

This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

KINETIC STUDY OF THE REACTIONS OF TRIARYLPHOSPHINES WITH α -HALO SULFONES

Bruce B. Jarvis^a; Bruce A. Marien^a

^a University of Maryland, College Park, Maryland, U.S.A.

To cite this Article Jarvis, Bruce B. and Marien, Bruce A.(1976) 'KINETIC STUDY OF THE REACTIONS OF TRIARYLPHOSPHINES WITH α -HALO SULFONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 1: 2, 177 — 178

To link to this Article: DOI: 10.1080/03086647608073324

URL: <http://dx.doi.org/10.1080/03086647608073324>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

KINETIC STUDY OF THE REACTIONS OF TRIARYLPHOSPHINES WITH α -HALO SULFONES

by

Bruce B. Jarvis and Bruce A. Marien

University of Maryland, College Park, Maryland, 20742 U.S.A.

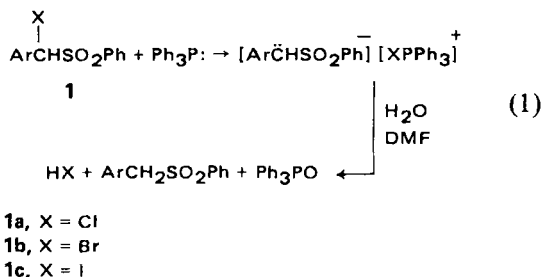
Received May 30, 1974

ABSTRACT

Reaction of a series of triarylphosphines with α -halo-*m*-cyanobenzyl phenyl sulfones gives the following Hammett ρ values: (Cl) $\rho = -1.84$; (Br) $\rho = -3.03$; (I) $\rho = -3.36$.

In a continuing investigation of S_N2 reactions on halogen atoms,¹⁻³ we wish to report the effect of systematic variation of the nucleophile in the reduction of α -halo sulfones. The reactions of triphenylphosphine with α -halo sulfones^{1,2} (eq 1) has been shown to be markedly sensitive to both the halogen atom (X) present and the substituents on the benzyl ring in the sulfone 1. For this reaction it was observed that $k_{Br} > k_I \gg k_{Cl}$, contrary to the typical S_N2 order of reactivity. This can be rationalized in terms of the relative strengths of the bonds formed and broken in the transition states.^{1,2}

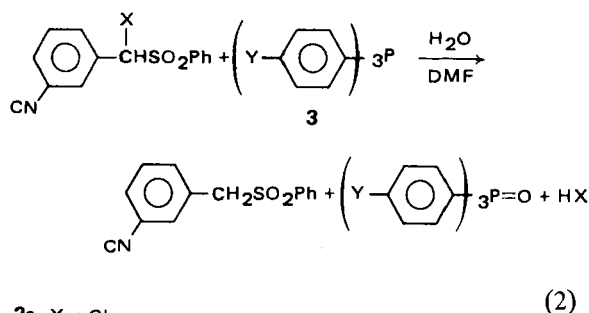
Hammett plots, which correlated with σ^- constants, gave the following ρ values: (Cl) +2.23, (Br) +5.97 and (I) +6.29. The large ρ 's for the reactions of the α -bromo and α -iodo sulfones indicate a great deal of carbon-halogen bond breaking in the transition states.



We have now examined the rate of reaction of α -halo-*m*-cyanobenzyl phenyl sulfones 2 as a function

of the substituents on the triarylphosphines in order to measure the degree of phosphorus-halogen bond making.

As can be seen from Table I, the rates vary considerably with the halogen atom as well as with the substituents on the phosphine. Again the observed order of reactivity is $k_{Br} > k_I \gg k_{Cl}$.



The Hammett ρ 's given in Table I can be contrasted with those determined for a) the acidity of triarylphosphines, $\rho = -1.11$ ⁴; b) S_N2 reactions of diethyl arylphosphines with ethyl iodide, $\rho = -1.11$ ⁵, and triarylphosphines with α -bromoacetophenone, $\rho = -1.26$ ⁶; and c) the initial step in the reactions of triarylphosphines with azides (Staudinger reaction), $\rho = -1.07$.⁷ Clearly, reaction (2) is significantly more sensitive to changes in the triarylphosphine than were

1. B. B. Jarvis and J. C. Saukaitis, *J. Am. Chem. Soc.*, **95**, 7708 (1973).
2. B. B. Jarvis and J. C. Saukaitis, *Tetrahedron Lett.*, 709 (1973).
3. B. B. Jarvis and M. Evans, *J. Org. Chem.*, **39**, 643 (1974).

4. H. Goetz and A. Sidhu, *Justus Liebigs Ann. Chem.*, **682**, 71 (1963).
5. W. C. Davis and W. P. G. Lewis, *J. Chem. Soc.*, 1599 (1934).
6. G. B. Borowitz *et al.*, *Phosphorus*, **2**, 91 (1972).
7. J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, **89**, 5235 (1967).

TABLE I

Rate Constants for the Reaction of α -Halo-*m*-cyanobenzyl Phenyl Sulfone, 2, with *p*-Substituted Triarylphosphines, 3, in 90% Aqueous Dimethylformamide (DMF) at 25°

X	Y	$k \text{ M}^{-1} \text{ sec}^{-1a}$	ρ^b
Cl	-N(CH ₃) ₂	5.76×10^{-3}	
Cl	-OCH ₃	1.06×10^{-4}	
Cl	-CH ₃	2.73×10^{-5}	
Cl	-H	2.75×10^{-6}	-1.84 (Cl)
Br	-OCH ₃	4.57×10^{-1}	
Br	-CH ₃	6.83×10^{-2}	
Br	-H	2.07×10^{-3}	
Br	-Cl	1.48×10^{-5}	-3.03 (Br)
I	-OCH ₃	4.06×10^{-2}	
I	-C(CH ₃) ₃	7.37×10^{-3}	
I	-CH ₃	2.61×10^{-3}	
I	-H	7.76×10^{-5}	-3.36 (I)

^a Determined in a manner previously reported with the same degree of accuracy.¹

^b Determined from Hammett σ constants: $\log k_X/k_H = \rho(\Sigma\sigma)$.

the above reactions.⁸ This strong interaction between the phosphorus and halogen atoms, particularly for bromine and iodine, in the transition states can be accounted for by the principle of hard and soft acids and bases.⁹

Experimental Section

The synthesis of the α -halo-*m*-cyanobenzyl phenyl sulfones and the kinetic measurements (by conductance) of their reactivity toward triarylphosphines have been described previously.¹ The triarylphosphines were synthesized as previously described.^{10,11}

8. The reactions of triarylphosphines with 7,7,8,8-tetracyanoquinodimethane and tetracyanoethylene [M. P. Naan, R. L. Powell and C. D. Hall, *J. Chem. Soc., (B)*, 1683 (1971)] exhibit a rather large negative ρ (-3.2), also. However, these reactions appear to involve the radical cations $\text{Ar}_3\text{P}^{\bullet+}$. We have no evidence that such species are involved in our reactions, but this point is being studied further.
9. a. R. G. Pearson and J. Söngstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).
b. R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N.Y., 1965, Chapter 4 and 5.
10. D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2933 (1930).
11. J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, **89**, 5232 (1967).