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Reactions of Alkylarenes, Benzyl Alcohols, Sulfides, and Phosphine with Manganese(III) Acetate-Chloride Ions

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The reactions of methoxytoluenes and methylnaphthalenes with a manganese(III) acetate-Cl$^-$ complex gave the corresponding aldehydes in 8 to 54% yields. In a similar reaction aromatic compounds having a methylene group were oxidized to the corresponding acetates and ketones. The primary and secondary benzyl alcohols gave aldehydes and ketones, respectively, in good yields. Sulfides and phosphine were oxidized to give oxides by the complex. The reaction of alkylarenes with lower ionization potentials can be explained in terms of an electron-transfer mechanism involving the manganese(III) acetate-Cl$^-$ complex.

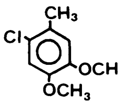
Several papers have been published concerning the complex formation and the reaction of manganese(III) acetate in the presence of chloride ions. The reaction of olefins with the complex yielded mainly addition products,[1,2] while α,β-unsaturated carboxylic acids gave addition and chlorine-substituted products accompanied by decarboxylation.[3] α,β-Unsaturated carboxylates also gave addition and chlorine-substituted products.[4] In a previous paper[5] we reported that the reaction of aryl ketones with manganese(III) acetate-lithium chloride gave α-chlorinated ketones in good yields. In the reaction of toluenes with manganese(III) acetate the addition of an equimolar portion of potassium bromide led to an appreciable rate enhancement and gave increased yields of benzyl acetates and benzaldehydes[6] instead of methyl-substituted benzyl acetates, which were the main products in the reaction of manganese(III) acetate alone. However, the reactions were examined only from the mechanistic point of view. This prompted us to investigate the reactions of aromatic compounds having methyl and methylene groups, benzyl alcohols, sulfides and phosphorus compounds with the manganese(III) acetate-Cl$^-$ complex in order to improve the yields of aldehydes, ketones, and oxides. We have examined the reactions of methoxy-substituted toluenes, methylnaphthalenes, diarylmethanes, xanthene, anthrone, methyl phenylacetates, fluorene, benzyl alcohols, diphenyl sulfide, dibenzothiophene, and triphenylphosphine. These compounds were chosen because they may provide a variety of products which reflect the nature of the reaction and that the products can be easily characterized by spectroscopy. The reaction were carried out under various reaction conditions by changing the molar ratio of the substrate, manganese(III) acetate and chloride ions. The effects of changing the source of the chloride ions, and of additives were also examined.

Results

Methoxy-Substituted Toluenes and Methylnaphthalenes. When 4-methoxytoluene (**1a**) was oxidized with the manganese(III) acetate-Cl$^-$ complex in AcOH in a molar ratio of **1a**:Mn(III):LiCl of 1:4:5 at 100 °C, it gave a mixture of 4-methoxybenzyl acetate (**2a**) and 4-methoxybenzaldehyde (**3a**). The reaction

$ArCH_3$	$ArCH_2OAc$	ArCHO	$ArCH_2OH$
1a~e	**2a~d**	**3a~e**	**4a,b**

a : Ar = 4-methoxyphenyl
b : Ar = 3,4-dimethoxyphenyl
c : Ar = 2,3,4-trimethoxyphenyl
d : Ar = 1-naphthyl
e : Ar = 2-naphthyl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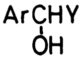
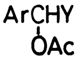
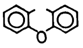
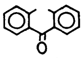
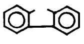
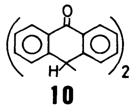
$ArCH_2Y$ **6a~g,i~l**


$ArCH(OH)Y$ **7c~g,j~l**


$ArCH(OAc)Y$ **8c,e~g,i~l**


$ArC(=O)Y$ **9a~g,i~k**

a : Ar, Y = 
b : Ar, Y = 
c : Ar = Y = phenyl
d : Ar = Y = 4-methoxyphenyl
e : Ar = 2-naphthyl, Y = methyl
f : Ar = 4-methoxyphenyl, Y = phenyl
g : Ar, Y = 
i : Ar = 4-methoxyphenyl, Y = methoxycarbonyl
j : Ar = 4-methoxyphenyl, Y = methyl
k : Ar = 4-chlorophenyl, Y = methyl
l : Ar = 4-methylphenyl, Y = methyl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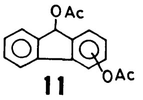
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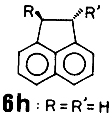
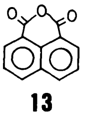

6h : R = R′ = H
8h : R = H, R′ = OAc
12 : R = R′ = Cl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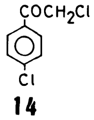
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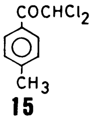
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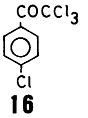
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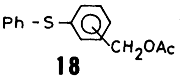
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Table 1. Oxidations of Alkylarenes and Methylene Compounds with Mn(III)–Cl$^-$ in AcOH

Entry	Substrate	Molar ratio[a]	Cl$^-$ source	Temp	Time	Recovery	Product (Yield/%)[b]		
				°C	h	%	Acetate	Aldehyde or Ketone	Others
1	**1a**	1:4: 5	LiCl	100	46		**2a**(14)	**3a**(50)	
2	**1a**	1:4:10	LiCl	100	14		**2a**(27)	**3a**(53)	**4a**(9)
3	**1a**	1:4:10	LiCl	Reflux	1		**2a**(31)	**3a**(34)	
4	**1a**	1:4:15	LiCl	100	16		**2a**(18)	**3a**(41)	
5	**1a**	1:4:20	LiCl	100	6		**2a**(12)	**3a**(45)	
6	**1a**	1:4:10[c]	LiCl	100	7		**2a**(60)	**3a**(4)	
7	**1a**	1:4:10[d]	LiCl	100	2.5		**2a**(31)	**3a**(54)	
8	**1a**	1:4:10	KCl	Reflux	2.5		**2a**(66)	**3a**(15)	
9	**1a**	1:4:10	NH_4Cl	Reflux	0.8		**2a**(68)	**3a**(17)	
10	**1a**	1:4:10	$CaCl_2$	Reflux	0.7		**2a**(37)	**3a**(29)	
11	**1a**	1:4:10	NaCl	Reflux	2.5		**2a**(67)	**3a**(10)	
12	**1a**	1:4:10	$ZnCl_2$	Reflux	0.7		**2a**(35)	**3a**(14)	
13	**1b**	1:4:10	LiCl	100	2	6	**2b**(31)	**3b**(17)	**5** (5)
14	**1c**	1:4:10	LiCl	100	3.4		**2c**(34)	**3c**(26)	
15	**1d**	1:4:10	LiCl	100	27		**2d**(35)	**3d**(39)	
16	**1e**	1:4:10	LiCl	100	2			**3e**(8)[e]	
17	**6a**	1:4:10	LiCl	100	3.5	16		**9a**(70)	
18	**6b**	1:4:10	LiCl	100	4			**9b**(56)	**10**(10)
19	**6c**	1:4:10	LiCl	Reflux	4	53	**8c**(12)		
20	**6d**	1:4:10	LiCl	100	4.5			**9d**(61)	**7d**(23)
21	**6g**	1:4:10	LiCl	Reflux	2	25	**8g**(55) **11**(3)		
22	**6h**	1:4:10	LiCl	100	0.5		**8h**(36)		**12**(15) **13**(9)
23	**6i**	1:4:10	LiCl	Reflux	0.8		**8i** (76)	**9i** (11)	

a) Substrate: Mn(III): Cl$^-$. b) Yields are based on the substrate added. c) Ac_2O (20 cm^3) was added. d) Water (1 cm^3) was added. e) Isolated as a 2,4-DNP.

was conducted at various molar ratios of **1a**:Mn(III):LiCl until all Mn(III) was consumed, and the best yield for **3a** was attained when the molar was 1:4:10 (Table 1, Entry 2). When Ac_2O was added to the reaction medium, the yield of **3a** decreased (Entry 6). The addition of water did not cause any significant change in the yield (Entry 7). It was found that changing the Cl$^-$ source affects the yield of the products in the reaction of **1a** (Entries 8—12). All other salts lowered the yield of **3a**, but increased that of **2a**. In a similar reaction with the manganese(III) acetate–Cl$^-$ complex 3,4-dimethoxytoluene (**1b**) and 2,3,4-trimethoxytoluene (**1c**) gave the corresponding aldehydes (**3b** and **3c**) in poor yields (Entries 13 and 14). In the reaction of **1b** 2-chloro-4,5-dimethoxytoluene (**5**) was obtained in minor quantity. The reaction of 1-methyl- (**1d**) and 2-methylnaphthalene (**1e**) yielded the corresponding (acetoxymethyl)naphthalenes (**2d** and **2e**) and naphthalenecarbaldehydes (**3d** and **3e**).

Methylene Group Flanked by One or Two Aryl Groups. The reaction of xanthene (**6a**), anthrone (**6b**), and bis(4-methoxyphenyl)methane (**6d**) gave the corresponding carbonyl compounds (**9a**, **9b**, and **9d**) in moderate yields (Entries 17, 18, and 20) together with some other products (**7d** and **10**). Diphenylmethane (**6c**) and fluorene (**6g**) did not give ketonic products, but yielded acetates, **8c** and **8g**, respectively (Entries 19 and 21). Acenaphthene (**6h**) gave 1-acetoxyacenaphthene (**8h**), 1,2-dichloroacenaphthene (**12**), and 1,8-naphthalenedicarboxylic anhydride (**13**). The configuration of the chlorine atoms in **12** is determined as a trans, since the melting point and the IR and ^{1}H NMR spectrum of **12** were identical with those reported.[7]

Benzyl Alcohols. The reaction of 4-methoxybenzyl alcohol (**4a**) with the complex gave a mixture of **2a** and **3a**, the latter being predominant. 3,4-Dimethoxybenzyl alcohol (**4b**) yielded 3,4-dimethoxybenzaldehyde (**3b**) exclusively (Entry 25). Diphenylmethanol (**7c**) yielded a mixture of an acetate (**8c**) and benzophenone (**9c**). The presence of an electron-donating group, such as a methoxyl group in the aromatic ring, slightly increased the yield of the ketone, as shown in the reaction of (4-methoxyphenyl)phenylmethanol (**7f**) (Entry 28). The reaction of **7f** with manganese(III) acetate alone gave **8f** and **9f** in poor yields (Entry 29). The reaction of 1-(4-methoxyphenyl)ethanol (**7j**) yielded an acetate (**8j**) and 4′-methoxyacetophenone (**9j**), the latter being the major product (Entry 31). Similarly, 1-(4-chlorophenyl)ethanol (**7k**) gave an acetate (**8k**), 4′-chloroacetophenone (**9k**), and 2,4′-dichloroacetophenone (**14**). 1-(2-Naphthyl)ethanol (**7e**) yielded an acetate (**8e**) and 2-acetylnaphthalene (**9e**). The chlorination of acetophenones with the Mn(III)–Cl$^-$ complex has already been reported to give α-chlorinated

Table 2. Oxidations of Benzyl Alcohols, Disulfides, and Phosphine with Mn(III)–LiCl in AcOH

Entry	Substrate	Molar ratio[a]	Temp	Time	Recovery	Product (Yield/%)[b]		
			°C	h	%	Acetate	Aldehyde or ketone	Others
24	**4a**	1:3:10	100	0.8		**2a**(6)	**3a**(70)	
25	**4b**	1:3:10	100	1			**3b**(71)	
26	**7c**	1:6:10	Reflux	8		**8c**(33)	**9c**(63)	
27	**7e**	1:3:10	Reflux	0.2	11	**8e**(28)	**9e**(29)	
28	**7f**	1:3:10	Reflux	0.2	21		**9f**(72)	
29	**7f**	1:3: 0	Reflux	9		**8f**(18)	**9f**(12)	
30	**7g**	1:3:10	Reflux	0.8			**9g**(80)	
31	**7j**	1:3:10	Reflux	0.2		**8j**(7)	**9j**(39)	
32	**7k**	1:3:10	Reflux	0.3	43	**8k**(11)	**9k**(18)	**14** (2)
33	**7l**	1:3:10	Reflux	0.3		**8l**(45)		**15** (10)
34	**17a**	1:4:10	Reflux	3	11			**19a**(76)
35	**17a**	1:4: 0	Reflux	7	55	**18**(28)		
36	**17b**	1:4:10	Reflux	6	9			**19b**(21)
37	**20**	1:4:10	Reflux	46				**21** (97)

a) Substrate: Mn(III): LiCl. b) Yields are based on the substrate added.

acetophenones.[5]

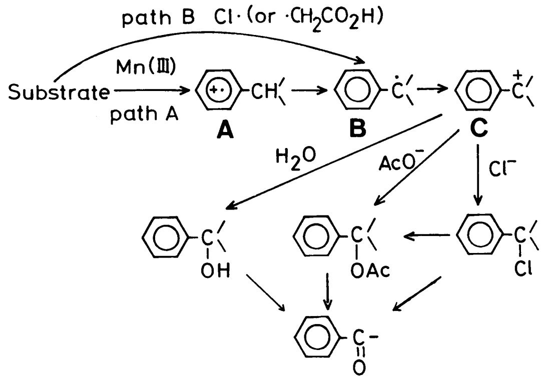
Sulfides and Triphenylphosphine. The reaction of diphenyl sulfide (**17a**) with the complex yielded diphenyl sulfoxide (**19a**) in good yield (Entry 34). The reaction of **17a** with manganese(III) acetate in the absence of Cl^- ions gave an acetate (**18**) in 28% yield and a large amount of **16a** was recovered unchanged (Entry 35). Dibenzothiophene (**17b**) afforded dibenzothiophene oxide (**19b**) in 21% yield (Entry 36). The reaction of triphenylphosphine (**20**) gave triphenylphosphine oxide (**21**) in excellent yield (Entry 37).

Discussion

The oxidation of alkylarenes with manganese(III) acetate afforded aldehydes in minor quantities.[8] The addition of alkali halides as catalysts has been reported to improve the yields of carbonyl compounds.[9] However, these reactions were carried out primarily for mechanistic studies using a large excess of the substrate. By contrast, we used a large amount of the manganese(III) acetate–Cl^- complex compared with those in the previous studies.[6,9] Methoxy-substituted toluenes and methylnaphthalenes gave the corresponding aldehydes in 8 to 54% yields, which are better than those reported. When the acetoxymethyl derivative is stable towards Mn(III)–Cl^-, the yields of the aldehydes are not sufficiently high. The oxidation of benzyl alcohols, on the other hand, gave better yields of the aldehydes.

The oxidation of methylene compounds (**6a**—**d**,**g**) with the complex gave ketonic compounds in good yields, except for diphenylmethane (**6c**) and fluorene (**6g**). Secondary benzyl alcohols (**7c**, **7f**, and **7g**) also gave the corresponding ketones (**9c**, **9f**, and **9g**). However, the reaction of 1-arylethanols (**7k** and **7l**) gave α-chlorinated ketones (**14** and **15**) along with an aryl methyl ketone (**9k**) and acetates (**8k** and **8l**) and seems to have a less synthetic value.

Gilmore and Mellor[10] have proposed that the potassium bromide-catalyzed oxidation of toluenes using manganese(III) acetate proceeds via radical intermediates. The reaction of norbornene with manganese(III) acetate–$CaCl_2$ gave no rearranged products, suggesting that the radical process is conceivable.[2] However, it is known that the reaction of manganese(III) acetate with aromatic compounds having relatively lower ionization potentials readily takes place via an electron-transfer process.[8] It was found that the reaction of manganese(III) acetate–Cl^- gave a better yield of the aldehyde in the absence of Ac_2O, which normally facilitates a free-radical process; the addition of water has no appreciable effect on the product distribution. We also found that the presence of electron-donating groups in the aromatic rings changes the product distribution in favor of ketonic compounds, as can be seen in the cases of **6a** and **6d**; also, methyl (4-methoxyphenyl)acetate (**6i**) yielded α-acetoxy ester (**8i**) and methyl (4-methoxyphenyl)glyoxylate (**9i**), while ethyl phenylacetate, which may have a higher ionization potential than **6i**, was totally unreactive.[4] These facts suggest that the reaction of aromatic substrates of lower ionization potentials may proceed via an electron-transfer mechanism (path A in Scheme 1), although the mechanism need not to be operating in all reactions. The benzyl radical (B), once formed, is further oxidized to the benzyl cation (C), as shown in Scheme 1. The benzyl cation (C) is then combined with a chloride ion, acetate ion, and water molecule to give chloro derivatives, acetates, and alcohols, respectively. The substitution of the benzylic chlorine by an acetate ion should be very fast to give the acetate. Although it has been reported that methyl-substituted benzyl acetate is less reactive towards



Scheme 1.

manganese(III) acetate than methoxytoluene,8) the acetates in the reactions can still be oxidized in a similar process to give carbonyl componds. In harmony with the above-mentioned mechanism, 4-methoxybenzyl chloride was readily converted to 4-methoxybenzyl acetate (**2a**, 77%) through a treatment with manganese(II) acetate in AcOH at 100 °C for 50 min; in turn, **2a** was converted to **3a** (45%) by oxidation with the manganese(III) acetate–$\mathrm{Cl^-}$ complex at 100 °C in 9 h. A direct oxidation of the benzyl alcohols to the carbonyl compounds is indicated by its faster reaction time (0.8 h at 100 °C) than methyl and methylenes. The route from benzyl chloride to the carbonyl compounds could not be ruled out.

Conclusion

Aldehydes and ketones have been obtained in minor quantities in the reaction of alkylarenes with manganese(III) acetate. We found that when a large excess of the manganese(III) acetate–$\mathrm{Cl^-}$ complex is used, the aldehydes and ketones become the major product. Moreover, the primary and secondary benzyl alcohols give the corresponding carbonyl compounds in excellent yields. Sulfoxide and phosphine oxide are also prepared by the reaction of the complex. These reactions can be useful in organic syntheses.

Experimental

Measurements. All of the ^{1}H NMR spectra (60 MHz) were taken with a Hitachi Perkin-Elmer R-24 and a JMN PMX-60SI NMR spectrometer with tetramethylsilane as the internal standard. The IR spectra were measured in chloroform solutions on a JASCO A-102 IR spectrometer. The mass spectra were obtained on a JMS-O1SG-2 instrument. The melting points were determined with a Yanagimoto micromelting point apparatus and were not corrected.

Materials. Methoxytoluenes (**1a**—**c**), xanthene (**6a**), diphenylmethanes (**6c** and **6d**), fluorene (**6g**) were obtained from the corresponding aldehydes and ketones by Wolff-Kischner reduction.11) Methylnaphthalenes (**1d** and **1e**), anthrone (**6b**), acenaphthene (**6h**), and triphenylphosphine (**20**) were commercially available from Wako Pure Chemical Industories. Diphenyl sulfide (**17a**) and dibenzothiophene (**17b**) were purchased from Tokyo Kasei Co., Ltd. Methyl (4-methoxyphenyl)acetate (**6i**) was prepared from the acid by esterification. Primary and secondary alcohols (**4a**, **4b**, **7c**, **7e**—**g**, and **7j**—**k**) were prepared by the sodium borohydride reduction12) of the corresponding aldehydes and ketones.

Reactions of Manganese(III) Acetate in the Presence of Chloride Ions. The typical procedure for the oxidation of manganese(III) acetate in the presence of chloride ions is as follows. To a heated solution of manganese(III) acetate, $[\mathrm{Mn_3O(OAc)_6(OAc)(HOAc)}]\cdot 5\mathrm{H_2O}$,13) (3—4 milliequivalents for Mn(III)) and $\mathrm{Cl^-}$ (10 mmol) in AcOH a substrate (1 mmol) was added. The mixture was then heated under reflux until the dark-brown color turned opaque white. The reaction mixture was diluted with water (60 cm^3) and then extracted with benzene (30 cm^3) twice. The combined benzene solution was washed with aqueous sodium hydrogencarbonate solution and then evaporated in vacuo. The resulting products were purified on TLC with either benzene or chloroform as the eluting solvent, and recrystallized or distilled. The yields are summarized in Tables 1 and 2. The structures of the products were determined by means of IR, ^{1}H NMR, and mass spectra. Known compounds were also identified by comparisons of their melting points with those reported in the literature and with authentic samples.

Oxidation Products. **4-Methoxybenzyl Acetate (2a)**: Liquid. **3,4-Dimethoxybenzyl Acetate (2b)**: Liquid. **2,3,4-Trimethoxybenzyl Acetate (2c)**: Liquid; IR ν (cm^{-1})=1732 (>C=O); ^{1}H NMR (CCl$_4$) δ=1.98 (3H, s, OAc), 3.78 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 3.94 (3H, s, OCH$_3$), 4.95 (2H, s, -CH$_2$-), 6.52 (1H, d, J=7.8 Hz, H-5), 6.89 (1H, d, J=7.8 Hz, H-6). Found: m/z=240.1001. Calcd for $\mathrm{C_{12}H_{16}O_5}$: M, 240.0998. **1-(Acetoxymethyl)naphthalene (2d)**: Liquid. **4-Methoxybenzaldehyde (3a)**: Liquid. **3,4-Dimethoxybenzaldehyde (3b)**: Mp 41—42 °C. **2,3,4-Trimethoxybenzaldehyde (3c)**: Liquid. **1-Naphthalenecarbaldehyde (3d)**: Liquid. **2-Naphthalenecarbaldehyde (3e)**: **2,4-Dinitrophenylhydrazone**, mp 271 °C (lit,14) mp 270—271 °C). **4-Methoxybenzyl Alcohol (4a)**: Liquid. **6-Chloro-3,4-dimethoxytoluene (5)**:15) Liquid; ^{1}H NMR (CDCl$_3$) δ=2.28 (3H, s, CH$_3$), 3.82 (6H, s, 2×OCH$_3$), 6.68 (1H, s, H-2), 6.82 (1H, s, H-5). **Bis(4-methoxyphenyl)methanol (7d)**: Mp 71—72 °C (lit,16) mp 72 °C). **Diphenylmethyl Acetate (8c)**: Liquid (lit,17) mp 40.5—41.5 °C). **1-(2-Naphthyl)ethyl Acetate (8e)**: Liquid (lit,18) bp 130 °C/120 Pa). **(4-Methoxyphenyl)phenylmethyl Acetate (8f)**: Liquid (lit,19) bp 158 °C/119.7 Pa). **9-Fluorenyl Acetate (8g)**: Mp 68—69 °C (lit,20) mp 68.5—69 °C). **1-Acetoxyacenaphthene (8h)**: Liquid (lit,21) bp 166—168 °C/665 Pa). **Methyl α-Acetoxy(4-methoxyphenyl)acetate (8i)**: Liquid;4) IR ν (cm^{-1})=1742 (-COO-); ^{1}H NMR (CCl$_4$) δ=2.09 (3H, s, OAc), 3.64 (3H, s, OCH$_3$), 3.75 (3H, s, OCH$_3$), 5.79 (1H, s, >CH-), 6.78 (2H, m, H-3′ and H-5′), and 7.29 (2H, m, H-2′ and H-6′). Found: m/z=238.0884. Calcd for $\mathrm{C_{12}H_{14}O_5}$: M, 238.0837. **1-(4-Methoxyphenyl)ethyl Acetate (8j)**: Liquid (lit,18) bp 153—154 °C/3.59×10^3 Pa). **1-(4-Chlorophenyl)ethyl Acetate (8k)**: Liquid (lit,18) bp 88 °C/146 Pa). **1-(4-Methylphenyl)ethyl Acetate (8l)**: Liquid (lit,18) 105—106 °C/2.79×10^3 Pa). **9-Xanthenone (9a)**: Mp 172—174 °C. **9,10-Anthraquinone (9b)**: Mp 279—280 °C. **Benzophenone (9c)**: Mp 48 °C. **4,4′-Dimethoxybenzophenone (9d)**: Mp 142—143 °C. **2-Acetylnaphthalene (9e)**: Mp 51—52 °C.

4-Methoxybenzophenone (9f): Mp 58—59 °C. **9-Fluorenone (9g)**: Mp 83—84 °C. **Methyl (4-Methoxyphenyl)glyoxylate (9i)**: Mp 49—50 °C (lit,[22] mp 54 °C); IR ν (cm^{-1})=1675 (>C=O); ^{1}H NMR ($CDCl_3$) δ=7.94—7.79 (2H, m, H-2′ and H-6′), 6.92—6.77 (2H, m, H-3′ and H-5′), 3.84 (3H, s, OCH_3), 3.82 (3H, s, OCH_3). **4′-Methoxyacetophenone (9j)**: Mp 33—34 °C. **4′-Methylacetophenone (9k)**: Liquid. **10,10′-Bianthrone (10)**: Mp 261—263 °C (lit,[23] mp 235—250 °C). **Diacetoxyfluorene (11)**: Liquid; IR ν (cm^{-1})=1732 (OAc); ^{1}H NMR ($CDCl_3$) δ=7.70—6.94 (7H, m, arom. H), 6.71 (1H, s, >CH-), 2.29 (3H, s, OAc), 2.16 (3H, s, OAc). Found: m/z=282.0861. Calcd for $C_{17}H_{14}O_4$: M, 282.0892. ***trans*-1,2-Dichloroacenaphthene (12)**: Mp 66 °C (lit,[7] mp 66.5—68 °C). **1,8-Naphthalenedicarboxylic Anhydride (13)**: Mp 267 °C. **2,4′-Dichloroacetophenone (14)**: Mp 99 °C (lit,[24] mp 100—101 °C). **2,2-Dichloro-4′-methylacetophenone (15)**: Liquid (lit,[25] bp 110 °C/1.33×10^3 Pa). **(Acetoxymethyl)-phenyl Phenyl Sulfides (18)**: Isomer ratio 9.8 : 7.0; Liquid; IR ν (cm^{-1})=1732 (OAc); ^{1}H NMR ($CDCl_3$) δ=1.91 (3H, s, OAc), 1.97 (3H, s, OAc), 4.94 (2H, s, $-CH_2-$), 5.13 (2H, s, $-CH_2-$), 7.03—7.54 (18H, m, ar. H); MS m/z (rel intensity)=258 (M^+, 100), 215 (23), 197 (79), 137 (42). Found: m/z=258.0687. Calcd for $C_{15}H_{14}O_2S$: M, 258.0715. **Diphenyl Sulfoxide (19a)**: Mp 70 °C (lit,[26] mp 71 °C). **Dibenzothiophene Oxide (19b)**: Mp 183 °C (lit,[27] mp 183.5—184.5 °C). **Triphenylphosphine Oxide (21)**: Mp 152—153 °C (lit,[28] mp 154—155 °C).

4-Methoxybenzyl Acetate (2a) from 4-Methoxybenzyl Chloride. A mixture of 4-methoxybenzyl chloride (1 mmol), manganese(II) acetate tetrahydrate (8 mmol), and lithium chloride (10 mmol) in acetic acid (25 cm^3) was heated at 100 °C for 50 min. After working up in a manner similar to that for the above, 4-methoxybenzyl acetate (**2a**) was obtained in 77% yield.

Oxidation of 4-Methoxybenzyl Acetate (2a) with Manganese(III)-Cl$^-$. A mixture of 4-methoxybenzyl acetate (**2a**) (1 mmol), manganese(III) acetate (2 mmol), lithium chloride (10 mmol) in acetic acid (25 cm^3) was heated at 100 °C for 9 h. After working up in a manner similar to that mentioned above, the resulting mixture was chromatographed on TLC with chloroform as the eluting solvent to give 4-methoxybenzaldehyde (**3a**) (45%) and *p*-anisic acid (5%) with 4% recovery of **2a**.

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