= 8 Hz, 1 H, H-4), 7.65 (d, J = 8 Hz, 1 H, H-6).

Anal. Calcd for $C_{18}H_{19}Cl_3O_5$: C, 51.26; H, 4.54; Cl, 25.23. Found: C, 51.33; H, 4.69; Cl, 25.41.

(1*R*)-1-(2-Hydroxy-3-methylphenyl)-2,2,2-trichloroethyl (1*S*)-Camphanate (5Ae). The title compound was prepared following the above procedure. Recrystallization from 8:2 petroleum ether/CH_2Cl_2 afforded 0.79 g (70%) of **5Ae** as colorless needles: mp 152-153 °C; $[\alpha]_{589}$ -12.8 (c 0.3, 95% ethanol); IR (KBr) 3360, 1756 cm^{-1}; ^{1}H NMR ($CDCl_3$/200 MHz) δ 1.01 (s, 3 H, CH_3), 1.13 (s, 6 H, CH_3), 1.6-2.6 (m, 4 H, CH_2), 2.28 (s, 3 H, CH_3), 5.40 (s, 1 H, CH), 6.90 (t, J = 8 Hz, 1 H, H-5), 6.98 (s, 1 H, OH), 7.20 (d, J = 8 Hz, 1 H, H-4), 7.50 (d, J = 8 Hz, 1 H, H-6).

Anal. Calcd for $C_{19}H_{21}Cl_3O_5$: C, 52.37; H, 4.86; Cl, 24.41. Found: C, 52.33; H, 4.97; Cl, 24.62.

Crystal Structure Determination of Compounds 5Aa and 5Ae. Crystal data for **5Aa**: $C_{18}H_{19}Cl_3O_5$, M_r = 421.7, trigonal space group $P3_2$ (from systematic absences and structural analysis), cell dimensions, $a = b$ = 11.635 (2) Å, c = 12.662 (2) Å, V = 1484.5 (4) Å^3, Z = 3, Cu Kα λ = 1.54178 Å, μ = 4.503 mm^{-1}, D_c = 1.415 g cm^{-3}, 3016 reflection measured, 1745 with $I > 2\sigma(I)$ used in refinement of 235 parameters, $(\Delta\rho)_{max}$ = 0.10, $(\Delta\rho)_{min}$ = -0.09, max 2θ = 140°.

Crystal data for **5Ae**: $C_{19}H_{21}Cl_3O_5$, M_r = 435.7, elongated prisms, monoclinic space group $P2_12_12_1$ (from systematic absences and structural analysis), cell dimension, a = 21.491 (3) Å, b = 15.277 (2) Å, c = 6.476 (1) Å, V = 2126.2 (5) Å^3, Z = 4, Cu Kα λ = 1.54178 Å, μ = 4.208 mm^{-1}, D_c = 1.361 g cm^{-3}, 2361 reflections measured, 1431 with $I > 2\sigma(I)$ used in refinement of 244 parameters, $(\Delta\rho)_{max}$ = 0.16, $(\Delta\rho)_{min}$ = -0.13, max 2θ = 140°.

Intensity data were collected at room temperature using Ni-filtered Cu Kα radiation and ω-2θ scan technique. In both types of data collection, the intensity of a standard reflections was measured every 20 reflections to check the stability of the crystal and the electronics. No correction for absorption was applied.

For both compounds the structure was solved by direct methods with Multan[12,13] and refined by full-matrix least-squares cycles using the SHELX-76[14] system of computer programs with initially isotropic and then anisotropic thermal parameters. For both compounds all the hydrogen atoms were located from a difference Fourier synthesis. The final conventional R_f index was 0.0406 for **5Aa** and 0.0562 for **5Ae** (observed reflections only). Scattering factors for Cl, C, H, and O were taken from ref 15, and both the real and imaginary components of anomalous dispersion were included.[15]

The molecular structures and numbering schemes of the two compounds are shown in Figure 1. Bond distances and angles are within normal ranges (see supplementary material). The geometry of camphanic groups well agree with previous X-ray works.[16,17]

An interesting aspect concerning the structure of the compounds **5Aa** and **5Ae** is their different conformation, emphasized from the following torsion angles: O(4)-C(10)-C(9)-O(3) = -147.7(6), O(4)-C(10)-C(9)-O(2) = 36.5 (6)° for **5Aa**; O(4)-C(11)-C(10)-O(3) = -20.4(1.3), O(4)-C(11)-C(10)-O(2) = 160.5 (6)° for **5Ae**. This behavior is probably determined by the steric hindrance of the phenolic o-methyl group in **5Ae**, which, favoring the formation of intramolecular H-bonds, prevents the intermolecular association.

In fact as shown in Figure 3 (in supplementary material) in **5Ae** an intramolecular hydrogen bond between O(1) and Cl(1) (O(1)...Cl(1) = 3.260 (7) Å) is formed determining a monomeric structure, while in **5Aa** an intermolecular H-bond, involving O(1)-H as donor and carbonyl O(5) ($x - 1, y - 1, z$) as acceptor (2.802 (4) Å) forms infinite chains of head-to-tail H-bonds. These chains run along three directions, [100], [010], and [110], at level z, $^2/_3 + z$, $^1/_3 + z$, respectively, due to the presence of the 3-fold screw axis.

The carbonyl groups have short intermolecular contacts: in **5Aa**, O(5) with C(5) ($x + 1, y + 1, z$) at 3.379 (6) Å; in **5Ae**, O(5) with C(9) ($x - {}^1/_2, {}^3/_2 - y, -z$) at 3.304 (12) Å. These weak interactions determine the connection of the chains in **5Aa** and the formation of chains running along the [100] direction in **5Ae**.

Acknowledgment. We are indebted to the Ministero della Pubblica Istruzione, Italy, for support of this work.

Supplementary Material Available: Bond distances and angles, final coordinates of the atoms and thermal parameters with their estimated standard deviation for the crystal structure determination of compounds **5Aa** and **5Ae**, tables of analytical and spectral data for compounds **4a-j**, and Figure 3, showing molecular packing of **5Aa,e** (11 pages) (the observed and calculated structure factors can be obtained from G.G.F. on request). Ordering information is given on any current masthead page.

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The Oxidation of Acetophenones to Arylglyoxals with Aqueous Hydrobromic Acid in Dimethyl Sulfoxide

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The reaction of acetophenones with aqueous hydrobromic acid (HBr) in dimethyl sulfoxide (Me_2SO) leads to the formation of arylglyoxals in good yield. Evidence has been obtained which suggests that this oxidation is mediated by a low concentration of molecular bromine, with the consecutive intermediacy of the α-bromo- and α-hydroxyacetophenones. The reaction of α-bromoacetophenone **2** with Me_2SO alone provides the arylglyoxal **4** with the glyoxylic acid **6** as the major products. The α-hydroxyacetophenone **3** and thiol ester **5** are intermediates leading to **4** and **6**, respectively, and may be isolated as minor products. The presence of water in the medium suppresses the formation of **5** and **6** and results in a cleaner conversion to **4**. Treatment of aryl aldehyde **13** with **14** followed by reaction of the resulting **15** with aqueous HBr in Me_2SO gave arylglyoxal **4** in good yield.

The oxidation of acetophenones to arylglyoxals or their corresponding hydrates (e.g., **1** → **4**; See Scheme I) is usually carried out with selenium dioxide (selenious acid). This method has a wide scope and provides the aryl-

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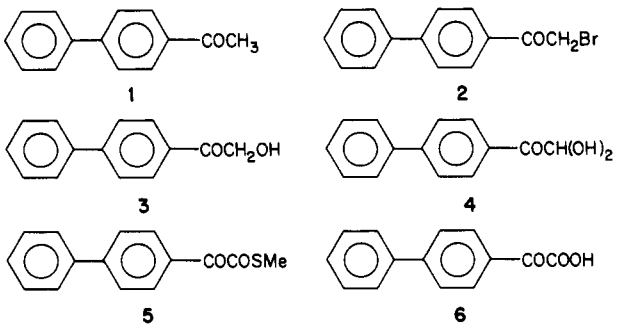
Scheme I



glyoxals in generally good yield.[1] However, we sought an alternative preparation of arylglyoxals to avoid the selenium-containing contaminants which too often accompany the product in this reaction. After consideration of several possibilities[2] we were attracted to the conversion of α-bromoacetophenones to arylglyoxals through the agency of dimethyl sulfoxide (Me_2SO), a reaction first reported by Kornblum and co-workers.[3]

In our preliminary work, treatment of the α-bromoacetophenone **2** with dry Me_2SO at room temperature did not result in a clean conversion to arylglyoxal **4**. The reaction was characterized by an induction period of several hours, during which the slow formation of α-hydroxyacetophenone **3** was the only change observable by TLC. As the other products began to appear, a slightly exothermic reaction was observed. A "spent" oxidation mixture consisted only of **4** and **6** in a ratio of ca. 3:2; examination of the products at an earlier stage, for example, shortly before complete consumption of the starting material **2**, also showed the presence of small amounts of **3** and **5**. Arylglyoxal **4** is not converted to glyoxylic acid **6** under the conditions of the reaction and therefore is not an intermediate in the formation of the latter.

It was found that the formation of **5** and **6** from **2** could be suppressed by the addition of water to the medium. As little as 25 mol %, based on **2**, was sufficient to effect this change. The induction period was not perceptibly shortened, and indeed there appears to be a retardation in the rate of disappearance of **2** as water is added.

The above observations suggest that the mechanism of the oxidation of α-bromoacetophenones (e.g., **2**) to arylglyoxals (e.g., **4**) does *not* involve the intermediacy of alkoxydimethylsulfonium salts,[4] as shown in Scheme II.

Scheme II

$$\underset{\mathbf{2}}{ArCOCH_2Br} + Me_2SO \rightleftarrows ArCOCH_2OS^+Me_2Br^- \quad (1)$$

$$ArCOCH_2OS^+Me_2Br^- \rightarrow ArCOCHO + HBr + Me_2S \quad (2)$$

$$ArCOCHO + H_2O \rightarrow ArCOCH(OH)_2 \quad (3)$$

$$Ar = 4\text{-}C_6H_5C_6H_4$$

Evidence obtained in this work and literature precedents support instead a chain reaction involving molecular bromine, as shown in Scheme III.

Scheme III

$$\underset{\mathbf{2}}{ArCOCH_2Br} + H_2O \rightarrow \underset{\mathbf{3}}{ArCOCH_2OH} + HBr \quad (4)$$

$$2HBr + Me_2SO \rightleftarrows Br_2 + H_2O + Me_2S \quad (5)$$

$$\mathbf{3} + Br_2 \rightarrow \underset{\mathbf{7}}{ArCOCHBrOH} + HBr \quad (6)$$

$$\mathbf{7} + H_2O \rightarrow \underset{\mathbf{4}}{ArCOCH(OH)_2} + HBr \quad (7)$$

$$\mathbf{2} + Br_2 + \rightarrow \underset{\mathbf{8}}{ArCOCHBr_2} + HBr \quad (8)$$

$$\mathbf{8} + H_2O \rightarrow \mathbf{7} + HBr \quad (9)$$

$$Ar = 4\text{-}C_6H_5C_6H_4$$

The α-hydroxyacetophenone **3**, an observable intermediate, might be produced by solvolysis of **2** (reaction 4). The water necessary for this reaction, if not present initially, would have to arise from HBr and Me_2SO by reaction 5, the equation which expresses the relationship between the components of aqueous HBr in Me_2SO.[5] The low equilibrium concentration of bromine produced by reaction 5 (solvated by Me_2SO or complexed with dimethyl sulfide)[6] may react with **3** via its enolic form to give the unobservable intermediate **7** (reaction 6), which would be rapidly hydrolyzed to **4** (reaction 7).

An alternative pathway would be expressed by reactions 8 and 9 in which the bromo ketone **2** forms the dibromide **8** and the latter undergoes successive solvolyses through intermediate **7**, to yield **4**. The available evidence suggests that the sequence **2** → **3** → **7** (reactions 4 and 6) is the predominant pathway, rather than the sequence **2** → **8** → **7** (reactions 8 and 9). The relative contributions would be dependent on the rates of enolization, bromination, and solvolysis of the intermediates of Scheme III. We have found that bromo ketone **2** undergoes reaction with dry Me_2SO, in the manner noted above, at a much faster rate than the dibromo ketone **8**, which is substantially unchanged under the same conditions. After 3 weeks reaction, **8** provides **6** in 85% yield. In the aqueous HBr–Me_2SO system described below (See Table I), **2** also reacts at a much faster rate, to yield **4** (entry 2). The slower reaction of **8** (entry 4) gives a mixture of **4** (61%) and **6** (27%). The trace of **6** formed in the reaction of **2** with wet Me_2SO may result from the operation of reaction 8 to a small extent followed by oxidative conversion of the dibromide **8**. The arylglyoxal **4** is stable to the above conditions and does not appear to be the precursor of **6**.

The solvolysis reactions (reactions 4 and 9) appear to be acid catalyzed. A control experiment demonstrated that **2** was only slowly (ca. 30 h) converted at 55 °C to **3** (and **4**) in Me_2SO, which contained water (ca. 6.5 M). However, as noted above the initial presence of HBr in the medium resulted in an acceleration of the disappearance (ca. 1.5 h) of **2**. The hydrate form of the ketones may be intermediates in the solvolysis reactions.[7]

Molecular bromine has been proposed as a reactive intermediate in other reactions involving HBr in Me_2SO. Examples are the conversion of aniline hydrobromide to *p*-bromoaniline in hot Me_2SO[8] and the conversion of 1,3-indandione to ninhydrin with a sub-stoichiometric amount of aqueous HBr in Me_2SO.[9]

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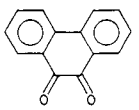
Table I. Oxidation of Aromatic Ketones ArCOCHXY to Glyoxals and Other Products with Aqueous Hydrobromic Acid in Me_2SO[a]

entry	reactant Ar	X	Y	product[b]	yield,[h] %	reactn time,[c] h
1	4-$C_6H_5C_6H_4$ (1)	H	H	$ArCOCH(OH)_2$ (4)	90	24
2	4-$C_6H_5C_6H_4$ (2)	H	Br	4	92	1.5
3	4-$C_6H_5C_6H_4$ (3)	H	OH	4	93	0.5
4	4-$C_6H_5C_6H_4$ (8)[d]	Br	Br	4	61	18
5	4-$C_6H_5C_6H_4$ (9)[e]	H	$SMe_2^+Br^-$	4	89	1.5
6	4-$C_6H_5C_6H_4$ (10)[e]	H	SMe	4	94	2
7	4-$C_6H_5C_6H_4$ (12)[e]	H	OSO_2Me	4	87	2
8	4-$C_6H_5C_6H_4COCOSCH_3$ (5)			6	85	5
9	4-$CH_3OC_6H_4$	H	H	$ArCOCH(OH)_2$	94	24
10	4-$O_2NC_6H_4$	H	H	ArCOCHO[f]	60	24
11	4-BrC_6H_4	H	H	$ArCOCH(OH)_2$	86	24
12	4-$C_6H_5NHC_6H_4$[e]	H	H	4-BrC_6H_4-4-$NHC_6H_4COCH_3$	90	1
13	C_6H_5	H	C_6H_5	$C_6H_5COCOC_6H_5$	99	24
14	C_6H_5	OH	C_6H_5	$C_6H_5COCOC_6H_5$	95	24
15	C_6H_5	H	COC_6H_5	$C_6H_5COC(OH)_2COC_6H_5$	70	24
				C_6H_5COOH	17	
16	2-$C_6H_5C_6H_4$	H	H	ArCOCHO[g]	42	24
					47	

[a] All reactions were carried out at ca. 55 °C with the reactant (ca. 0.5 M), HBr (ca. 1.5 M), and water (ca. 7.5 M). [b] Products were homogeneous by TLC and were identified by spectral means and where possible by comparison with authentic samples. [c] Reaction time corresponds roughly to that required for disappearance of reactant. [d] Reference 13. [e] See Experimental Section. [f] Isolated by bulb-to-bulb distillation [110 °C (0.06 mm)] and characterized as a quaterhydrate, mp 55–70 °C. [g] Isolated as the bisulfite addition product. [h] Isolated.

The pronounced decrease in the formation of the by-product acid **6** and its thiol ester precursor **5** when water is added to the medium is explained by the corollary mechanism shown in Scheme IV.

Scheme IV

$$\underset{\mathbf{2}}{ArCOCH_2Br} + Me_2S \rightarrow \underset{\mathbf{9}}{ArCOCH_2S^+Me_2Br^-} \quad (10)$$

$$\mathbf{9} + Me_2S \rightarrow \underset{\mathbf{10}}{ArCOCH_2SMe} + Me_3S^+Br^- \quad (11)$$

$$\mathbf{10}\ (\mathbf{9}) + 2Br_2 \rightarrow \underset{\mathbf{11}}{ArCOCBr_2SMe} + 2HBr\ (+\ MeBr) \quad (12)$$

$$\mathbf{11} + H_2O \rightarrow \underset{\mathbf{5}}{ArCOCOSMe} + 2HBr \quad (13)$$

$$\mathbf{5} + {}^1/_2Br_2 + H_2O \rightarrow \underset{\mathbf{6}}{ArCOCOOH} + HBr + {}^1/_2(MeS)_2 \quad (14)$$

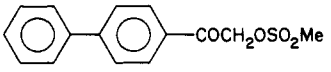
Ar = 4-$C_6H_5C_6H_4$

When a low concentration of water is present in the medium, the dimethyl sulfide (Me_2S) formed in reaction 5 competes effectively as a nucleophile and serves to convert **2** to the sulfonium salt **9** (reaction 10). Further reaction of **9** with Me_2S, when present in high enough concentration, to give **10** is possible (reaction 11).[10] Either **9** or **10** may undergo two stages of bromination to give dibromide **11** (reaction 12), and **11** is eventually hydrolyzed to the observed product **5** (reaction 13). Thiol ester **5** is finally oxidatively hydrolyzed to acid **6** (reaction 14).

To examine some of the proposed stages of Scheme IV, intermediates **9** and **10** were prepared and reacted with bromine (2 equiv) in Me_2SO. The thioether **10** afforded a mixture of **4** (40%) and **6** (50%). Sulfonium salt **9** afforded the glyoxylic acid **6** exclusively under the same conditions. The reaction of either **9** or **10** with the aqueous HBr–Me_2SO system resulted in formation of **4** only (Table I, entries 5 and 6). As expected the thiol ester **5** yielded **6** with this system (entry 8). It is clear that the presence of water and HBr can alter the course of the bromination of these sulfur-containing materials, although the details are not clear.[11] More importantly, it appears that the presence of water prevents the formation of sulfur compounds in the reactions we have studied. The formation of arylglyoxylic acids and their thiol esters from the reaction of α-bromoacetophenones with Me_2SO has been reported previously.[12]

The induction period observed in the reactions of **2** with Me_2SO might be a consequence of the need to build up sufficient concentrations of the reactive intermediates HBr, molecular bromine, and the α-hydroxyacetophenone **3**. Reactions 4 (solvolysis) and 6 (bromination) should both be autocatalytic in nature. The relative concentrations of HBr, bromine, and water would be regulated by reaction 5. The observed formation of **3** during the induction period supports its role as an intermediate in the oxidation. That reaction 6 occurs rapidly when there is sufficient bromine (and HBr for catalysis of enolization) is demonstrated by the facile conversion of **3** to **4** in Me_2SO containing aqueous HBr, with no induction period (Table I, entry 3).

Some reactions carried out with the mesylate **12** were pertinent to this study. If the alkoxydimethylsulfonium salt mechanism of Scheme II is operative, replacement of the α-bromo substituent by mesyloxy in the Me_2SO solvolysis reaction should also provide such an ion as the mesylate, with subsequent oxidative fragmentation to **4**.



12

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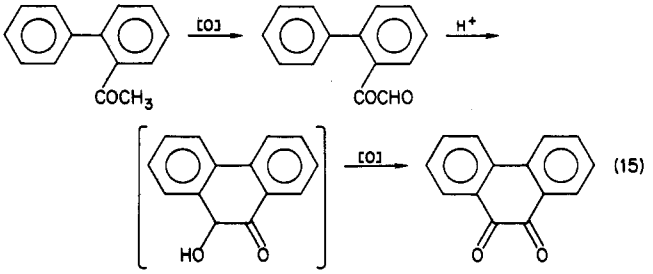
When 12 was dissolved in dry Me_2SO for several days at room temperature, there was no sign of reaction, and 12 was recovered unchanged. Solvolysis of 12 in Me_2SO which contained aqueous sulfuric acid resulted in the formation of 3 and other unidentified minor products, with negligible oxidation to 4. However, exposure of 12 to the action of Me_2SO containing aqueous HBr resulted in rapid formation of 4 (Table I, entry 7).

The above observations suggested that a direct conversion of acetophenones to arylglyoxals should be possible. After some experimentation it was found that the reaction could be conveniently carried out by heating the acetophenone and 48% aqueous HBr (ca. 0.5 and 1.5 M, respectively) in Me_2SO at 50–60 °C for several hours. Under these conditions bromination of the starting material appears to be the rate-determining step judged by the absence of detectable (TLC) amounts of intermediates (e.g., 2 and 3) during the reaction. As expected there is no induction period. While increasing the concentration of HBr or the temperature would probably increase the rate of reaction, we have chosen to operate in the range above since the glyoxal products would be expected to rearrange to mandelic acids under too strongly acid conditions.[11] The amount of water present in the above mixture (ca. 7.5 M for a solution 1.5 M in HBr) apparently does not suppress, through the equilibrium of reaction 5, the bromine concentration below that necessary for a smooth reaction. The net stoichiometry is presumed to be

$$ArCOCH_3 + 2Me_2SO \rightarrow ArCOCH(OH)_2 + 2Me_2S$$

The reaction has been applied to several acetophenones and other aromatic ketones with the results shown in Table I. Side reactions may prevail in cases where a moiety more reactive to bromine than the acetyl group is present. For example, reaction of 4-acetyldiphenylamine with the reagent resulted in rapid formation of the 4′-bromo derivative (entry 12). This reaction and others under study suggest that aqueous HBr in Me_2SO may function as a useful, selective brominating agent for aromatic amines.[8]

While the rearrangement of the arylglyoxal products to mandelic acids mentioned above has not been observed, other acid-catalyzed reactions have occurred under the conditions of the system. 2-Acetylbiphenyl affords 9,10-phenanthrenequinone (47%) as well as the expected glyoxal (42%) presumably as a result of the sequence in eq 15 (entry 16).

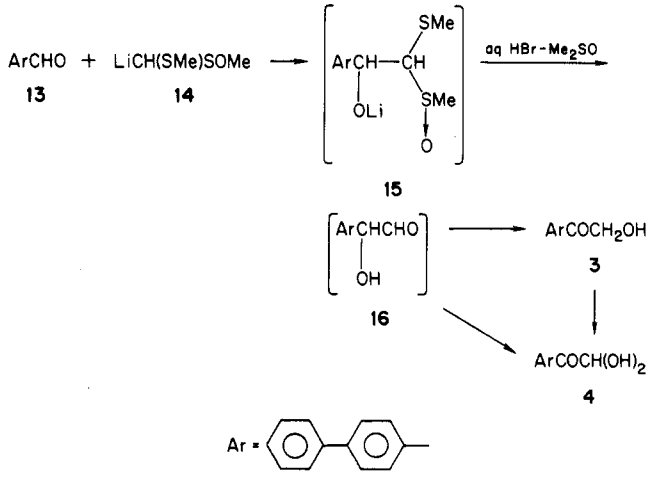


(15)

The oxidation system converted both deoxybenzoin and benzoin to benzil (entries 13 and 14). However in contrast to the acetophenones, in this case the α-hydroxy ketone (benzoin) was a clearly observable intermediate in the deoxybenzoin oxidation. Thus the rate of benzil appearance from deoxybenzoin is limited by the rate of benzoin enolization or the reaction of the enol with the brominating species.

Since α-hydroxyacetophenones such as 3 serve as substrates for the oxidizing reagent system, an efficient one-pot homologation of benzaldehydes to the corresponding arylglyoxals was examined (see Scheme V). The method

Scheme V



utilizes (methylthio)methyl sulfoxide (MMTS) for the conversion of benzaldehydes such as 13 to the requisite precursor 3.[14] The lithium salt of MMTS (14), prepared in THF–hexane, was reacted with 13 in the usual way. The solvents were evaporated to give a solid, presumably 15, which was treated while cooling initially with aqueous HBr in Me_2SO (5 molar equiv). After brief heating at ca. 55 °C and workup, 4 was obtained in 78% yield. The conversion may involve the oxidation of 16 directly or its rearrangement product 3 or both. The attempted use of sodium hydride in Me_2SO as the base and solvent for the MMTS reaction, followed by addition of aqueous HBr, was less efficient. Much residual aldehyde was observed because of the sluggish nature of the reaction of MMTS with sodium hydride.

In summary, we have attempted to point out some of the salient features of the reactions of aromatic ketones with Me_2SO in the presence of HBr, water, and bromine. In particular, the conversion of α-bromoacetophenone to arylglyoxals is interpreted as proceeding via solvolysis to α-hydroxyacetophenone intermediates. The formation of arylglyoxals from the latter is a result of the rapid bromination of the enediol form which is made available by the acidic medium. The conversion of acetophenones to arylglyoxals described here should find synthetic application in appropriate cases.

Experimental Section

General Methods. Melting points were determined in open capillary tubes with a Mel-Temp apparatus and are uncorrected. Infrared (IR) spectra were determined in KBr discs or as neat smears with a Nicolet 7199 FT-IR spectrometer. Ultraviolet (UV) spectra were determined with a Cary Model 219 spectrophotometer. Proton magnetic resonance (^1H NMR) spectra were determined in the indicated solvent with either the Varian HA-100 or the Varian FT-80 spectrometer. The thin-layer chromatographic (TLC) system employed was the solvent 60:30:1 heptane–ethyl acetate–acetic acid on Analtech Uniplate silica gel GF plates. Visualization of spots was achieved by observation under "short UV light" and by spraying with a 2,4-DNP reagent. The following R_f values were observed for compounds in the biphenyl series: 1, 0.68; 2, 0.70; 3, 0.40; 4, 0.30; 5, 0.75; 6, 0.08; 8, 0.75. Unless otherwise indicated, yield data refer to isolated, purified product.

Reaction of Bromoacetophenone 2 with Dry Me_2SO. A solution of 25.1 g (91.2 mmol) of 2 in 150 mL of Me_2SO (dried over 3A molecular sieves) was stirred at room temperature for 16 h. TLC showed no 2 remained. The solution was poured onto ice, and the resulting solid was filtered, washed with water, and dried, yielding 20.7 g. TLC showed a mixture of 4 and 6. An

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acetone solution of the mixture was poured into $NaHCO_3$ solution. The solution was cooled and filtered to provide 11.6 g (56%) of **4**. Recrystallization from aqueous acetone gave mp 113–125 °C. This material was identical (TLC, spectra) with that prepared by selenium dioxide oxidation.[15]

Arylglyoxylic Acid 6. The filtrate was acidified with HCl, and the resulting precipitate was extracted with ether. Workup of this extract gave 8.7 g (42%) of **6** as a light yellow solid. Recrystallization from petrol ether–ether gave light yellow crystals, mp 101–103 °C. This material was identical (TLC, ^1H NMR) with that prepared by an alternate method.[16]

In a separate run which employed the above conditions, the reaction was followed by TLC. After 1.5 h, only **2** and a trace of **3** were observed. After 6 h, **2** and small amounts of **3–5** were observed. A 15-mL aliquot was removed, partitioned with ice–water and EtOAc, and filtered. The EtOAc layer of the filtrate was worked up to give 1.1 g of yellow solid, which was chromatographed on a dry column of silica gel with the solvent system used for TLC. In addition to **2** and **4**, the following compounds were isolated from the segmented column.

Hydroxyacetophenone 3. The fractions which displayed R_f 0.4 on TLC were pooled to give 0.12 g of solid. Recrystallization from EtOH gave mp 121–128 °C; this material was identical (TLC, ^1H NMR) with that prepared by an alternate method.[17]

Thiol Ester 5. The fractions which displayed R_f 0.75 on TLC were pooled to give 0.10 g of yellow solid. This material was identical with **5** prepared by the alternate route described below.

4-Phenylbenzonitrile (8.96 g, 50 mmol) was condensed with methyl (methylthio)methyl sulfoxide through the agency of NaH in THF as previously described[18] to provide 12.0 g (79%) of enamino sulfoxide. To a solution of 6.07 g (20 mmol) of the enamino sulfoxide in 100 mL of CH_2Cl_2 and 30 mL of $CHCl_3$ was added 5.1 g (30 mmol) of $CuCl_2 \cdot 2H_2O$.[19] After the mixture was stirred for 5 h at room temperature conversion to **5** was complete by TLC. The solids were filtered off, and the filtrate was washed with water, dried, and evaporated. The crude product was recrystallized from petrol ether–acetone to provide 2.91 g (58%) of greenish yellow solid: mp 61–68 °C; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3 H). Anal. Calcd for $C_{15}H_{12}SO_2$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.25; H, 4.84; S, 12.91.

Reaction of Bromoacetophenone 2 with Wet Me_2SO. A solution of 121 g (0.44 mol) of **2** in 720 mL of Me_2SO which contained 7.9 mL (0.44 mol) of water was stirred at room temperature. After 1.5 h only **2** and a trace of **3** were observed by TLC. After 3 h the formation of **4** was observable. After 24 h no **2** remained, and the product **4** was accompanied by trace contaminants including **3** and **6**. The solution was poured onto ice, and the resulting solid was filtered, washed with water followed by ether to remove organic impurities, and dried, yielding 83.6 g (84%), homogeneous on TLC.

General Procedure for Oxidation of Acetophenones to Arylglyoxal Hydrates. To a stirred solution of the ketone (50 mmol) in 85 mL of Me_2SO was added slowly 17 mL (150 mmol) of 48% aqueous HBr (8.8 M). The solution was stirred in an open flask at 55 °C,[20] and the reaction was followed by TLC. When the starting material was consumed, the solution was poured onto ice. In most cases the solid products were filtered, washed with water, and dried under vacuum at room temperature over P_2O_5. For some water-soluble compounds or oils the crude product was extracted into EtOAc, and the solution was washed with water, dried, and concentrated. Usually the products obtained showed a single spot on TLC. All products were recrystallized for comparison with authentic samples or determinations of physical data.

In cases where acidic materials were produced as products, a partition with aqueous $NaHCO_3$ and EtOAc was carried out. The acidic materials were recovered by reacidification with HCl and appropriate workup.

Results are summarized in Table I.

Dimethylsulfonium Salt 9. A stirred mixture of 19.0 g (69 mmol) of **2**, 15.2 mL of dimethyl sulfide, and 70 mL of dioxane was heated at 65 °C for 60 min, cooled, and diluted with ether. The white solid was filtered, washed with ether, and dried under vacuum over P_2O_5 at 25 °C: yield, 19.0 g (82%); mp 148–152 °C. Anal. Calcd for $C_{16}H_{17}SOBr$: C, 55.98; H, 5.08; S, 9.50; Br, 23.69. Found: C, 57.45; H, 5.26; S, 9.28; Br, 23.85.

Reaction of 9 with Bromine in Me_2SO. To a stirred suspension of 1.69 g (5.0 mmol) of **9** in 20 mL of Me_2SO was added 1.60 g (10 mmol) of bromine during 15 min at 25 °C. A solution formed. After 30 min at 25 °C no **9** was detectable by TLC and a small spot for **5** and a large spot for **6** were observed. After 2 h no **5** was detectable, and the bromine color was still present. Workup as for the reaction of **2** above afforded, after recrystallization from petroleum ether–ether, 0.85 g (75%) of **6**. The neutural fraction gave only traces of material.

Thioether 10. To a stirred mixture of 25.0 g (90.8 mmol) of **2** and 10 mL (ca. 180 mmol) of methanethiol in 120 mL of EtOH at 0 °C was added a solution prepared from 5.40 g (100 mmol) of sodium methoxide in 120 mL of EtOH during a 30-min period. After the addition the mixture was warmed to 25 °C and stirred for 18 h. The mixture was treated with 1.2 mL of glacial HOAc and concentrated. The residue was partitioned with water and EtOAc. Workup of the organic layer gave a solid, which was recrystallized from petroleum ether–EtOAc to give 21.2 g (96%) of white crystals: mp 93–97 °C; ^1H NMR ($CDCl_3$) δ 2.14 (s, 3 H), 3.78 (s, 2 H). Anal. Calcd for $C_{15}H_{14}SO$: C, 74.34; H, 5.82; S, 13.23. Found: C, 74.44; H, 5.77; S, 13.40.

Reaction of Thioether 10 with Bromine in Me_2SO. To a stirred solution of 1.21 g (5.0 mmol) of **10** in 20 mL of Me_2SO was added 1.60 g (10 mmol) of bromine during 15 min at 25 °C. After 18 h at 25 °C no **10** remained, and the bromine color was still present. Workup and separation of neutral and acidic products afforded 0.50 g of impure **4** and 0.58 g (51%) of **6**.

Mesylate 12. To a stirred solution of 3.18 g (15 mmol) of **3** in 75 mL of CH_2Cl_2 at −25 °C was added 2.57 mL (33 mmol) of methanesulfonyl chloride followed by 2.30 mL (16.5 mmol) of Et_3N dropwise during 3 min.[21] The mixture was stirred at −25 °C for 45 min. The mixture was partitioned at 0 °C with CH_2Cl_2 and H_2O. The organic layer was washed well with H_2O, dried, and concentrated. The crude product was recrystallized from CH_2Cl_2–Et_2O to give 3.62 g (83%) of light yellow solid: mp 141–142 °C; ^1H NMR ($CDCl_3$) δ 3.36 (s, 3 H), 5.60 (s, 2 H). Anal. Calcd for $C_{15}H_{14}SO_4$: C, 62.06; H, 4.86; S, 11.04. Found: C, 61.80; H, 4.73; S, 10.96.

Attempted Reaction of 12 with Dry Me_2SO. A solution of 145 mg (0.50 mmol) of **12** in 1.0 mL of dry Me_2SO was allowed to stand at room temperature for 5 days, during which time no evidence of reaction was detected (TLC). Workup of the reaction by partition with $CHCl_3$ and H_2O gave recovery of essentially pure **12** (TLC, NMR).

Reaction of 12 with Aqueous Sulfuric Acid in Me_2SO. To a stirred solution of 145 mg (0.50 mmol) of **12** in 0.84 mL of Me_2SO was added 0.17 mL (1.5 mmol) of 8.8 N H_2SO_4. The mixture was stirred at 55 °C for 16 h. Workup of the reaction by partition with $CHCl_3$ and H_2O gave impure **3** contaminated with three unknown mobile impurities by TLC. A trace at most of glyoxal **4** was present.

Bromination of 4-Acetyldiphenylamine with Aqueous Hydrobromic Acid in Me_2SO. A solution of 0.53 g (2.5 mmol) of 4-acetyldiphenylamine and 0.85 mL (7.5 mmol) of 48% HBr in 4.2 mL of Me_2SO was stirred at 55 °C. After 60 min TLC (3:1 heptane–EtOAc) showed no starting material (R_f 0.35), and a spot for product (R_f 0.32) was observed. The solution was poured onto ice and worked up by EtOAc extraction to give 0.66 g (91%) of amber solid. Recrystallization from petroleum ether–EtOAc gave an amber solid: mp 114–116 °C; ^1H NMR ($CDCl_3$) δ 2.55 (s, 3 H). Anal. Calcd for $C_{14}H_{12}NOBr$: C, 57.95; H, 4.17; N, 4.83; Br, 27.54. Found: C, 58.12; H, 4.20; N, 4.63; Br, 27.42.

Reaction of 13 with 14 and Conversion to 4 with Aqueous Hydrobromic Acid in Me_2SO. To a stirred solution of 9.3 g

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(75 mmol) of methyl (methylthio)methyl sulfoxide in 60 mL of THF was added 35.7 mL (75 mmol) of 2.1 M *n*-butyllithium in hexane at 10–15 °C. After 15 min a solution of 10.9 g (60 mmol) of **13** in 20 mL of THF was added at 0–10 °C, and the solution was stirred at 25 °C overnight. The solvents were removed under vacuum to give a yellow foam. TLC indicated no **13** was present.

This intermediate was dissolved in 120 mL of Me_2SO and treated while cooling with 34 mL of 48% HBr. The resulting solution was heated at 55 °C for 2 h and then worked up in the usual way to give the crude **4**. Recrystallization from aqueous acetone gave 11.4 g (78%) of material with single spot on TLC.

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Registry No. **1**, 92-91-1; **2**, 135-73-9; **3**, 37166-61-3; **4**, 1145-04-6; **5**, 99114-41-7; **6**, 5449-21-8; **8**, 28179-30-8; **9**, 5697-41-6; **10**, 46817-48-5; **12**, 99114-42-8; **13**, 3218-36-8; **15**, 99114-45-1; 4-$H_3COC_6H_4COCH_3$, 100-06-1; 4-$O_2NC_6H_4COCH_3$, 100-19-6; 4-$BrC_6H_4COCH_3$, 99-90-1; 4-$C_6H_5NHC_6H_4COCH_3$, 23600-83-1; $C_6H_5COCH_2C_6H_5$, 451-40-1; $C_6H_5COCH(OH)C_6H_5$, 119-53-9; $C_6H_5COCH_2COC_6H_5$, 120-46-7; 2-$C_6H_5C_6H_4COCH_3$, 2142-66-7; 4-$H_3COC_6H_4COCH(OH)_2$, 16208-17-6; 4-$O_2NC_6H_4COCHO$, 4974-57-6; 4-$BrC_6H_4COCH(OH)_2$, 80352-42-7; 4-$BrC_6H_4NHC_6H_4$-4-$COCH_3$, 99114-43-9; $C_6H_5COCOC_6H_5$, 134-81-6; $C_6H_5COC(OH)_2COC_6H_5$, 29574-75-2; $C_6H_5CO_2H$, 76-93-7; 4-$C_6H_5C_6H_4CH_2CN$, 31603-77-7; $H_3CSCH_2SOCH_3$, 33577-16-1; 4-$C_6H_5C_6H_4C(=NH)CH(SCH_3)SOCH_3$, 99114-44-0; H_3CSH, 74-93-1; 9,10-phenanthrenedione, 84-11-7.

Hydride Sponge: Complexation of 1,8-Naphthalenediylbis(dimethylborane) with Hydride, Fluoride, and Hydroxide

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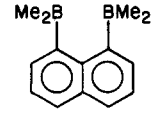
The syntheses of 1,8-naphthalenediylbis(dimethylborane) (**1**) (hydride sponge) and dimethyl-1-naphthylborane (**2**) are described. In solution, **1** abstracts hydride from KH and from a variety of other borohydrides, including **2**·KH, to give a complex, **1**·KH, that is unreactive toward moderately strong acids, benzaldehyde, and free **1**. The crystal structure of **1**·KH·(dioxane)$_3$ reveals the bridged hydride linkage that is primarily responsible for the kinetic and thermodynamic stability of **1**·KH. The complexes **1**·$F^-(NMe_2)_3S^+$ and **1**·$OH{\cdot}PPh_4^+$ are also characterized. These are the first hexaorgano $R_3BXBR_3^-$ species (X = F, OH) to be isolated as pure compounds. Thus, **1** is shown to be a neutral bidentate receptor for small anions.

The design of neutral, geometrically defined receptors for ions is an important goal of modern organic chemistry.[1] Enormous progress has been made in the study of rigid and semirigid polyethers[2] and polyaza compounds[3] interacting with positively charged metal ions and ammonium salts. In contrast, there have been only a few examples of multidentate complexation of anions reported. The best developed systems have been protonated[4] or alkylated[5] polycyclic bases forming inclusion complexes with complementarily sized counterions. The hosts in these systems are actually positively charged analogues of the kinds of compounds that are generally associated with cation complexation, while the "guests" are ions that would be paired with their hosts electrostatically even in the absence of inclusion phenomena.

Very few attempts have been made to arrange *neutral* Lewis acidic functionalities on an organic framework to cooperatively bind anions. One promising effort along these lines is that of M. Newcomb and his co-workers,[6] who have prepared cyclic polystannanes that are potential antipodes of crown ethers. A second group[7] has isolated and characterized complexes of bridging halide ions with *o*-phenylenedimercurials. Oligoboranes have not been extensively pursued in this regard, although 1,2-bis(difluoroboryl)ethane was reported[8] to be a chelating agent for oxygen bases on the basis of low-temperature vapor pressure measurements and precipitation experiments. A recent paper[9] from this laboratory proposed 1,8-diborylnaphthalenes as stereoelectronically defined "ligands" for anions and presented some preliminary data on the prototypical compound **1**.



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Herein we report the full details of our experiments on **1** and the interaction of **1** with hydride, fluoride, and hydroxide.

Experimental Section

General Procedures. All manipulations of air-sensitive liquids were performed by using standard syringe or vacuum line techniques. Air-sensitive solids were transferred in a nitrogen-filled glovebag. Solvents were distilled from the usual drying agents: ethers from Na or sodium benzophenone; hydrocarbons from sodium; CH_2Cl_2 and CD_3CN from P_2O_5. Acetonitrile and CD_2Cl_2

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