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THE CHEMISTRY OF CUMULATED DOUBLE BOND COMPOUNDS IV
THE REACTION OF SULFURDIIMIDES WITH TRIETHYLPHOSPHITE

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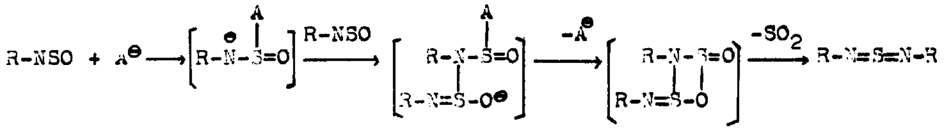
Various synthetic methods of sulfurdiimides have been reported so far (1). In this paper, new routes of aryl thionylamines to sulfurdiimides through the use of anionic catalysts and the reaction of triethylphosphite with sulfurdiimides are described. The general procedure of experimental was as follows: aryl thionylamines (0.2 mole) were added to a soultion of anionic catalysts (0.1 mole) in benzene (150 ml) and the mixture was heated at reflux temperature. When ethyl N, N-disodio carbamate was used as catalyst, the reaction proceeded very mild. In the case of methylsulfinylcarbanion, the reaction was exothermic. After evaporation of the benzene and unreacted thionylamines, the crude sulfurdiimides were purified by distillation under reduced pressure. These results are presented in Table I.

From the results of reaction between arylthionylamines and anionic catalysts, the following scheme could be proposed.



Scheme I

These sulfurdiimides reacted smoothly with triethylphosphite to form corresponding triethylphosphorimidates with O.O.O-triethylphosphorothioate in high yields at temperatures in the range of 120° to 140° (Table II). In these reactions, nitrene intermediate (Route B or Route C in Scheme II) seemed to be negligible as well as the reaction (2) of thionylamines with trialkylphosphites.

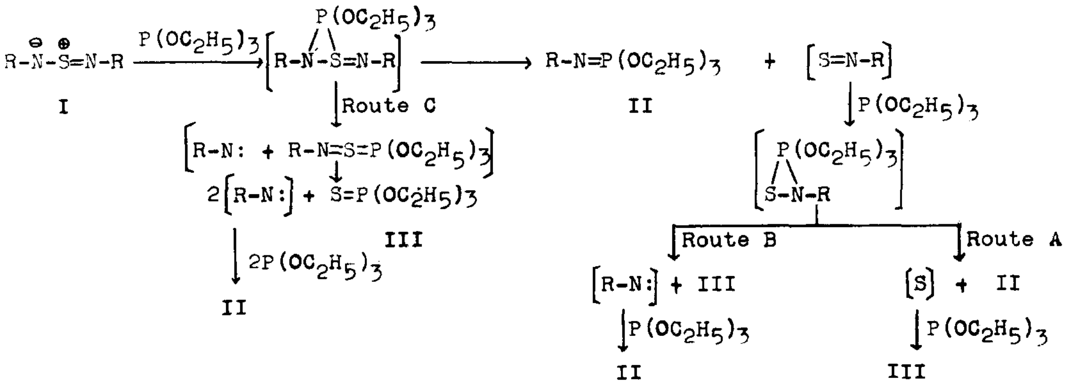
TABLE I

Reaction of arylthionylamines in the presence of anionic catalysts[a]

Run.	Reactants	Catalysts	Conditions		$R-N=S=N-R$[b]	
	R-NSO		temp. (°C)	time (hr.)	b.p. (°C/mmHg)	Yields (%)
1	C_6H_5-	$Na_2NCOOEt$	80	16	120/0.5	47.7
2	C_6H_5-	$Na_2NCOOEt$	80	24		65.0
3	C_6H_5-	C_2H_5ONa	80	16		65.2
4	C_6H_5-	$NaCH_2SOCH_3$	70-80	1		40.0
5	C_6H_5-	$NaNH_2$	80	9.5		22.0
6	C_6H_5-	Pyrrolylsodium	80	6		16.4
7	C_6H_5-	Sodium ethyldiethylmalonate.	80	6		28.0
8	o-Cl-C_6H_4-	$Na_2NCOOEt$	80	16	119/0.03	37.2
9	o-Cl-C_6H_4-	$NaCH_2SOCH_3$	70-80	1		50.0
10	m-CH_3-C_6H_4-	$Na_2NCOOEt$	80	19	110/0.005	57.0
11	m-CH_3-C_6H_4-	$NaCH_2SOCH_3$	70-80	1		33.7

a) 0.2 mole of R-NSO/0.1 mole of cat. in benzene.

b) Sulfurdiimides formed were identified by elemental analysis and i.r. spectrum of authentic samples prepared independently.



Scheme II

If the reaction is assumed to proceed via nitrene intermediate, the formation of carbazole should be expected in fairly large quantities (3) in the reaction of o-diphenylsulfurdiimide (I) with teiethylphosphite.

However, carbazole was not obtained, but triethyl-N-(o-diphenyl)-phosphorimidate (II) was isolated in 67.5% yields with O.O.O-triethylphosphorothioate (III).

Based on this observation, route A seemed to be probable.

Although 2.1.3-benzothiadiazole was heated with triethylphosphite in a sealed tube for six hours at 180 , the corresponding phospherimidate and phosphorothioate were not obtained.

TABLE II

Reaction of sulfurdiimides with triethylphosphite[a]

$$R{-}N{=}S{=}N{-}R + 3P(OC_2H_5)_3 \longrightarrow 2R{-}N{=}P(OC_2H_5)_3 + S{=}P(OC_2H_5)_3$$

Run.	Reactants	Conditions		$R{-}N{=}P(OC_2H_5)_3$[c]	
	R-N=S=N-R	temp. (°C)	time (hr.)	b.p.(°C/mmHg)	yields (%)
1	$R=C_6H_5-$	120	3.0	107/1.0	88.6
2	$R=o-Cl-C_6H_4-$	120	0.5	117/0.5	84.0
3	$R=m-CH_3-C_6H_4-$	120	2.0	115-117/0.5	67.7
4[b]	$R=o-C_6H_5-C_6H_4-$	140	4.5	160/0.4	67.5
5	2.1.3-benzothiadiazole	180	6.0	-----	0

a) 0.05 mole of sulfurdiimides/0.15 mole of triethylphosphite.

b) o-diphenylsulfurdiimide used was synthesized in the method of Leandri (1a).

c) Triethylphosphorimidates formed were identified by comaprison to n.m.r and i.r. spectrum of authentic samples (2) prepared independently.

References

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