few minutes, and NaBr precipitated.

**"Trapping" of $Br_2$ with Anisole.** A mixture of 20 mmol **1e** and 10 mmol of anisole was oxidized as described in the general procedure ($AcOH/Ac_2O/KBr$) by using 2 g of $KMnO_4$. Analysis of the reaction products gave 59% recovered **1e**, 8% **3e**, and 32% **4e**. 4-Bromoanisole was also formed.

**Registry No. 1a**, 591-17-3; **1b**, 108-41-8; **1c**, 100-84-5; **1d**, 621-32-9; **1e**, 3586-14-9; **1f**, 122-46-3; **2a**, 3132-99-8; **2b**, 587-04-2; **2c**, 591-31-1; **2d**, 22924-15-8; **2e**, 39515-51-0; **3a**, 615-59-8; **3b**, 14495-51-3; **3c**, 27060-75-9; **3d**, 68155-69-1; **3e**, 77317-53-4; **3f**, 22012-59-5; **4e** (R = $C_2H_5$), 78514-43-9; **4e** (R = $C_3H_7$), 78514-44-0; **4e** (R = $CH_3$), 50789-44-1; **5e**, 52322-81-3; **6e**, 51632-16-7; $KMnO_4$, 7722-64-7; 2-bromo-5-(phenoxy-$d_5$)toluene, 78514-45-1.

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# Unusual Photochemical Rearrangement of a Carbonyl Compound

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*Received April 14, 1981*

As a part of a study of the photochemical oxidation of carbohydrates and nucleosides, we reported several years ago[1] that an effective method for conversion of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) to 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose (**2**) consisted of the synthesis and photolysis of the pyruvate ester **3** (Scheme I). Although compound **2** was obtained in 74% yield from reaction of **1**, irradiation of **3** beyond that required to consume this pyruvate ester (**3**) caused a gradual decrease in the isolated yield of **2**. Recently, we became interested in investigating the photochemical reactivity of **2** to determine whether it was a suitable starting material for synthesis of branched-chain sugars. This study has led to the finding, described below, that **2** experiences exten-

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