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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

PUMMERER REARRANGEMENTS OF ETHYL ETHYLTHIOMETHYL SULPHOXIDE

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To cite this Article Wladislaw, B. , Marzorati, L. , Andrade, F. A. C. and Andrade, M. A.(1979) 'PUMMERER REARRANGEMENTS OF ETHYL ETHYLTHIOMETHYL SULPHOXIDE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 6: 1, 333 — 334

To link to this Article: DOI: 10.1080/03086647908080440

URL: <http://dx.doi.org/10.1080/03086647908080440>

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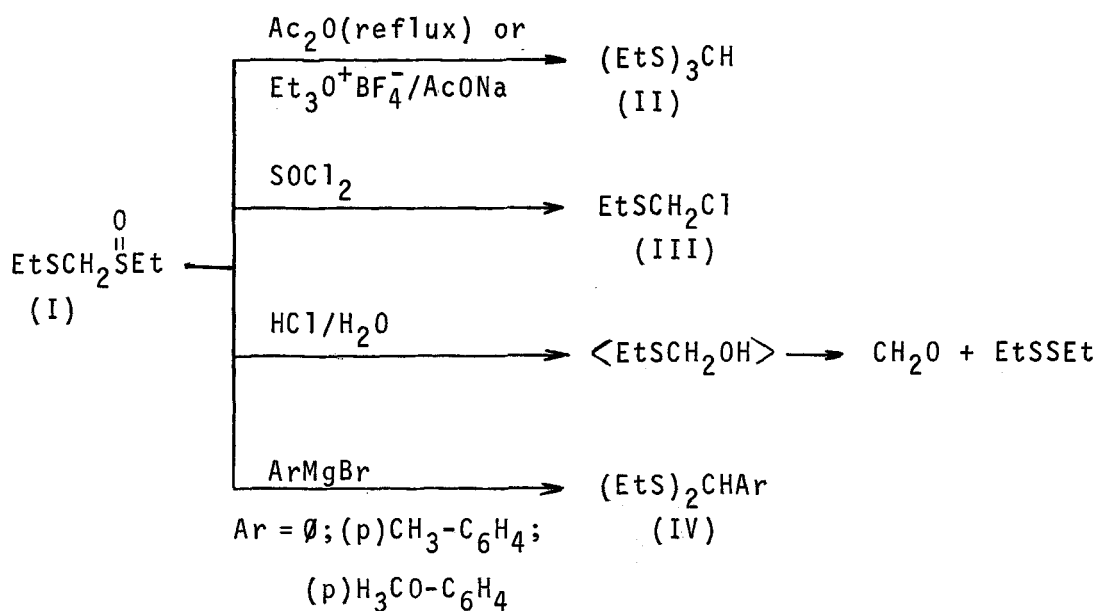
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PUMMERER REARRANGEMENTS OF ETHYL ETHYLTHIOMETHYL SULPHOXIDE

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Some Pummerer rearrangements, in which ethyl ethylthiomethyl sulphoxide (I) is supposed to react initially as a nucleophile, were investigated in connection with the observed decrease of basicity in this compound, due to electronic interaction between α -sulphur atom and sulphinyl group. In fact, it proved to be quite resistant to the acetic anhydride induced rearrangement, being totally recovered under conditions in which DMSO reacts. In more drastic condition, or when triethyloxonium tetrafluoroborate and sodium acetate was substituted for acetic anhydride, instead of the normal Pummerer product, ethyl orthotriithioformate (II) was produced. Although ethyl ethylthiomethyl sulphoxide appeared to be susceptible, in mild condition, to aqueous acid, instead of Pummerer reaction, hydrolysis to formaldehyde and diethyl disulphide took place. The suppression of the Pummerer rearrangement was also found to occur in the reaction with thionyl chloride, to afford ethyl chloromethyl sulphide (III). However, normal Pummerer rearrangement occurred in the reaction of ethyl ethylthiomethyl sulphoxide with excess of some phenyl and para-phenylsubstituted magnesium bromides to lead to diethylmercaptals of the corresponding benzaldehydes (IV), in good yields.



The results are discussed in terms of decreased nucleophilicity of the oxygen atom of the title sulfoxide and sensibility of the methylene group, bonded to two sulphur atoms, one of them positively charged, in the reactions intermediates, to the nucleophiles. A general mechanism for the reaction of sulfoxides with Grignard reagents is also proposed.

We thanks the "Fundação de Amparo à Pesquisa do Estado de São Paulo" for the fellowship (to L.M.) and the "Universidade Federal da Bahia" for the leave of absence (to F.A.C.A. and M.A.A.).