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Preliminary communication

REACTION OF SULFONIUM YLIDES COMPLEXED WITH TRICARBONYLCHROMIUM

A. CECCON*, F. MICONI and A. VENZO
Istituto di Chimica-Fisica, Università di Padova, 35100 Padova (Italy)

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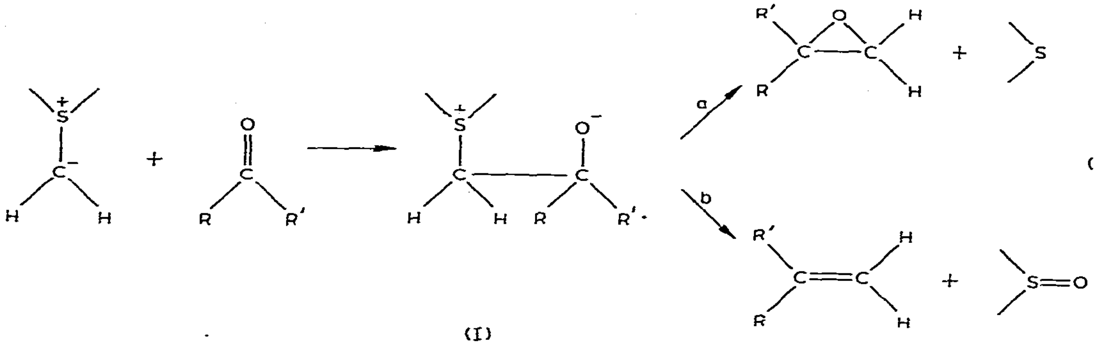
Summary

Oxiranes and olefins are obtained from the reactions of free and complexed phenylmethylsulfonium methylides with tricarbonylchromium with benzophenone, benzaldehyde and cyclohexanone. Good yields of olefins are obtained from the $Cr(CO)_3$ complexes with benzophenone, but yields of 0.1—0.5% are obtained with benzaldehyde and cyclohexanone.

Sulfonium ylides react with aldehydes and ketones to give oxiranes, exclusively (path "a") [1], the reaction taking place through the formation of the betaine intermediate, I.



(1)

In contrast, phosphonium ylides give olefins (path "b"-like) as the only product [2].

In our program aimed at determining the influence of the tricarbonylchromium (TCC) group on the chemical and spectroscopic properties of ionic intermediates bearing a charge in the side chain of an arene ring, we have begun an in-

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*To whom correspondence should be addressed.

vestigation on the reaction of phenylmethylsulfonium methylide, free and complexed with TCC, with carbonyl compounds. This communication reports the preliminary results obtained with two benzophenones, benzaldehyde and cyclohexanone.

Phenyldimethylsulfonium [3], tricarbonylchromiumphenyldimethylsulfonium [4] and 4-nitrophenyldimethylsulfonium [4] tetrafluoroborates were treated with the carbonyls in anhydrous DMSO containing potassium t-butoxide at room temperature under nitrogen following the procedure suggested by Franzen [5]. The results are shown in Table 1.

TABLE 1

PRODUCTS OF THE REACTIONS OF Ar$\overset{+}{S}$Me$_2$ BF$_4^-$ WITH SOME CARBONYL COMPOUNDS IN DMSO/KOBu-t AT ROOM TEMPERATURE[a]

Ar	Carbonyls	Oxirane[b] (%)	Olefin[b] (%)	Unreacted carbonyl[b] (%)
C_6H_5	Benzophenone	94	<0.1	<0.1
TCC-C_6H_5	Benzophenone	15	52[c]	18
4-$NO_2C_6H_5$	Benzophenone	38	8	17
C_6H_5	4,4′-Dimethylbenzophenone	80[d]	<0.1	<0.1
TCC-C_6H_5	4,4′-Dimethylbenzophenone	26[d]	33	20[d]
C_6H_5	Benzaldehyde	34	<0.1	<0.1
TCC-C_6H_5	Benzaldehyde	2.5	0.5	8
C_6H_5	Cyclohexanone	62	<0.1	28
TCC-C_6H_5	Cyclohexanone	3.3	<0.1	14

[a] The products are stable in the reaction medium. [b] Determined by GLC analysis by comparison with authentic samples using internal standards. [c] In one experiment, 1,1-diphenylethylene was recovered by preparative GLC and its NMR spectrum was identical to that of an authentical sample. [d] Yield determined by NMR integration.

High yields of oxiranes were obtained in the reaction of the "ligand" ylide, $Ph(CH_3)^+S{-}CH_2^-$, with all carbonyls investigated, and no olefin could be detected by GLC analysis.

Complexation of the sulfonium salt with TCC changes drastically the course of the reaction. With benzophenone, both 1,1-diphenylethylene oxide and 1,1-diphenylethylene are formed, with the alkene as the major product. The alkene is formed in high yields also with 4,4′-dimethylbenzophenone, but only in 0.5% yield with benzaldehyde, and is absent with cyclohexanone. Finally, the oxirane is obtained in very poor yield both with benzaldehyde and with cyclohexanone.

The high yields of olefin formed in the reaction with the highly polarized benzophenones can be explained by the strong electron-withdrawing effect of TCC, which makes the attack at the sulfur atom by the negative oxygen (path "b") competitive with the attack of the same oxygen at the carbon atom (path "a") in the betaine intermediate. This is supported by the finding that 4-nitrophenylmethylsulfonium methylide affords a small but definite amount of 1,1-diphenylethylene.

The percentage of olefin decreases drastically on passing from benzophenones to benzaldehyde and cyclohexanone. It thus appears that the presence of substituents able to stabilize the incipient carbon—carbon double bond in the transition state of step "b" may be of importance in determining the yield of olefin.

Finally, the lower percentage of oxirane obtained with cyclohexanone and benzaldehyde upon complexation may be explained by the lower carbanionic character of the complexed ylide as a result of the $-I$ effect of $Cr(CO)_3$. This effect increases the extent of *d*-orbital resonance between the carbanion and sulfur, so decreasing the nucleophilic character of the ylide [6].

In conclusion, the sulfonium ylides can afford the "Wittig" product only if the sulfur atom is sufficiently electrophilic in character to undergo attack by the negatively charged oxygen of the betaine, and if the double bond of the olefin is sufficiently stabilized by substituents.

Researchers are in progress to elucidate the many aspects of the reactions of the tricarbonylchromium-complexed sulfonium ylides.

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