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Abstract

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CHEMISTRY

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THIONYLAMIDE OF DIETHYLPHOSPHORIC ACID IN THE DIENE SYNTHESIS REACTION

(Presented by Academician B. A. Arbuzov on 12 IV 1965)

Aromatic thionylamides of the type Ar—N = SO ([1]) are usually synthesized in high yields by the interaction of thionyl chloride with the corresponding amine or by a "perthionylation" reaction between a thionylamide of a weak base and a free amine of greater basicity ([2]). Subsequently, these methods were successfully used for the synthesis of thionylamides of a series of aryl- and alkylsulfonic acids ([2]) of the type R—SO_2—N = SO, which proved to be very active in various addition reactions at the double bond —N = SO. At the same time, an attempt to synthesize analogous thionylamides of carboxylic and thiocarboxylic acids gave no results: the reaction led to the formation of acid nitriles and 1,2,4-thiadiazoles, respectively.

We undertook an attempt to synthesize thionylamide of diethylphosphoric acid by the interaction of thionyl chloride with the amide of diethylphosphoric acid:

$$(C_2H_5O)_2P(=O)—NH_2 + SOCl_2 \xrightarrow[-2HCl]{} (C_2H_5O)_2P(=O)—N=SO$$

(TAP)

Indeed, the formation of phosphorylthionylamide (TAP) is confirmed by the following data. When an equimolar amount of thionyl chloride was added to a benzene solution of diethylphosphoric acid amide, followed by half an hour of heating of the reaction mixture (careful protection from atmospheric moisture is necessary), evolution of hydrogen chloride was observed. Vacuum distillation of the reaction solution yielded a yellow liquid with b.p. 72°/0.03 mm (yield 70%). The substance obtained contained 15.40% phosphorus and 15.81% sulfur (calculated for TAP –$C_4H_{10}NO_4PS$: phosphorus 15.49%, sulfur 16.08%). On hydrolysis of 3.7 g of this substance with an ether–water azeotrope, 2.84 g of a crystalline substance with m.p. 46° was isolated; a mixed sample of it with

diethylphosphoric acid amide showed no depression of the melting point (theoretically, 2.58 g of diethylphosphoramide should be formed from TAP). Finally, if this is thionylamide of diethylphosphoric acid, then on interaction with an amine more strongly basic than diethylphosphoric acid amide, thionylamine of the base taken should be obtained; this was indeed observed when equimolar amounts of aniline and the obtained substance were mixed; as a result, thionylaniline with b.p. 80°/12 mm, n_D^{20} 1.6253 ([2]), and solid diethylphosphoric acid amide with m.p. 46° were isolated:

$$(C_2H_5O)_2P(=O)—N=SO \begin{cases} \xrightarrow{HOH} (C_2H_5O)_2P(=O)—NH_2 + SO_2 \\ \xrightarrow{C_6H_5NH_2} (C_2H_5O)_2P(=O)—NH_2 + C_6H_5—N=SO \end{cases}$$

Table 1

Adducts of thionamide of diethylphosphoric acid with dienes

Diene	Compound no. in text	R_1	R_2	R_3	R_4	Adduct	Formula	P, % found	P, % calculated
Butadiene-1,3	I	H	H	H	H	1-oxo-2-diethylphosphor-3,6-dihydro-1,2-thiazine	$C_8H_{16}O_2NSP$	13.80	12.25
Piperylene	II	CH_3(H)	H	H	H(CH_3)	1-oxo-2-diethylphosphor-3(6)-methyl-3,6-dihydro-1,2-thiazine	$C_9H_{18}O_2NSP$	11.30; 11.36	11.61

Diene	Compound no. in text	R_1	R_2	R_3	R_4	Adduct	Formula	P, % found	P, % calculated
1-Phenylbutadiene-1,3	III	C_6H_5	H	H	H	1-oxo-2-diethylphosphor-3(6)-phenyl-3,6-dihydro-1,2-thiazine	$C_{14}H_{20}O_2NSP$	9.80; 9.10	9.42
Isoprene	IV	H	CH_3	H	H	1-oxo-2-diethylphosphor-4-methyl-3,6-dihydro-1,2-thiazine	$C_9H_{18}O_2NSP$	11.15; 11.31	11.61
Hexadiene-2,4	V	CH_3	H	H	CH_3	1-oxo-2-diethylphosphor-3,6-dimethyl-3,6-dihydro-1,2-thiazine	$C_{10}H_{20}O_2NSP$	10.86; 10.31	11.00
2,3-Dimethylbutadiene-1,3	VI	H	CH_3	CH_3	H	1-oxo-2-diethylphosphor-4,5-dimethyl-3,6-dihydro-1,2-thiazine	$C_{10}H_{20}O_2NSP$	10.80; 10.86	11.00

Diene	Compound no. in text	R_1	R_2	R_3	R_4	Adduct	Formula	P, % found	P, % calculated
1,1/5-Cyclooctadiene [[unclear: diene name]]	VII	– $(CH_2)_4$ –	– $(CH_2)_4$ –	– $(CH_2)_4$ –	– $(CH_2)_4$ –	1-oxo-2-diethylphosphor-3,4,5,6-dibenz-3,6,7,8,9,10,11,12,13,14-decahydro-1,2-thiazine [[unclear: compound name]]	$C_{16}H_{32}O_2NSP$	7.84; 8.00	8.58
Chloroprene	VIII	H	Cl	H	H	1-oxo-2-diethylphosphor-4-chloro-3,6-dihydro-1,2-thiazine (m.p. 52°)	$C_8H_{15}O_2NSPCl$	10.76; 10.67	10.78

Thus, it may be considered that the reaction carried out leads to the formation of the thionamide of diethylphosphoric acid; this is in basic agreement with the results obtained independently of us by Vlecherkovskii ([3]).

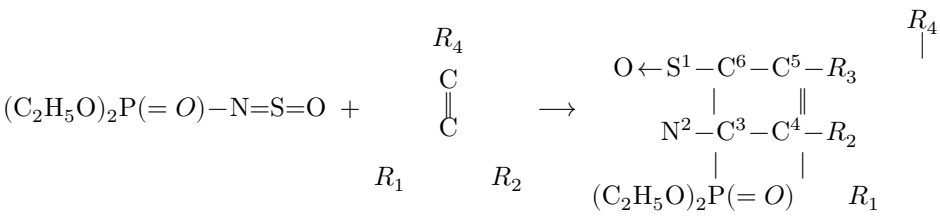
Thionylamides of the aromatic series, especially those with electron-acceptor groups in the phenyl ring, and thionylsulfonamides react rather actively with various dienes according to the scheme of diene synthesis ([2,4,5]); therefore it could be expected that TAF would also prove to be an active dienophile. This possibility was confirmed by us in the reactions of TAF with a series of dienes (see Table 1).

The reactions were carried out by mixing TAF with an excess of diene; the mixture was allowed to stand for several hours at room temperature in a closed vessel, after which it was diluted with dry benzene and filtered through a chro-

matographic column with neutral alumina of activity grade I. The adducts were examined directly after evaporation of the solvent and excess diene (an attempt to distill the adducts in a high vacuum did not give a greater degree of purity, since boiling was accompanied by decomposition). In all cases the adducts were oily liquids of varying degrees of mobility, colored in various shades of yellow, and only the adduct

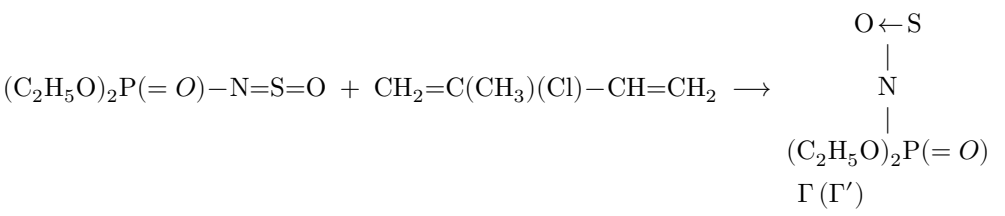
TAP with chloroprene (VIII) was isolated in crystalline form, m.p. 52°.

Quantitative elemental analysis for phosphorus showed that in all cases 1 : 1 adducts are formed, with yields from 50 to 80%. In the IR spectrum taken from adduct (I), frequencies of the P=O group (1260 cm^{-1}), of the P–O–C_2H_5 group (1030 cm^{-1}, 1165 cm^{-1}), and also a frequency at 1655 cm^{-1}, which may be assigned to an isolated C=C cis bond, were detected. On the basis of these data, and also in agreement with previous studies ([2–5]), the adducts may be assigned an ortho-thiazine structure, and the reaction represented by the following scheme:



Additional confirmation of the thiazine structure was obtained from the NMR spectra of adducts I, II, IV, VI, VIII. All spectra had peaks with chemical shifts $\tau_1' = 8.50$—8.55 ppm, $\tau_1'' = 8.70$—8.80 ppm, $\tau_1''' = 9.10$ ppm, corresponding to the methyl protons of the ethoxy group; peaks with chemical shifts $\tau_2' = 5.80$—5.86 ppm, $\tau_2'' = 6.05$—6.15 ppm, corresponding to the methylene protons of the ethoxy group; peaks with chemical shifts $\tau_3' = 6.36$—6.40 ppm, $\tau_3'' = 6.70$ ppm, assigned to the methylene protons (in the case R_1 and $R_4 = H$) of the thiazine ring in positions 3- and 6- ([5,7]).

In the interaction of TAP with unsymmetrically substituted dienes, two structural isomers may be expected for each reaction. 2-Substituted dienes (isoprene and chloroprene in our case) with TAP can give adducts of structures (G) and (D)



Γ (Γ′) (′)

Fig. 1. NMR spectra of TAF adducts with butadiene-1,3 (I) (a) and isoprene (IV) (b)

Figure 1: Fig. 1. NMR spectra of TAF adducts with butadiene-1,3 (I) (a) and isoprene (IV) (b)

From the NMR spectra of adducts I and II (Fig. 1a), the values of the chemical shifts for the protons at the double bond were found: $\tau(H_4) = 4.70$ and 5.00 ppm, $\tau(H_5) = 4.20$ and 4.30 ppm, respectively. From the spectrum of the adduct of thionylaniline with isoprene, whose structure was proved by chemical and physical methods ([5]), the magnitude of the chemical shift for the proton (H_5) at the double bond is 4.54 ppm. The spectrum of the TAP adduct with isoprene IV has a similar peak with a value of $\tau = 4.45$ ppm (Fig. 1b), which differs from the model compound by only 0.09 ppm, whereas for the isomeric product this difference should be on the order of 0.5–0.7 ppm. Thus, it may be concluded that adduct IV has structure G.

A similar structural directionality is also observed in the interaction of TAP with chloroprene. Since Cl in the β-position changes the magnitude of the chemical shift by 0.3–0.4 ppm toward smaller values ([7]), for structure G′ one may expect a value of τ for the proton at the double bond equal to 3.9–4.1 ppm, and for structure D′, 4.4–4.7 ppm. In the spectrum of adduct VIII we have a chemical-shift value for the proton at the double bond equal to 4.00 ppm, which supports structure G′.

For the adduct of TAF with piperylene (II), two structures are possible:

$$(C_2H_5O)_2\overset{O}{P} - N = S = O \; + \; \text{piperylene} \; \longrightarrow \; (E) \qquad (Zh)$$

From the NMR spectrum of adduct II, owing to its insufficient resolution, it is difficult to choose in favor of one or the other structure. However, the formation of the adduct having structure E may be regarded as preferable, on the basis of data obtained previously for thionylaniline ([^]5), thionylsulfonamides ([2,]8), and bisarythionylimino sulfur dioxide ([^]9).

As do thionylsulfonamides, thionylphosphonamides display greater dienophilic activity than thionylamines of the aromatic series. This is illustrated by the fact that TAF reacts both with 1-substituted dienes (adducts II, III) and with 1,2-substituted dienes (adducts V, VII). In reactions with 1,4-diphenylbutadiene-1,3 and with cyclopentadiene, the corresponding adducts could not be isolated, although in the latter case heating the reaction mixture upon mixing the components indicates the presence of interaction. But the adduct, evidently, decomposes immediately with strong resinification. These data are in agreement with the works of Kresze ([^]2) and Kollins ([^]6).

Fig. 1. NMR spectra of TAF adducts with butadiene-1,3 (I) (*a*) and isoprene (IV) (*b*).

The NMR spectra were recorded on a KGU-1 NMR spectrometer designed by Yu. Yu. Samitov (⌒10) with a permanent magnet at 25 MHz, with $Sn(CH_3)_4$ as reference. IR spectra were recorded on a two-beam H-800 spectrometer (Hilger) with a NaCl prism, as films.

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Note: Figure translations are in progress. See original paper for figures.