Reactions of Sulphones with Grignard Reagents

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WALLACE and his co-workers[1] have recently reported the conversion of benzyl sulphide, benzyl sulphoxide, and benzyl disulphide into stilbene by treatment with potassium t-butoxide in dimethylformamide. A similar conversion with sulphones has not been reported. We have found that treatment of sulphones with a Grignard reagent in toluene or xylene will effect a similar, but mechanistically different, conversion.

Thus, when benzyl β-phenethyl sulphone (18·7 mmoles) was treated with ethylmagnesium bromide (56·1 mmoles) in dry xylene at 105° for 19 hrs., 1,3-diphenylpropene (*cis* 25·6%, *trans* 27·3%) and stilbene (*cis* 6·3%, *trans* 23·1%) were obtained. A similar reaction in toluene produced the same products plus a mixture of the isomeric phenyltolylmethanes[2] (15·3%). In order to determine the fate of the sulphur atom from the starting sulphone, dibenzyl sulphone was treated with phenylmagnesium bromide. Besides the expected stilbenes (*cis* 28·2%, *trans* 37·4%), diphenyl sulphide[3] (25·3%) was isolated. Reaction of benzyl α-phenethyl sulphone with ethylmagnesium bromide in toluene gave *trans*-stilbene (7·7%), α-methylstilbene (*cis* 28·6%, *trans* 17·5%) and 1-phenyl-1-*p*-tolylethane[4] (12·2%). The above products were separated and determined by gas–liquid chromatography, and were identified by comparison of retention times (g.l.c.) and infrared spectra with authentic samples.

Considerable evidence has accumulated recently discounting the intermediacy of a carbene *per se* in the reactions of an organometallic reagent (carrying a labile alkoxide, halide, or other Lewis base in the α-position) with a nucleophilic reagent.[5] These reactions are now formulated as a direct reaction between the nucleophilic reagent (olefin) and the α-substituted organometallic reagent.[5b] We believe that the above reactions of sulphones proceed by a similar mechanism. In this instance the organometallic derivative plays both roles, that of the nucleophilic reagent and that of the α-substituted organometallic reagent.

The yield of 1,3-diphenylpropene (II) obtained from (I) and the large amount of *cis*-1,3-diphenylpropene so obtained (compare with III) indicate

$$\underset{\text{(I)}}{\text{Ph.CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Ph}} + 3\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{\text{xylene}} \underset{\text{(II)}}{\text{Ph}\cdot\text{CH}{=}\text{CHCH}_2\cdot\text{Ph}} + \underset{\text{(III)}}{\text{Ph}\cdot\text{CH}{=}\text{CH}\cdot\text{Ph}}$$

	(II)	(III)
cis	25·6%	6·3%
trans	27·3%	23·1%

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[1] T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1965, 1271. T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1963, **85**, 2739.

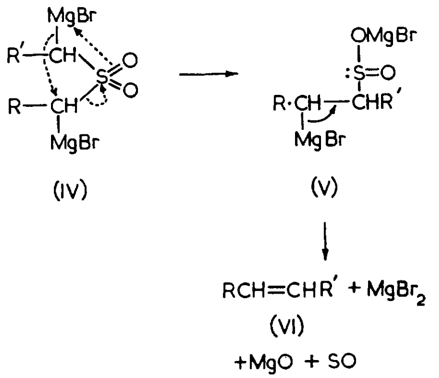
[2] P. Kovacic and K. E. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 427.

[3] J. R. Campbell, *J. Org. Chem.*, 1964, **29**, 1830.

[4] A. Spilker and W. Schade, *Ber.*, 1932, **65**, 1686.

[5] (*a*) M. J. Goldstein and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, 1965, **87**, 2293. (*b*) W. T. Miller, Jr. and D. M. Whalen, *ibid.*, 1964, **86**, 2089. (*c*) G. L. Close and R. A. Moss, *ibid.*, 1964, **86**, 4042.

the probability of an intramolecular, as well as an intermolecular, reaction. The intramolecular reaction could proceed *via* the magnesium derivative (IV) of a dicarbanion of the sulphone. One possible mechanism for the formation of the olefin is illustrated. The intermediacy of (IV) is supported by (1) the evolution of approximately two moles of ethane on reaction of α-phenethyl β-phenylpropyl sulphone with excess of ethylmagnesium bromide and by (2) the previous demonstration of the formation of the dianion of dibenzyl sulphone by Hauser and Harris.[6] The diphenyl sulphide isolated in one reaction could be formed by the reaction of phenylmagnesium bromide with sulphur monoxide. Although there is little precedent for it, we at present believe that the phenyltolylmethanes and the 1-phenyl-1-*p*-tolylethane formed above result from the reaction of the magnesium derivative of the sulphone with solvent.[7]



(*Received, June 28th,* 1965; *Com.* 402.)

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[6] C. R. Hauser and T. M. Harris, *J. Amer. Chem. Soc.*, 1959, **81**, 1154.

[7] For an example of the formation of 2- and 4-methyldiphenylmethanes from a reaction possibly involving "phenylcarbene" and toluene, see H. Nozaki, R. Noyori, and K. Sisido, *Tetrahedron*, 1964, **20**, 1125.