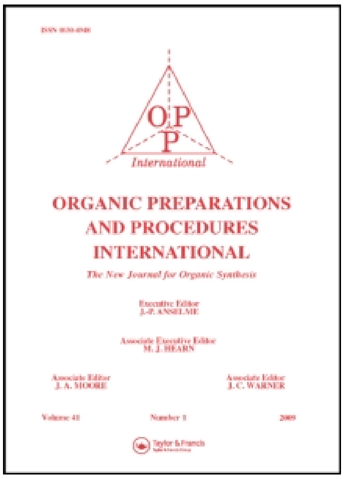

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CARBONYL COMPOUNDS FROM THE OXIDATION OF BENZYLAMMONIUM BROMIDES WITH DIMETHYL SULFOXIDE

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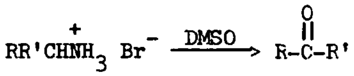
The successful utilization of dimethyl sulfoxide (DMSO) as an oxidant has been reported for a variety of reactions.[1] Scheit and Kampe[2] reported that carbonyl compounds can be obtained by diazotization of benzylamines in DMSO. More recently Traynelis and Ode[3] reported that carbonyl compounds could be obtained in low to moderate yields by heating benzylammonium chlorides in DMSO for a prolonged period of time. Prior to the published results of Traynelis and Ode,[3] we had observed that carbonyl compounds could be obtained from the reaction of benzylammonium bromides with DMSO employing short reaction times (10-30 min.) at an elevated temperature.[4] These results are summarized in Table I. In each case good to moderate yields of the corresponding carbonyl compounds were observed.



$$\underset{\text{I}}{\mathrm{RR'CH\overset{+}{N}H_3}}\ \mathrm{Br^-} \xrightarrow{\text{DMSO}} \mathrm{R{-}\overset{\displaystyle O}{\overset{\Vert}{C}}{-}R'}$$

Table I. - Oxidation of Benzylammonium Bromides to Aldehydes

Amine (I)		Product	% Yield
R	R'		
C_6H_5	H	benzaldehyde	69[a]
p-ClC_6H_5	H	p-chlorobenzaldehyde	84
p-$CH_3OC_6H_5$	H	p-methoxybenzaldehyde	83[a]
2-C_4H_3S	H	2-thiophenecarboxaldehyde	72[a,b]
2-C_4H_3O	H	2-furaldehyde	53[a,b]
C_6H_5	C_6H_5	benzophenone	88

[a] A trace of the corresponding nitrile was also detected.
[b] Isolated as its 2,4-dinitrophenylhydrazone.

The reaction of the hydrobromide salt with DMSO appears to be unique since under identical reaction conditions (150°, 10 min), the corresponding benzylammonium chloride,[3] iodide and acetate afforded less than 10% benzaldehyde. It has also been demonstrated that a DMSO·Br_2 adduct[5] (addition of Br_2, to cold DMSO followed by washing the complex with (CCl_4)) reacts with benzylamine under the above reaction conditions to afford benzaldehyde in 59%. This yield is similar to that obtained from the reaction of benzylammonium bromide with dimethyl sulfoxide.

A conceivable pathway that might possibly account for carbonyl formation could involve the DMSO-Br_2 adduct[5] as the oxidant to form the imine III as depicted below.[6] Although the DMSO-Br_2 adduct is depicted as the oxidant, we have no direct evidence of its participation.

$$2HBr + Me_2SO \longrightarrow Me_2S + H_2O + Br_2{}^{7}$$

$$Br_2 + Me_2SO \rightleftarrows Me_2SO\text{-}Br_2 \ (II)$$

$$C_6H_5CH_2\ddot{N}H_2 + II \longrightarrow \underset{III}{[C_6H_5CH{=}\ddot{N}H]} \xrightarrow{H_2O} PhCHO$$

Alternatively free bromine could also act as an oxidant to afford III. However, the reaction of bromine , benzylamine and water in diglyme or ethyl carbitol under conditions identical to those described above afford a negligible amount of benzaldehyde thus indicating that DMSO plays a vital role in the oxidation of the amine hydrobromide salt. The reaction of cyclohexylammonium bromide with DMSO did not afford cyclohexanone; only a tarry residue was observed after work up.

EXPERIMENTAL

<u>Benzophenone</u>. <u>General procedure</u>. - A mixture of benzhydrylammonium bromide (13.2 g, 0.05 mol) and dimethyl sulfoxide (100 ml) was heated to reflux. The internal reaction temperature[9] fell from 160 to 100° during a thirty minute reflux period. The reaction mixture was cooled to room temperature and poured into 750 ml of water. The resulting mixture was extracted with four (150 ml) portions of a 5:1 Skelly B:ethyl ether mixture. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed with a rotary evaporator. Distillation of the resulting residue gave 9.1 g (88%) of benzophenone, bp. 132-33°/1.5 mm, mp. 47.9-48.5.

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†. Undergraduate research participants.

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5. For an analogous DMSO-Cl_2 adduct see E. J. Corey and C. U. Kim, Tetrahedron Lett. 919 (1973).
6. If a S_N1 type mechanism (eq. 1), as suggested by Traynelis and Ode,[3]

or a S_N2 type (eq. 2) is operative one would anticipate that the yield

$$C_6H_5CH_2\overset{+}{N}H_3\ X^- \rightleftarrows C_6H_5\overset{+}{C}H_2 + \ddot{N}H_3 + X^- \qquad (1)$$

$$C_6H_5CH_2\overset{+}{N}H_3\ X^- \xrightarrow{DMSO} C_6H_5CH_2O\overset{+}{S}Me_2 + X^- + \ddot{N}H_3 \qquad (2)$$

of benzaldehyde from the reaction of benzylammonium bromide, iodide, chloride and acetate respectively with dimethyl sulfoxide would be comparable, since the leaving group ability of the ammonium grouping should not be affected by the counter ions. As pointed out above only the hydrobromide salt affords a high yield of benzaldehyde.

Since dimethyl sulfoxide is known to solvate cations, the anion X^- in dimethyl sulfoxide should be a good nucleophile. Therefore, another possible pathway to aldehyde formation might be envisioned by anion (X^-) displacing the NH_3^+ group to give ammonia and $C_6H_5CH_2$-X. The latter compound could then be oxidized by dimethyl sulfoxide[8] to give benzaldehyde. Our results are also inconsistent with this alternative mechanism.

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9. The drop in internal temperature is presumably due to the generated dimethyl sulfide.

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