HETEROCYCLES, Vol. 2, No. 5, 1974

# DERIVATIVES OF 1,2-DITHIOLE-3-THIONES. VIII.[1]
# REDUCTION OF N-BENZENESULFONYL THIONE S-IMIDES WITH TRIVALENT PHOSPHINES

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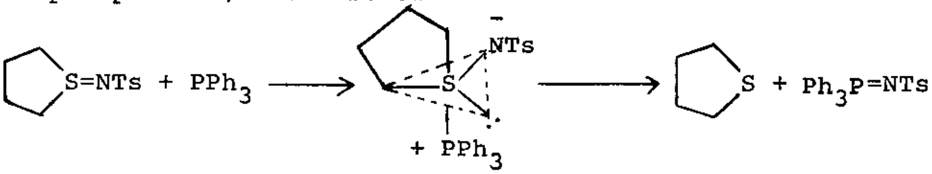
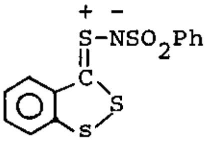
The reduction of N-benzenesulfonyl thione S-imide (I) with trivalent phosphines was kinetically studied. The reaction is considered to proceed via the formation of a metastable 1,3-dipolar adduct of (I) and the phosphine. Meanwhile, the addition of protic acid to the reaction mixture was found to change the pattern of the reaction.

Evidence to support the formation of tetracoordinate tetravalent sulfurane-like intermediates has recently been compiled[2] and sometimes even the extremely stable compounds[3] of this type have been isolated. In the course of the study of nucleophilic substitution reaction on tetravalent sulfur atom, the N-toluenesulfonylsulfilimide has been found to react readily with a trivalent phosphine to give a 1,3-dipolar adduct as an initially formed intermediate which eventually collapses to afford the corresponding sulfide and iminophosphorane, shown below.[4]



In this report we wish to present the results obtained upon the examination of the reaction between phosphines and N-benzenesulfonyl thione S-imides (I)[5] which bear a dicoordinate tetravalent sulfur atom and isoelectronically resemble the sulfilimide.



(I)

Like other common S-imides, the treatment of the thione S-imide (I) with an equimolar amount of a trivalent phosphine gives the corresponding reduced benzotrithione (II). This reduction also appears to involve the formation of the adduct between the thione S-imide and the phosphine, in view of the kinetic data obtained. Furthermore, addition of protic compound such as acetic acid, water, and alcohol into the reaction system was found to change the mode of the reaction, i.e., both products and kinetics.

When a typical reaction of tri-n-butylphosphine (352mg, 1.74mM) with an equimolar amount of the N-benzenesulfonyl thione S-imide (472mg, 1.39mM) was carried out in either

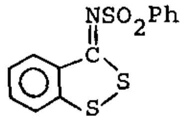
$CH_3CN$ or chloroform at room temperature for ten minutes, the corresponding reduced benzotrithione was obtained along with the equimolar amount of N-benzenesulfonyliminophosphorane in quantitative yields. The latter product was identified by means of spectroscopic and elemental analyses.[4] The products thus obtained are summarized in Table I. In the case with triphenylphosphine the addition of excess triphenylphosphine was necessary for the reduction to proceed smoothly at room temperature. Meanwhile, with an arylphosphine bearing p-methoxy group, a facile reduction was found to take place under the condition as employed in the case of common alkylphosphines and gave the similar reaction products like in the case with alkylphosphines.

Table I. Product Analyses (Yield %) of Reaction of Thione S-Imide (I)[a] with Phosphine in $CH_3CN$ at Room Temperature.

| phosphine (mM) | addend (mM) | II | $R_3P{=}NSO_2Ph$ | $Ph_3PO$ ($Ph_3PS$) | III[b] | $PhSO_2NH_2$ |
|---|---|---|---|---|---|---|
| n-$Bu_3P$ (1.7) |  | 84.1 | 99.3 |  |  |  |
| (p-MeO-$C_6H_4$)$_3$P (1.0) |  | 98.6 | 99.1 |  |  |  |
| $Ph_3P$ (1.0) | AcOH (10.0) | 88.4 |  | 75.4 | 5.0 | 92.8 |
| $Ph_3P$ (1.0) | $CH_3OH$ (10.0) | 83.9 |  | (5.4) | trace | 277[c] |
| $Ph_3P$ (1.0) | $H_2O$ (10.0) | 85.0 |  | (13.6) | 5.0 | 333[c] |

a: 1.0 mM

b:

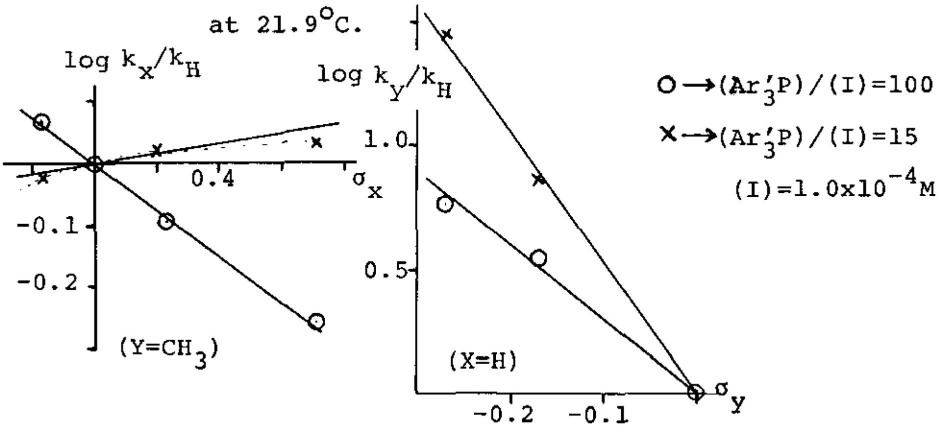


(III)

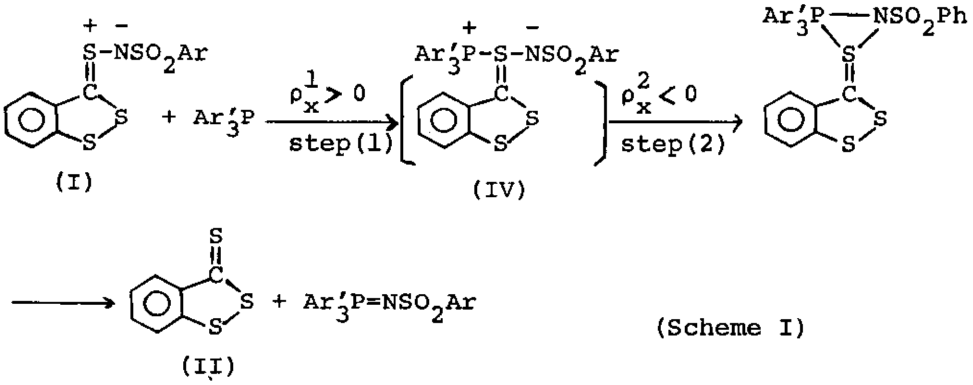
c: Unit in mg. The structural elucidation of this product was not yet completed, however, the product is considered to be a complex between $Ph_3P{=}O$ and $PhSO_2NH_2$ with ir stretching band at 1130 $cm^{-1}$ (P=O), 3280, 3090 $cm^{-1}$ ($NH_2$), and 1340, 1160 $cm^{-1}$ ($SO_2$). See ref. 4 on the complexes of this type.

In order to gain insight into the mechanism of the reaction, a kinetic study of the reaction of p-X-substituted N-benzenesulfonyl thione S-imides with arylphosphines was performed in $CH_3CN$ at about 22°C, keeping the pseudo-first-order condition with regard to the phosphine concentration. The reaction was found to be nearly second-order each in thione S-imide and phosphine concentrations. The results obtained are depicted in Fig. I with Hammett plots.

Fig. I Hammett Plots for The Reduction of Thione S-Imides with Para-substituted Tri-phenylphosphines in $CH_3CN$ at 21.9°C.



Inspection of Fig. I indicates that, in the region of low phosphine concentrations employed, the Hammett $\rho_x$ value is very small but evidently positive. The $\rho_y$ value obtained by the change of electron-donating p-substituent (Y) in arylphosphine is -5.30. Thus, the reduction apparently involves an initial, rate-determining, nucleophilic attack (step 1 in Scheme I) of the phosphine on the sulfur atom.



(Scheme I)

However, it is noteworthy to mention that no straight line plot but a concave curvature is obtained when the values of log $k_x/k_H$ are plotted against $\sigma_p$ values. In general such a downward concave of Hammett plots is a characteristic not of the change of the mechanism, but rather of that of the rate-determining step, and the failure to fit a linear Hammett equation undoubtedly indicates that the reaction is composed essentially of two consecutive stages, i.e., (1) and (2), which are of quite comparable in energies; namely, the electron-withdrawing substituent is expected to shift the rate-determining step from step (1) to step (2).

Meanwhile, in the reaction with high phosphine concentrations the overall value of $\rho_x$ drastically changes the sign where $\rho_x=-0.35$ ($Y=CH_3$) and $\rho_y=-3.0$ (X=H). Here, the plot no longer gives any deviation from a linearity. This means that the rate-determining step of the reaction under a large excess of the phosphine relative to the imide concentration shifts from the step (1) to the step (2).

Based on these kinetic results, the reaction is considered to proceed through an intervention of a metastable tricoordinate 1,3-dipolar adduct bearing a structure like **IV** shown in Scheme I.

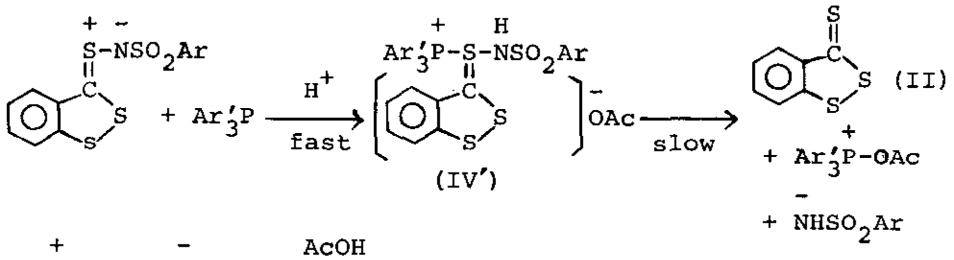
As shown in the products analyses in Table I, the addition of protic compounds such as acetic acid to the reaction mixture gave a different pattern of the formation of products. In order to elucidate the mechanism, the rate study was performed with an excess acetic acid, and it was found that at a constant concentration of acetic acid the reaction was strictly second-order each in the phosphine and the imide concentrations, while the rate increased with increase of the amount of the added acetic acid. The apparent second-order rate constants ($k_2$) obtained with varying acetic acid concentrations are listed in Table II.

Table II. Effect of Acetic Acid on the Second-order-rate Constants ($k_2$) in $CH_3CN$ at 21.9°C.

| (AcOH)x$10^2$ | 0.00 | 0.83 | 1.65 | 3.30 | 4.95 | 6.60 |
|---|---|---|---|---|---|---|
| $10^3k_2$, $M^{-1}sec^{-1}$ | 1.77 | 2.52 | 4.04 | 7.07 | 12.5 | 20.3 |

(AcOH)=$3.3\times10^{-2}$M, (I)=$1.0\times10^{-4}$M, ($(p\text{-}CH_3C_6H_4)_3P$)=$1.0\times10^{-3}$M, and $\rho_x=-0.44$ ($Y=CH_3$), $\rho_y=-8.4$ ($X=H$).

These results also imply that, under the reaction condition employed, the reduction apparently involves an incipient formation of the protonated phosphine adduct (IV′), which receives the relatively slower rate-determining attack of acetate anion on the phosphorus atom as shown below:



$$Ar'_3\overset{+}{P}\text{-}OAc + \overset{-}{N}HSO_2Ar \xrightarrow{AcOH} Ar'_3P{=}O + Ac_2O + NH_2SO_2Ar$$

REFERENCES

1. Part VII; to be published in Bull. Chem. Soc. Japan, 1974.
2. E. Ciuffarin and G. Guarraldi, J. Amer. Chem. Soc., 1969, **91**, 1745; F.A. Davis, S. Divald, and A.H. Confer, Chem. Comm., 1971, 294.
3. E.F. Perozzi, J.C. Martin, and I.C. Paul, J. Amer. Chem. Soc., 1974, **96**, 578; O.A. Musher, Angew. Chem., Internat. Edn., 1969, **8**, 54.
4. S. Oae, T. Aida, M. Nakajima, and N. Furukawa, Tetrahedron Letters, 1974, 947; T. Aida, N. Furukawa, and S. Oae, Chemistry Letters, 1974, 121.
5. S. Tamagaki, K. Sakaki, and S. Oae, Bull. Chem. Soc. Japan, 1973, **46**, 2608.

Received, 22nd August, 1974