[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STEVENS INSTITUTE OF TECHNOLOGY]

SULFONE FORMATION DURING SULFINATION OF THE ALKYL GRIGNARD REAGENT[1]

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The reaction between sulfur dioxide and the Grignard reagent has been widely used for the preparation of aliphatic and aromatic sulfinic acids (1). As a by-product, small quantities of sulfoxides, Ar_2SO, have been obtained from the sulfination of phenylmagnesium bromide (1b) and *p*-tolylmagnesium bromide (2). An excess of sulfur dioxide will bring about another secondary reaction, formation in good yield of thiolsulfinate, $RSO_2{\cdot}SR$ (3).

The formation of sulfone as a by-product of sulfination of alkyl or aryl magnesium bromide has not heretofore been described.

Sulfones were detected in the salts of aliphatic sulfinic acids prepared in earlier work (4). Their formation has now been studied at several temperatures and in the presence of excess alkyl halide. They are produced in small amount at room temperature and above but only in traces or not at all at low temperature. A considerable excess, 50%, of alkyl halide present before the introduction of sulfur dioxide increases the quantity of sulfone, whereas halide added after the sulfur dioxide does not increase it. The presence of air during the reaction does not seem to affect it. No sulfoxide was detected.

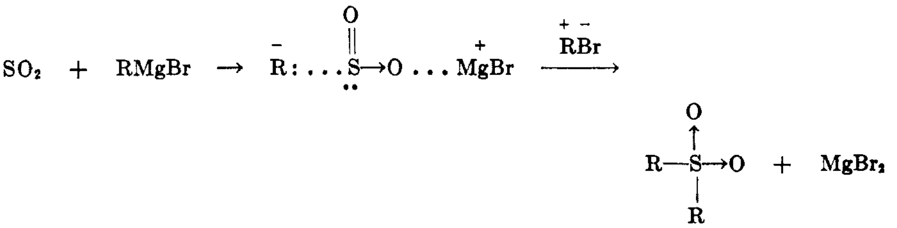
A possible reaction sequence for sulfone formation during sulfination of the alkyl Grignard reagent is given by equations 1 and 2.

1. $$C_{12}H_{25}MgBr + SO_2 \rightarrow C_{12}H_{25}SO_2MgBr$$

2. $$C_{12}H_{25}SO_2MgBr + BrC_{12}H_{25} \rightarrow (C_{12}H_{25})_2SO_2 + MgBr_2$$

This is similar to sulfone formation by the action of Grignard reagents with aromatic sulfonyl chlorides (5, 6), in which, however, sulfoxide was also formed. The addition of excess halide (Run 4) after formation of the sulfonylmagnesium bromide, however, effected no improvement in yield; this indicates a more complex mechanism suggested by equation 3.

3.



$$SO_2 + RMgBr \rightarrow \overset{-}{R}:\ldots\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}\rightarrow O\ldots\overset{+}{MgBr} \xrightarrow{\overset{+\ -}{RBr}} R-\overset{\overset{O}{\uparrow}}{\underset{\underset{R}{|}}{S}}\rightarrow O + MgBr_2$$

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TABLE I

YIELD OF SULFONE

Run No.	Mg g.-atoms reacted	Moles of RX		Temp, °C.	RSO_2R obtained		$(RSO_2)_2Mg \cdot 2H_2O$ % based on Mg
		Initial	Added		g.	% based on RX	
	$C_8H_{17}Br$				$(C_8H_{17})_2SO_2$		
1	0.183	0.201		−55	0		
2	.187	.201		−5–0	0.02	0.07	68
3	.189	.201		35	1.1	3.8	
4	.156	.156	0.078	35	.36	1.1	76
5	.182	.201		135	<.01		
	$C_{12}H_{25}Br$				$(C_{12}H_{25})_2SO_2$		
6	.251	.300		−60	0		83
7	.5 appr.	.500		−60	trace[a]		67
8	.178	.201		−55	0		64
9	.167	.201		0–10	0		60
10	.181	.201		8–16	0		64
11	.177	.190		10–18	.08	.2	
12	.181	.201	.096	27–37	3.58	6.0	82
13	.179	.201		33	.70	1.7	60
14	.178	.201		135	.31	.77	11
	$C_{16}H_{33}Br$				$(C_{16}H_{33})_2SO_2$		
15	.31 appr.	.311		25	.2 appr.	.3	

[a] Material lost in a fire before purification and weighing.

EXPERIMENTAL

Standard procedure. The Grignard reagent was formed in 250 ml. of ether by reaction between equimolar amounts of alkyl halide and magnesium, 0.2 mole of each. The unreacted magnesium was removed by forcing the solution through a cotton plug by nitrogen pressure into the reaction flask, which was nitrogen filled. The amount of Grignard present was determined (7) and the calculated quantity (weighed) of dried sulfur dioxide slowly was bubbled in with rapid stirring. (Before sulfination in Runs 5 and 14, *n*-butyl ether was added and the ethyl ether was distilled off.) The reaction mixture was poured into ammonium chloride solution and ice. The ether layer was removed and the white precipitate from the hydrolysis was washed with weak ammonium chloride and water and dried in the air at room temperature. When dry, the solid was extracted with ether or methyl ethyl ketone (or acetone) or both. The extract and the ether layer from the hydrolysis were examined for sulfone, identified by mixture melting point with an authentic sample.

In several cases the standard procedure was modified:

Runs 4, 9, 11, 12, 15: air in the reaction flask was not replaced by nitrogen.

Runs 7, 15: unreacted magnesium was not removed.

Runs 7, 15: a slight excess of sulfur dioxide was used.

Run 11: 50% excess sulfur dioxide was used.

Run 12: 50% more alkyl halide was added after formation of the Grignard, before sulfur dioxide was run in.

Run 4: 50% more alkyl halide was added after the sulfur dioxide had been run in; then the mixture was stirred for an hour.

SUMMARY

Small amounts of sulfone are formed in the reaction between sulfur dioxide and alkyl Grignard reagents, provided the temperature is about 15° or higher. Only traces are formed at lower temperatures.

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