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OXIDATION OF CARBENES BY DIMETHYL SULFOXIDE

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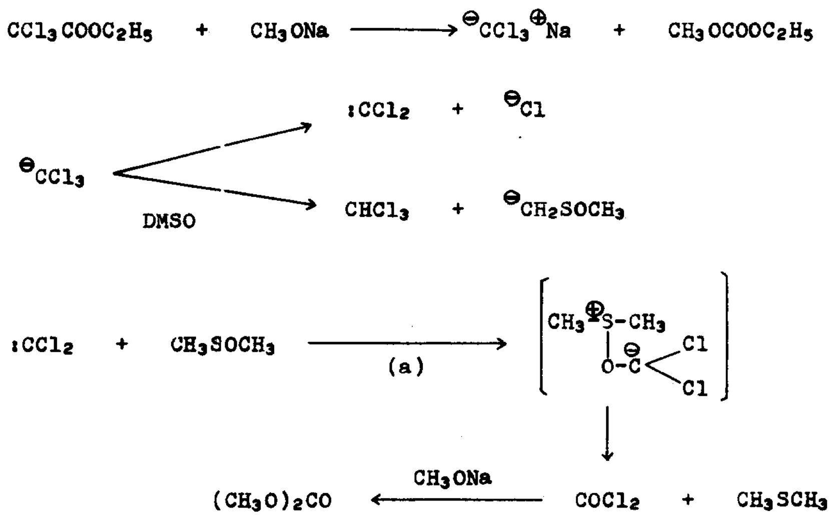
We wish to report the oxidation of some carbenes by dimethyl sulfoxide (DMSO) to the corresponding carbonyl compounds. In the case of dichlorocarbene, the products are phosgene and dimethyl sulfide. Phosgene was identified by conversion into dimethyl carbonate, while dimethyl sulfide was identified as $[(CH_3)_2S]_2 \cdot 3HgCl_2$.(1) The reaction was carried out by adding sodium methoxide (25g) to a cold DMSO (60g) solution of ethyl trichloroacetate (25g). After standing for one hour at ice-cooled temperature, the mixture was poured into ice-water and extracted with ether. The ether was evaporated and the residual solution was distilled.

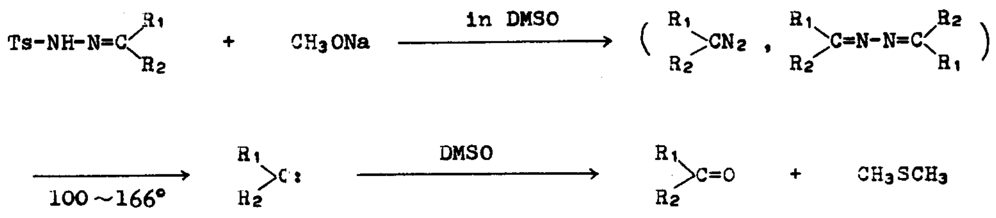
Vapor phase chromatographic analysis (V.P.C) of this distillate (17g), indicated the yields of the products and recovered starting material to be as follows; dimethyl carbonate (17%), methyl ethyl carbonate (33%), chloroform (38%), ethyl trichloroacetate (8%). The four components were identified by comparison of thier IR, NMR and V.P.C. with authentic samples after separation of each component by V.P.C. It was found that methyl ethyl carbonate underwent transesterification to dimethyl carbonate to the extent of 7% under the reaction conditions described above, although the two carbonates were mostly hydrolysed to sodium salts. This is one of the reasons that the combined yield of chloroform and dimethyl carbonate was higher than that of methyl ethyl carbonate.

On the other hand, dimethyl sulfide was isolated as $[(CH_3)_2S]_2 \cdot 3HgCl_2$ in 20% yields from the reaction mixture before ether extraction.



The chloroform is presumably formed through the deprotonation of DMSO by the trichloromethyl anion. Step (a) corresponds to the reaction of dichlorocarbene with pyridine N-oxide.(2),(3)

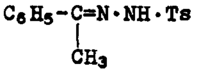
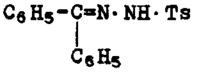
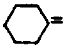
Other carbenes prepared by alkaline cleavage of tosylhydrazones(4),(5),(6) were also oxidized by DMSO to the corresponding ketones or aldehyde.



The tosylhydrazone (10~15g)(see Table I) was dissolved in DMSO (100g) and sodium methoxide (3g, 0.0556 mole) was added to the solution. The mixture was heated with stirring for about ten to eighteen minutes at 100~166° in nitrogen atmosphere. The reaction mixture (except cyclohexanone tosylhydrazone) began to turn wine-red at about 100°. The reaction mixture was poured into ice-water and extracted with ether. The carbonyl compounds of the products were compared with authentic specimens by V.P.C., IR and semicarbazones. Experimental data are shown in Table I. When the tosylhydrazones were decomposed in ethylene-glycol instead of DMSO under similar reaction conditions, no carbonyl compounds were formed. Dimethyl sulfide was also isolated as its mercuric chloride complex in yields comparable to those of the corresponding carbonyl compounds.

In the decomposition of acetophenone and benzophenone tosylhydrazone, the corresponding azines were isolated in 10% and 6% yields, respectively, besides the carbonyl compounds. The yields of the carbonyl compounds were found to drop rapidly if the reaction time is longer than that mentioned in Table I.

TABLE 1 Alkaline Cleavage of Tosylhydrazones in DMSO

	Tosylhydrasone (mole)	Temperature	Time (min)	Product	Yield
1).	 $C_6H_5-C(CH_3)=N\cdot NH\cdot Ts$ (0.052)	100 ~ 160°	15	$C_6H_5COCH_3$	46%
2).	 $C_6H_5-C(C_6H_5)=N\cdot NH\cdot Ts$ (0.0286)	100 ~ 150°	10	$C_6H_5COC_6H_5$	67%
3).	 =N·NH·Ts (0.0352)	100 ~ 166°	18	 =O	12%
4).	$C_6H_5\cdot CH=N\cdot NH\cdot Ts$ (0.0365)	100 ~ 133°	10	C_6H_5CHO	40%

For example, the yield of acetophenone was only 0.8% when the reaction mixture of acetophenone (10g), DMSO (100g) and sodium methoxide (3g) was heated at 100 ~ 160° for 18 minutes. A possible cause for this phenomenon is the reaction between the carbonyl compounds and the methylsulfinyl carbanion.

References

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