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## THE REACTION OF DIVINYLSULPHONE WITH AMINES AND PHOSPHINES

A. C. Bellaart<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry, Eindhoven University of Technology, The Netherlands

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THE REACTION OF DIVINYLSULPHONE WITH AMINES AND PHOSPHINES

## A.C. Bellaart

Department of Organic Chemistry, Eindhoven University of Technology, The Netherlands

<u>Primary amines</u> react with divinylsulphone (I) according to the following equation:

Several 4-alkyl-1,4-thiazane-1,1-dioxides and derivatives were obtained by Ford-Moore 1,2 and Bellaart 3. Ethyl-1,4-thiazane-1,1-dioxide-4-acetate (II) was obtained from I and glycine ethyl ester, III by saponification of II; 1,4-thiazane-1,1-dioxide-4-undecanoic acid (IV) from I and 11-amino undecanoic acid.

Secondary amines react with I as follows:

$$O_2 S < \frac{C = C}{C = C} + 2 HN < \frac{R_1}{R_2} \longrightarrow O_2 S < \frac{C - C - N < \frac{R_1}{R_2}}{C - C - N < \frac{R_1}{R_2}}$$

Tertiary amines do not react with I.

Primary phosphines, such as n-nonylphosphine, t-butylphosphine and tetradecylphosphine, react with I in an alcoholic solution in the following way:

The structure of V was proved by the following synthesis:

As yet we have no idea about the reaction mechanism:

A similar reaction was found by Davies<sup>4</sup>, who obtained, in an attempt to prepare bis-[2-cyanoethyl] sulphide from bis-[2-chloroethyl] sulphide and potassium

cyanide, 3,6-dithiaoctane-1,8-dinitrile. A possible reaction mechanism was given by Bell<sup>5</sup>:

$$2 \quad S \stackrel{C-CCI}{\underset{C-CCI}{\leftarrow}} + KCN \longrightarrow 2 \quad S \stackrel{C-CCN}{\underset{C-CCI}{\leftarrow}} \longrightarrow \begin{bmatrix} S \stackrel{C-C-CN}{\underset{C-CCI}{\leftarrow}} \\ S \stackrel{C-C-CN}{\underset{C-CCI}{\leftarrow}} \end{bmatrix} \stackrel{S-C-CCN}{\underset{S-C-CCN}{\leftarrow}} + c_2H_4CI_2$$

Diphenylphosphine reacts with divinylsulphone in concentrated hydrochloric acid in the following way:

$$O_2S \stackrel{C=C}{\underset{C=C}{\stackrel{H}\overset{+}{\underset{P}\varnothing}_{CI}}} + \stackrel{H}{\underset{P}\overset{+}{\underset{QI}{\stackrel{-}}}} = O_2S \stackrel{C-C}{\underset{C-C}{\stackrel{+}{\underset{P}\varnothing}_{2}}} \longrightarrow O_2S \stackrel{C-C}{\underset{C-C}{\stackrel{+}{\underset{P}\varnothing}_{2}}}$$

Triphenylphosphine also reacts with divinylsulphone in concentrated hydrochloric acid yielding the following compound:

$$O_2S < c = c$$
 $C = c$ 
 $C = c$ 
 $C + c + c + c$ 
 $C + c$ 

Quite recently  $^6$  we synthesized the phosphite triesters of methyl  $\alpha$ -D-ribopyranoside and methyl  $\beta$ -D-ribopyranoside (VI):

By heating VI for 15 hrs on 175° with sulphur we obtained the corresponding thiophosphate VII in a very good yield.

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