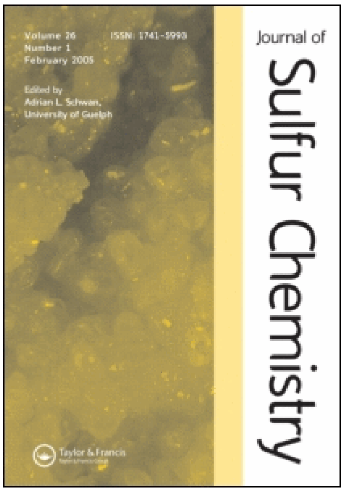

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Sulphur Nitrides in Organic Chemistry

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SULPHUR NITRIDES IN ORGANIC CHEMISTRY

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The present review describes the reactions of sulfur nitrides with a variety of organic compounds.

I. INTRODUCTION

Since the first synthesis in 1835,[1] the geometrical structure of tetrasulfur tetranitride (N_4S_4) had been a subject of controversy for a long time. Its unique spherical structure involving abnormally long sulfur-sulfur bonding was established by X-ray analysis in 1963.[2]

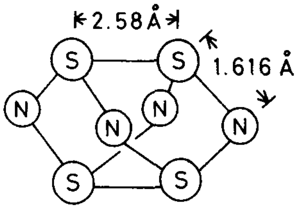
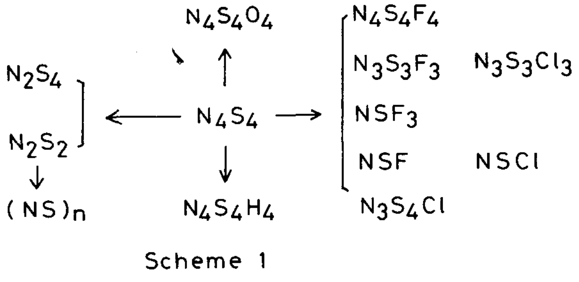


Figure 1
Structure of N_4S_4

Many sulfur nitrides can be prepared starting from N_4S_4 as shown in Scheme 1. Recently, a metallic, crystalline, covalent polymer, $(NS)_n$, possessing high electric conductivity has been synthesized.[3]



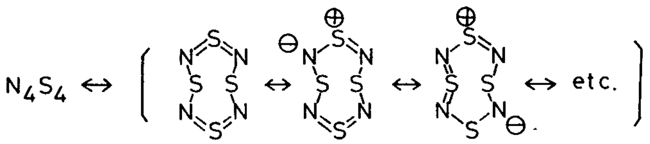
Scheme 1

Of the chemical behavior of N_4S_4, complex formation with metal halides has been widely studied. On the other hand, reactions with organic substances have been less studied. It is only recently that N_4S_4 has come under intensive scrutiny in organic chemistry.

Several reviews[4-6] are available concerning various aspects of sulfur nitride chemistry. The objective of the present review is to summarize the reactions of N_4S_4 with organic compounds. Reactions of other sulfur nitrides, though less studied than those of N_4S_4, will be also mentioned.

II. REACTIONS OF N_4S_4 WITH NUCLEOPHILES

As is to be expected from the resonance structures, nucleophilic attack occurs at the sulfur atoms of N_4S_4 and usually, cleavage of the N_4S_4 ring takes place.



II.1. *Reactions with Amines*

Benzylamine, *p*-methoxy-, and *p*-chlorobenzylamine give the corresponding tetrasulfides ($\mathbf{1}$: $x = 4$) and anils ($\mathbf{2}$).[7,8] A small amount of trisulfide ($\mathbf{1}$: $x = 3$) is obtained in the reaction with *p*-methoxybenzylamine.

$$ArCH_2NH_2 + N_4S_4 \longrightarrow \underset{\underline{1}}{(ArCH{=}N)_2{-}S_x} + \underset{\underline{2}}{ArCH_2{-}N{=}CH{-}Ar}$$

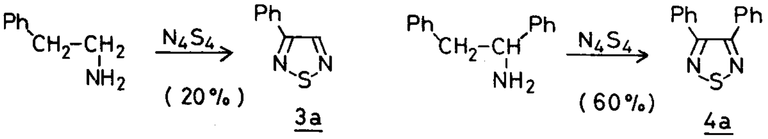
The reaction is quite sensitive towards structural change. *p*-Methylbenzylamine and allylamine do not give oligosulfides. Aromatic amines are unreactive towards N_4S_4.

TABLE I

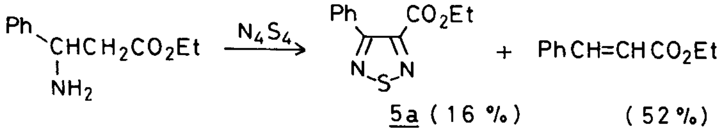
Reaction with benzylamines

Ar	Products Yield (mol %) 1	2
Ph	102	93
p-$CH_3OC_6H_4$	77 (x = 4) 3 (x = 3)	quant.
p-ClC_6H_4	79 (x = 4)	79

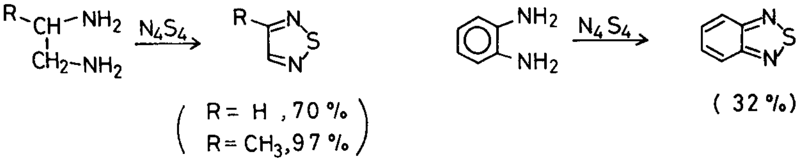
In the reactions with β-phenyl- and α, β-diphenylethylamine, none of the corresponding oligosulfide are obtained and, interestingly, 1,2,5-thiadiazoles (**3a** and **4a**) are formed.[9]



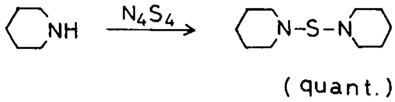
Ethyl β-amino-β-phenylpropionate affords the 1,2,5-thiadiazole-3-carboxylate **5a**.[10]



Diamines give the corresponding 1,2,5-thiadiazoles in good yields,[11,12] but since 1,2,5-thiadiazoles are prepared by the reaction of diamines with S_2Cl_2, and N_4S_4 is prepared from S_2Cl_2, there is no advantage over the direct S_2Cl_2 procedure.

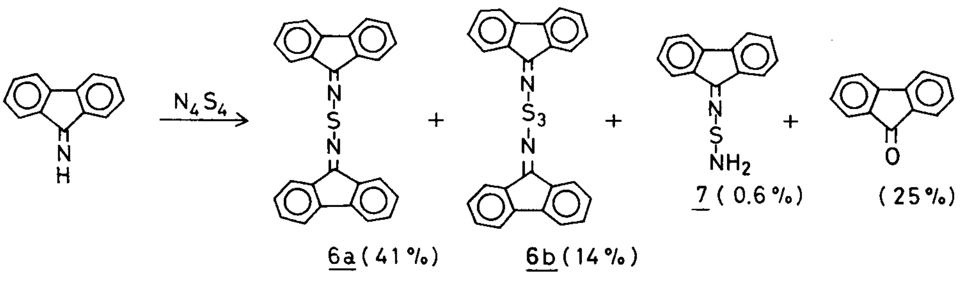


Piperidine gives bis(piperidino) sulfide.[13]

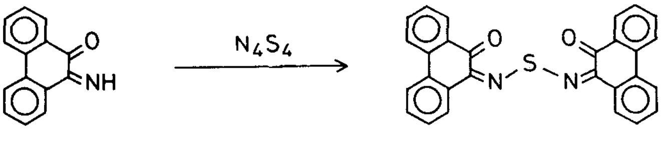


II.2. Reactions with Imines

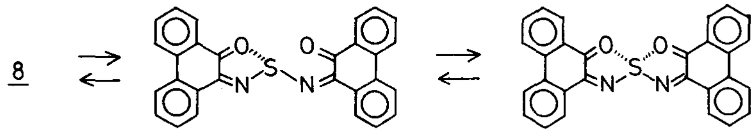
As in the case in the reaction with piperidine, imines react with N_4S_4 to give bis(imino) sulfides.[14]



Fluorenoneimine affords mono-(**6a**) and the trisulfide (**6b**) together with **7** and fluorenone. Reaction with phenanthrenequinoneimine gives the monosulfide (**8**) in good yield. From the infrared spectrum, the presence of a partial bond between the sulfur and oxygen atoms of **8** is suggested.

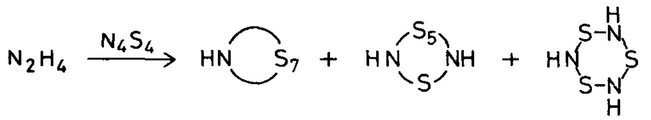


8 (83 %)



II.3. Reactions with Hydrazines

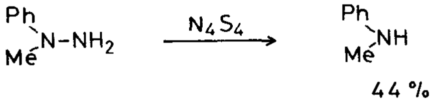
Three cyclic amino polysulfides are obtained in the reaction with hydrazine.[15]



Phenylhydrazine gives diphenyl di- and monosulfide.[8]

$$\mathrm{PhNHNH_2} \xrightarrow{N_4S_4} \underset{55\ \%}{\mathrm{PhSSPh}} + \underset{19\ \%}{\mathrm{PhSPh}}$$

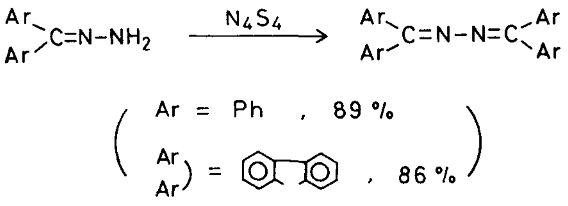
N—N bond fission occurs in the reaction with 1-methyl-1-phenylhydrazine to give *N*-methylaniline.[16] Reaction with benzoylhydrazine also gives the product of N—N bond cleavage, benzamide, together with *N*,*N*′-dibenzoylhydrazine.[16]



$$\mathrm{PhCONHNH_2} \xrightarrow{N_4S_4} \underset{27\ \%}{\mathrm{PhCONH_2}} + \underset{28\ \%}{\mathrm{PhCONHNHCOPh}}$$

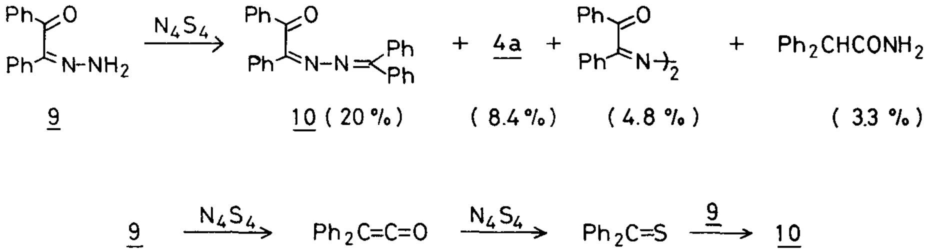
II.4. Reactions with Hydrazones

The hydrazones of fluorenone and benzophenone give the corresponding azines in their reaction with N_4S_4 in refluxing toluene.[16]



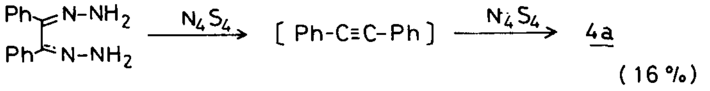
Thiatrithiazyl chloride ($N_3S_4Cl_3$) reacts with benzophenone hydrazone in refluxing benzene, affording the corresponding azine.[17]

In the reaction of N_4S_4 with benzil monohydrazone (**9**), the mixed azine (**10**), **4a**, benzil azine and diphenylacetamide are obtained.[18,19] The structure of **10** was at first erroneously assigned as 2-benzoyl-2,4,5-triphenyl-2*H*-imidazole by the authors and later corrected by Daley *et al.* The reaction pathway for the formation of **10** is given in Scheme 2.



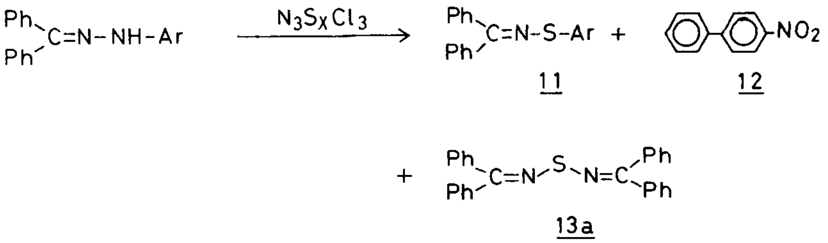
Scheme 2

Benzil bishydrazone gives **4a** which could be formed via diphenylacetylene.[18] Reaction of N_4S_4 with acetylenes gives 1,2,5-thiadiazoles as will be described later.



Reactions of thiazyl chlorides with benzophenone arylhydrazones have been investigated.[17]

$N_3S_4Cl_3$ gives **11** in its reaction with the phenylhydrazone. In the reaction with the *p*-nitrophenylhydrazone, $N_3S_4Cl_3$ and trithiazyl chloride ($N_3S_3Cl_3$) afford the same compounds, **11**, **12** and **13a**, in the yields shown in Table II.



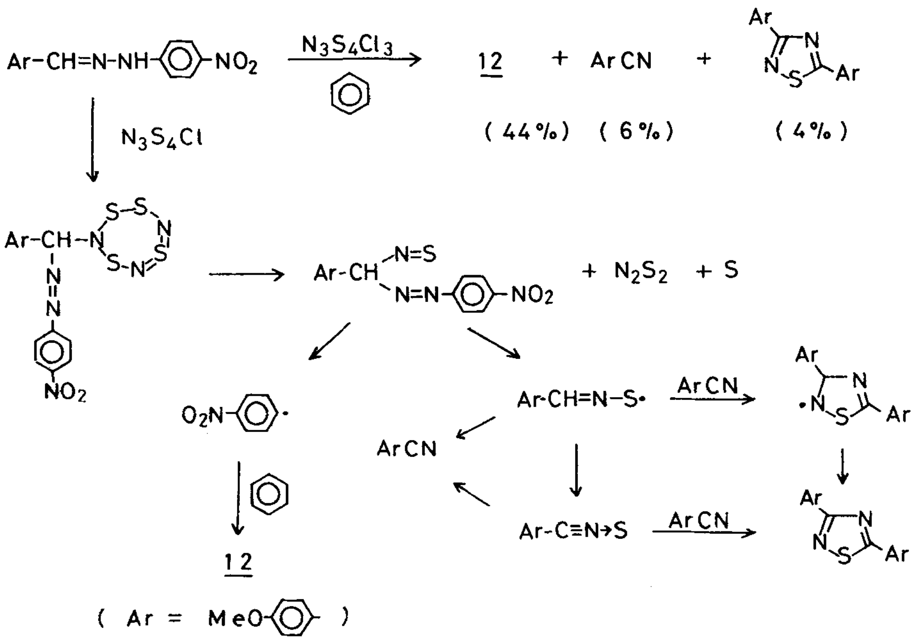
The 2,4-dinitrophenylhydrazone is unreactive towards $N_3S_4Cl_3$.

TABLE II

Reaction with benzophenone arylhydrazones

Ar	X	Products Yield (%) 11	12	13a
Ph	4	10.5		
p-$NO_2C_6H_4$	4	33	7	3
p-$NO_2C_6H_4$	3	23	47	23
p-$NO_2C_6H_4$	3	23	17	19

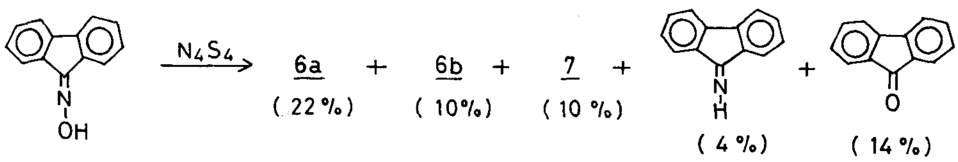
Reaction of $N_3S_4Cl_3$ with *p*-anisaldehyde *p*-nitrophenylhydrazone in refluxing benzene gives **12**, accompanied by anisonitrile and the corresponding 1,2,4-thiadiazole. A pathway involving a thionitroso intermediate has been presented.

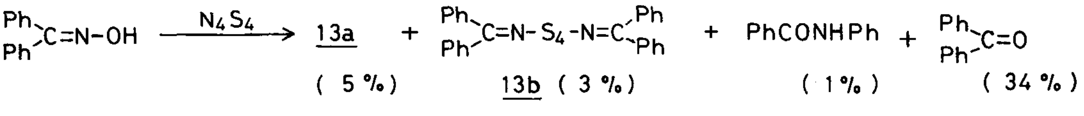


Scheme 3

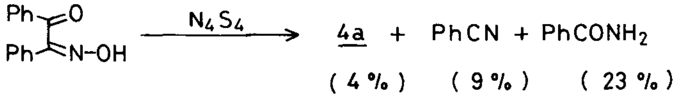
11.5. Reactions with Oximes

N—O bond cleavage of oximes by N_4S_4 is expected as a logical extension of the N—N bond fission of hydrazines. Reaction with fluorenone oxime gives **6a**, **6b**, **7**, fluorenone, and the expected fluorenoneimine.[14] The compounds **6a**, **6b**, and **7** are formed via the imine. Though the expected imine has not been isolated, the compounds **13a** and **13b** are formed in the reaction of N_4S_4 with benzophenone oxime.[14] Cyclohexanone oxime affords only an intractable tar.

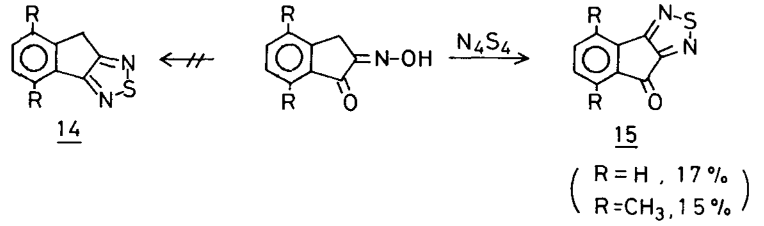




C—C bond cleavage is observed in the reaction with benzil monoxime, giving benzonitrile and benzamide[14] with a small amount of **4a**.

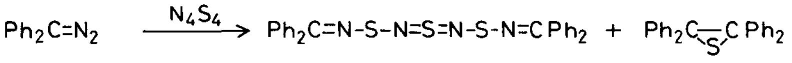


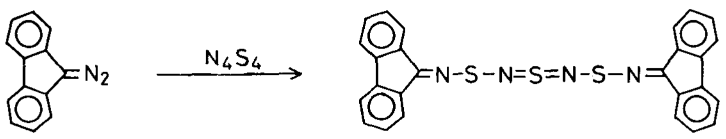
In the reaction with 1,2-indanedione 2-oxime, formation of **14** is expected, but **15** is obtained.[20]



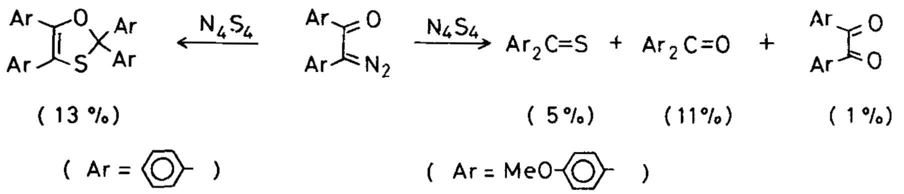
II.6. Reactions with Diazo Compound

Reaction with diphenyldiazomethane and 9-diazofluorene gives novel heterocumulenes.[21]

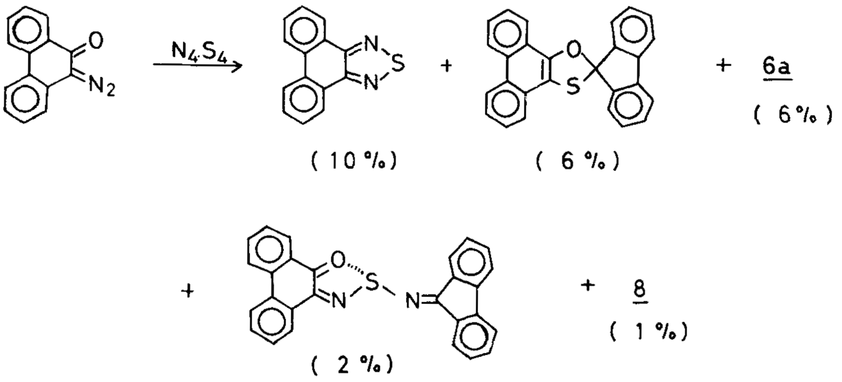




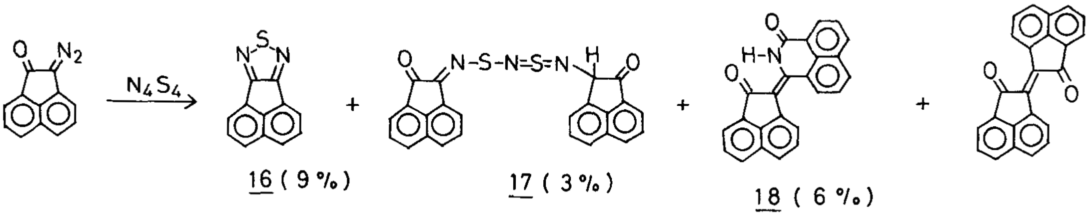
In the expectation of formation of 1,2,5-thiadiazoles via the intramolecular ring closure of the corresponding sulfur diimide derivatives (Scheme 4), the reaction with diazoketones was investigated.[22] Azibenzil gives 2,2,4,5-tetraphenyl-1,3-oxathiole, while 4,4′-dimethoxyazibenzil gives 4,4′-dimethoxythiobenzophenone, 4,4′-dimethoxybenzophenone, and 4,4′-dimethoxybenzil.



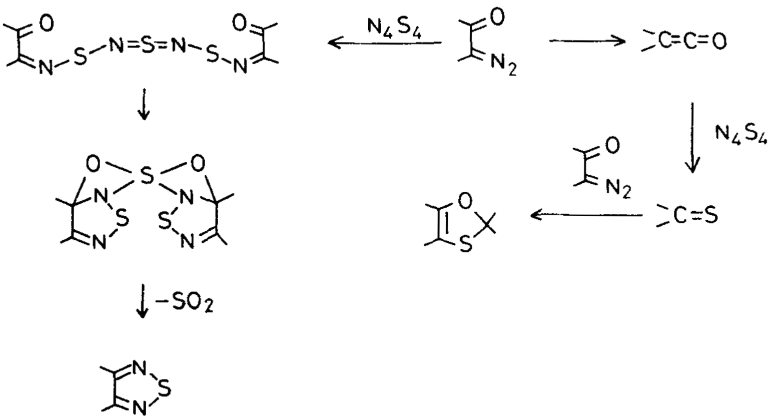
In the reaction with α-diazophenanthrone the expected 1,2,5-thiadiazole is obtained together with the 1,3-oxathiole, **6a**, as well as **8** and an unsymmetrical bis(imino) sulfide.



α-Diazoacenaphthenone gives the corresponding 1,2,5-thiadiazole **16**, together with **17**, **18**, and diacenaphthylidenedione.



The pathway of the reaction of N_4S_4 with α-diazoketones is shown in Scheme 4. The reactions of an α-diazoketone with a thioketone gives the corresponding 1,3-oxathiole.[23]



Scheme 4

II.7. Reactions with Organometallics

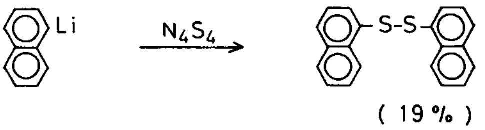
The reaction with arylmagnesium bromide is reported to give 1,5-diaryl-1,3,5,2,4-trithiadiaza-2,3-pentadiene (**19**).[24] Detailed reinvestigation reveals that the reaction products and their yields are dependent on the decomposition conditions of the reaction mixture.[25]

$$RMgX \xrightarrow{N_4S_4} \underset{\underline{19}}{R\text{-}S\text{-}N{=}S{=}N\text{-}S\text{-}R} + \underset{\underline{20}}{R\text{-}S\text{-}S\text{-}R} + \underset{\underline{21}}{R\text{-}S\text{-}NH\text{-}S\text{-}R} + \underset{\underline{22}}{RSSO_3^{\ominus}NH_4^{\oplus}}$$

$$+ \underset{\underline{23}}{R\text{-}S\text{-}SO_2\text{-}R}$$

As shown in Table III, the disulfide (**20**) is obtained in good yield and the reported **19** is isolated when the reaction mixture is decomposed under mild conditions. Alkyl derivative corresponding to **19** are not obtained. Compounds **21**, **22**, and **23** are formed by the decomposition of **19**. Hydrolysis of **19** and **21** gives **23**.

Naphthyllithium affords dinaphthyl disulfide.[25]



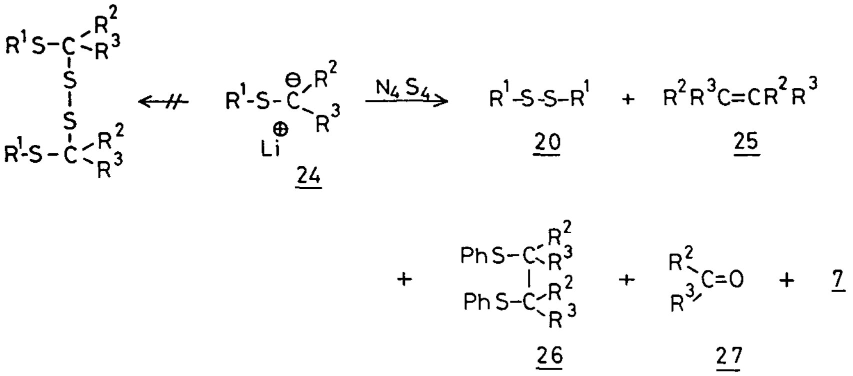
(19 %)

TABLE III

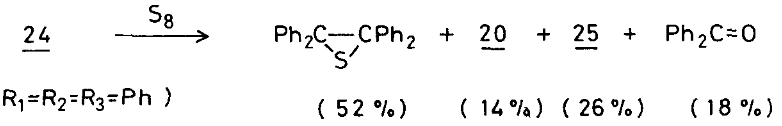
Reaction with Grignard reagents

R	Decomp. Condns.	Products, Yield (mol %) 19	20	21	22	23
Ph	A	8	72	5	18	-
p-ClC_6H_4	A	6	92	19	27	-
p-$CH_3C_6H_4$	A		71		59	-
$PhCH_2$	A	-	66	-	4	-
cyclo-C_6H_{11}	A	-	30	-	19	-
Ph	B	-	94	-	-	-
p-ClC_6H_4	B	34	85	-	-	3
p-BrC_6H_4	B	29	80	-	-	6
Ph	C	-	92	-	-	-
p-ClC_6H_4	C	-	98	-	-	14
p-BrC_6H_4	C	-	72	-	-	-
o-$CH_3C_6H_4$	C	-	63	-	-	5
p-$CH_3C_6H_4$	C	-	90	-	-	10
p-$CH_3OC_6H_4$	C	-	99	-	-	-
$PhCH_2$	C	-	82	-	-	12

The sulfur-stabilized organolithium compounds (**24**)[25] do not give the expected tetrasulfides. Disulfides (**20**) and ethylene (**25**) are obtained together with the coupling products (**26**), **27**, and **7**. Compounds **20** and **25** arise from the C—S bond fission of **24**.



Participation of sulfur, which could be formed by the decomposition of N_4S_4, is excluded because the reaction of sulfur with **24** ($R_1 = R_2 = R_3 = Ph$) gives tetraphenylthiirane in 52 % yield. Thiobenzophenone is trapped in the reaction with α-diazoacenaphthenone. Though the reaction mechanism is obscure, the intermediate formation of the corresponding thioketone in the reaction of N_4S_4 or sulfur with **24** is suggested.

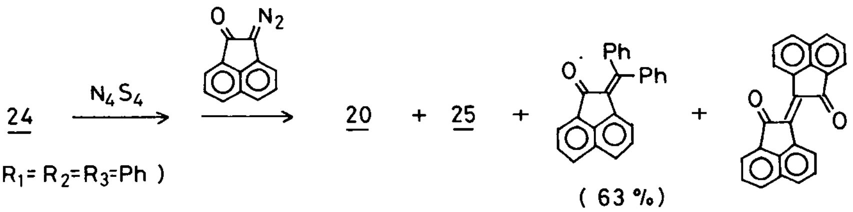


Metalated amines give sulfur diimide derivatives in their reaction with N_4S_4.

TABLE IV

Reaction with 24

R^1	R^2	R^3	Products, Yield (%) 20	25	26	27	7
Ph	H	H	20				
Ph	Ph	H	43	1	4		
Ph	H	$p\text{-}ClC_6H_4$	33	6			
$p\text{-}ClC_6H_4$	H	Ph	29	1			
Ph	H	$p\text{-}CH_3C_6H_4$	24		7		
$p\text{-}CH_3C_6H_4$	H	Ph	22				
Ph	Ph	Ph	14	11		31	
Ph			33	20	32	19	13



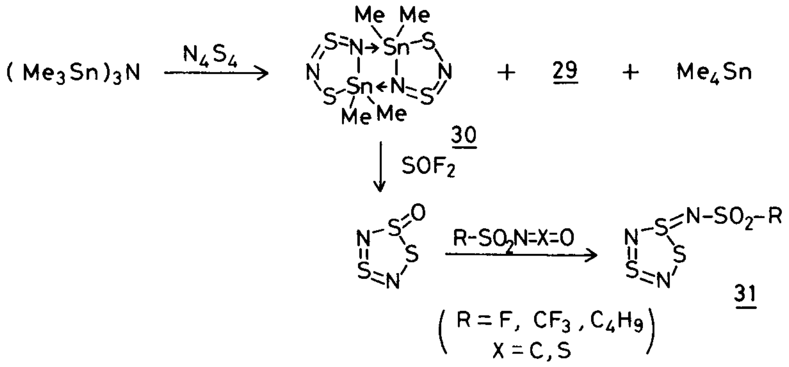
Trimethylsilyldimethylamine gives bis(dimethylamino) sulfide and **28** (R = Me), while trimethylsilyldiethylamine affords only **28** (R = Et)[26,27]

$$\mathrm{Me_3Si{-}NR_2} \xrightarrow{\mathrm{N_4S_4}} \mathrm{Me_2N{-}S{-}NMe_2} + \underset{\underline{28}}{\mathrm{R_2N{-}S{-}N{=}S{=}N{-}SiMe_3}}$$

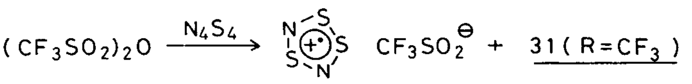
Bis(trimethylstannyl) sulfur diimide (**29**) and bis(dimethylamino) sulfide are obtained in the reaction with the corresponding stannylamine.[28]

$$\mathrm{Me_3Sn{-}NMe_2} \xrightarrow{\mathrm{N_4S_4}} \mathrm{Me_2N{-}S{-}NMe_2} + \underset{\underline{29}}{\mathrm{Me_3Sn{-}N{=}S{=}N{-}SnMe_3}}$$

Reaction with tris(trimethylstannyl)amine gives tetramethyltin, **29**, and the dimer (**30**). In the reaction with thionyl fluoride, **30** affords a cyclic sulfur diimide which, on reaction with sulfonyl isocyanates, gives the sulfilimines (**31**).[29–31]



Compound **31** (R = CF_3) is also formed in the reaction of N_4S_4 with trifuloromethansulfonic anhydride together with the five-membered cyclic radical cation of N_2S_3.[32]

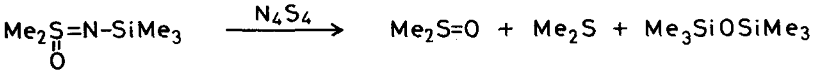


II.8. Reaction with Miscellaneous Nucleophiles

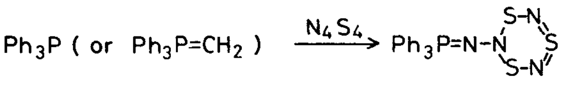
Treatment with cyanide anions results in ring contraction of N_4S_4 and thiocyanate ions are produced.[33]

$$\mathrm{CN}^{\ominus} \xrightarrow{\mathrm{N_4S_4}} \mathrm{SCN}^{\ominus}$$

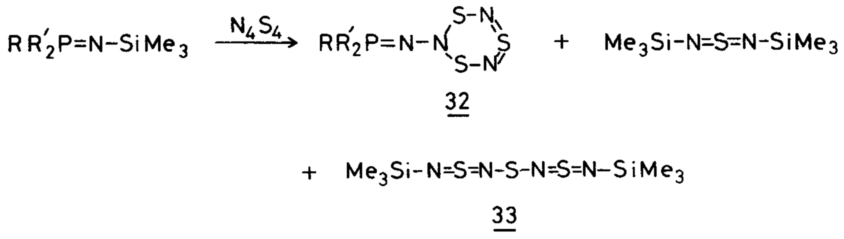
No nitrogen-containing product can be isolated in the reaction with trimethylsilylimino dimethyl sulfoxide.[34]



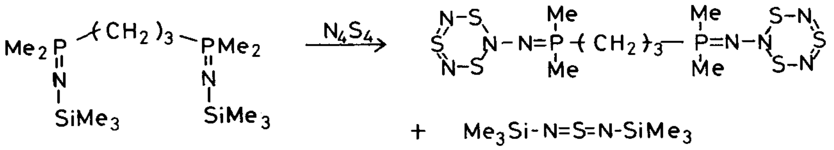
Triphenylphosphine and methylenetriphenylphosphorane react with N_4S_4 to afford trithiazyliminophosphorane.[33]



Though simple iminophosphoranes are unreactive towards N_4S_4, trimethylsilylated iminophosphoranes give **32** together with bis(trimethylsilyl)sulfur diimide and **33**. In the presence of trimethylsilyliminophosphorane, the compounds **33** gradually decompose, affording **32**. A bis(trithiazyl) derivative is similarly prepared.



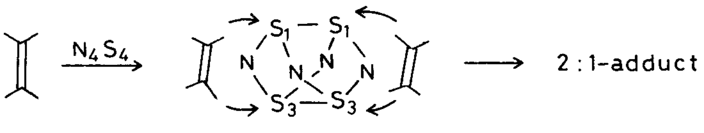
$$RR'_2P{=}N{-}SiMe_3 + \underline{33} \longrightarrow \underline{32}$$



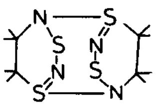
III. REACTION WITH MULTIPLE BONDS

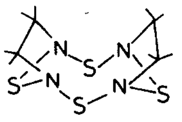
III.1. Addition Reactions with Strained Olefins

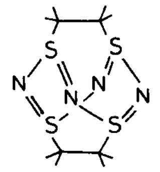
Strained olefins such as norbornadiene, norbornene, 5-norbornenol, 5-methylenenorbornene, cyclopentadiene, and *trans*-cycloctene add across the S(1)-N(2)-S(3) bond of N_4S_4, giving 2 : 1-adducts.[35–38]



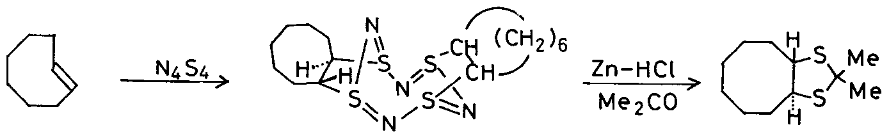
Such an adduct formation was first reported in 1968 and since then the following structures have been proposed for the adducts.



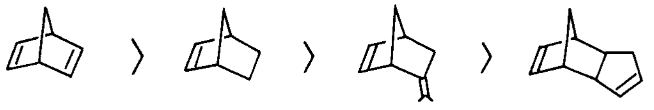




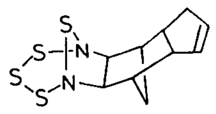
Their structures have been established by means of X-ray analysis[39] and chemical conversion leading to the corresponding thioketals.[38]



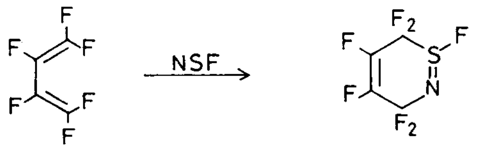
The color of the solution of the adducts changes from colorless to red at room temperature, suggesting dissociation of the adducts. Olefin exchange reactions can be observed and a competition experiment gave the following order of reactivity:[37]



No reaction takes place with maleic anhydride, tetracyanoethylene, cyclohexene, and cyclopentene. Cycloocta-1,5-diene is inactive. The strained single bond of 3-bromotricyclo-2,2,1,$0^{2,6}$ -heptene is also unreactive. A 1:1-adduct is isolated in the reaction of N_2S_4 with dicyclopentadiene.[40]



The first Diels-Alder reaction of a sulfur nitride was recently reported with the reaction of NSF with perfluorobutadiene.[41] 2,3-Dimethylbutadiene reacts explosively with NSF.



(quant.)

III.2. Reactions with Heterocumulenes

Sulfonyl isocyanates forms 1:1-adducts, though the structure of the adducts is not known.[42]

$$X\text{-}SO_2\text{-}N{=}C{=}O \xrightarrow{N_4S_4} 1:1\text{-adduct}$$

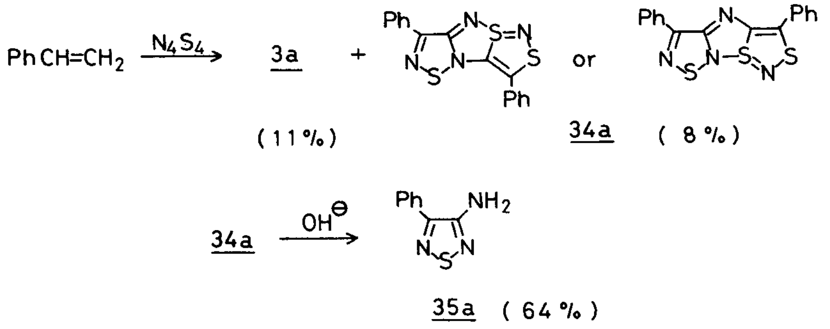
$$(X = Cl, F, NCO)$$

Reaction with diphenylketene give thiobenzophenone in quantitative yield.[19]

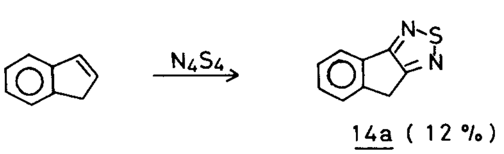
$$Ph_2C{=}C{=}O \xrightarrow{N_4S_4} Ph_2C{=}S \quad \text{(quant.)}$$

III.3. Reaction with Olefinic Compounds, Giving 1,2,5-Thiadiazoles

1,2,5-Thiadiazole ring formation by reaction of sulfur nitride with olefinic compound has scarcely been reported. Styrene reacts with N_4S_4 in refluxing toluene to give **3a**.[43] Though its structure is not yet fully established, the novel compound **34a** is also obtained in this reaction. On hydrolysis in alkaline medium **34a** gives 3-amino-4-phenyl-1,2,5-thiadiazole (**35a**).[44]



Thiadiazoloindene (**14a**) is formed in the corresponding reaction with indene.[45]



Silyl enol ethers derived from aromatic and heteroaromatic methyl ketones give, interestingly, 3-aryl-4-hydroxy-1,2,5-thiadiazoles (**36**), though the yields are low.[46] 3-Amino-1,2,5-thiadiazoles (**35**) are formed as by-products.

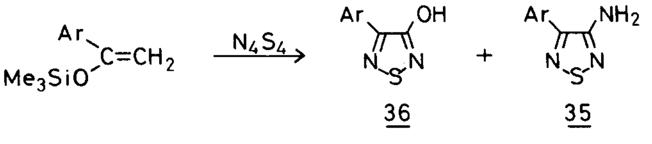
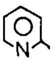
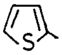
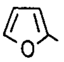
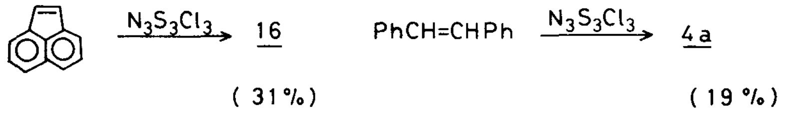
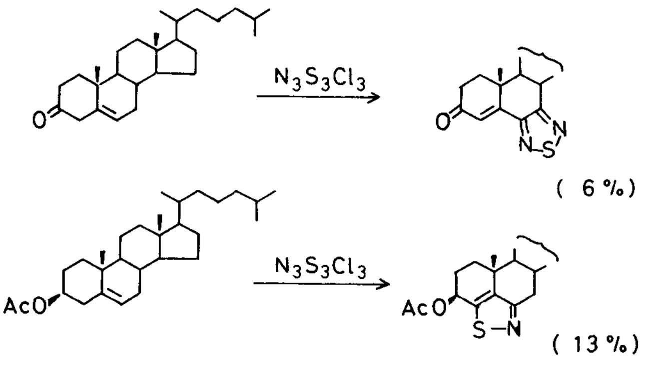


TABLE V
Reaction with 1-aryl-1-trimethylsiloxyethylenes

Ar	Products Yield (%) 36	35
Ph	12	–
p-ClC_6H_4	14	–
p-BrC_6H_4	11	–
p-$CH_3C_6H_4$	19	–
	18	–
	11	4
	3	2

Reaction of $N_3S_3Cl_3$ with acenaphthylene and *trans*-stilbene gives the corresponding 1,2,5-thiadiazoles (**16** and **4a**).[17] The (N—S—N) unit of $N_3S_3Cl_3$ can be introduced into cholesterone.[17] On the other hand, in the corresponding reaction with cholesteryl acetate, an (N—S) unit is introduced and an isothiazole ring is formed.





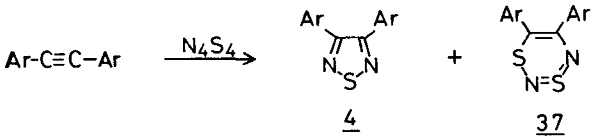
III.4. Reactions with Acetylenes

The reaction of N_4S_4 with acetylenes is useful for the preparation of symmetrically substituted 1,2,5-thiadiazoles.[47] Diaryl- and diaroylacetylenes afford the corresponding 1,2,5-thiadiazoles (**4**) in fair to good yields, as shown in Table VI. Novel compounds **37** are obtained in the reaction with di(*p*-chlorophenyl)- and diphenylacetylene.

TABLE VI

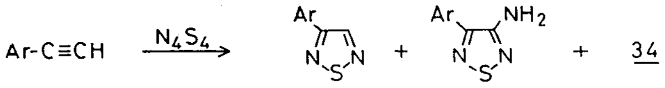
Preparation of 4

Ar	Yield (%)	Ar	Yield (%)
Ph	87	PhCO	39
p-Cl C_6H_4	46	p-Cl C_6H_4CO	45
p-$CH_3C_6H_4$	56	p-CH_3 C_6H_4CO	49
p-$CH_3OC_6H_4$	56		



4 37

The expected 3-aryl-1,2,5-thiadiazoles (**3**) are obtained in the reaction with arylacetylenes, but only in low yields.[44] Compounds **35** are formed as by-products.



3 35

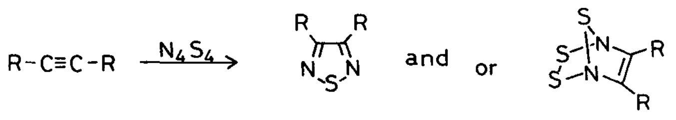
In the reaction with phenylacetylene, compound **34**, which also is obtained in the reaction with styrene, is isolated.

TABLE VII

Reaction with arylacetylenes

Ar	Products, Yield (%)		
	3	35	34
Ph	16	3	8
p-$CH_3C_6H_4$	12	4	+
p-Br-C_6H_4	6	–	–

Reaction with symmetrical electron-deficient acetylenes is reported to give 1,2,5-thiadiazoles and/or the 1:1-adduct of acetylenes with N_2S_3.[48] Bicyclic structures have been proposed for the adducts.



(R = CO_2Me , CN) (R = CN, CF_3)

Recently, reactions with three acetylenic esters have been studied in detail.[47] The expected 1,2,5-thiadiazoles (**5**) are obtained together with other products, as shown in Table VIII. Dimethyl acetylenedicarboxylate gives dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**5**: R = CO_2Me) in 60 % yield. The yields of the corresponding **5** are lower in the reactions with methyl propiolate and methyl phenylpropiolate. The molecular formula of **41** corresponds to the 1:1-adduct of N_2S_3 and the acetylenic ester. In the ^1H NMR spectrum of **41** (R = H), an azomethine proton is observed and a trithiadiazepine structure is proposed for **41**.

Interestingly, compound **43** is considered to arise from the fission of the triple bond; however, its structure has not yet been clarified.

The isomeric 1,2,3- and 1,2,4-thiadiazoles **38** and **39** are obtained in the reaction with phenylpropiolate. Transposition reactions between **5**, **38**, and **39** do not take place under the reaction conditions. Methyl propiolate gives the 3-amino-1,2,5-thiadiazole **40**.

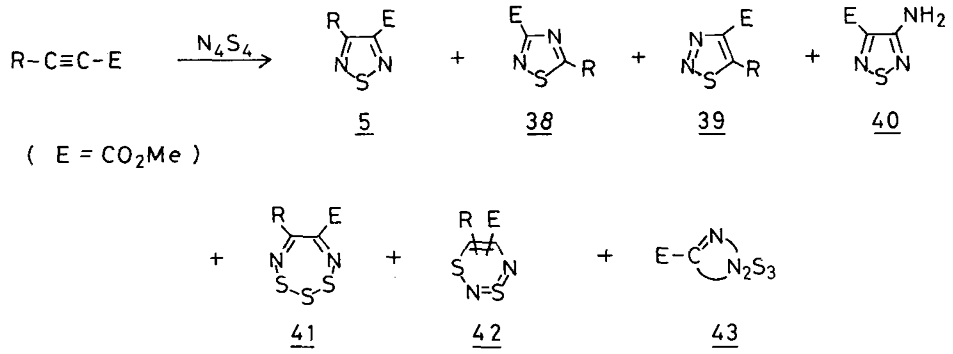
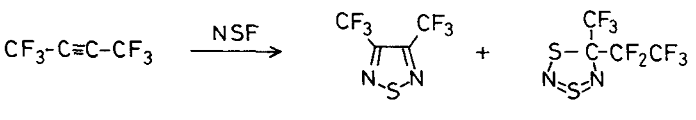


TABLE VIII

Reaction with acetylenic esters

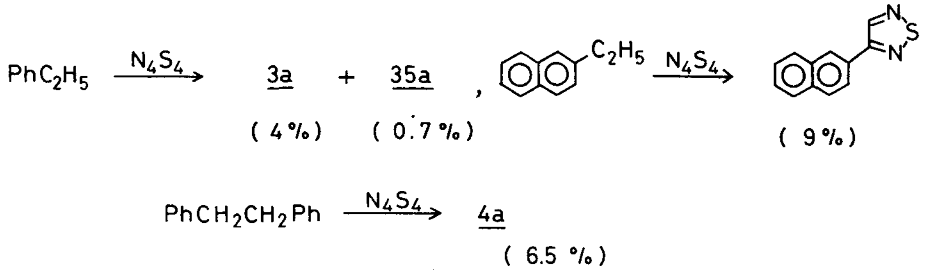
R	Products			Yield (%)			
	5	38	39	40	41	42	43
CO_2Me	60	8	–	–	5	–	6
Ph	22	3	9	–	2	+	6
H	7	–	–	9	2	–	6

In the reaction with perfluoro-2-butyne, thiazyl fluoride gives the corresponding 1,2,5-thiadiazole and dithiadiazole.[49]

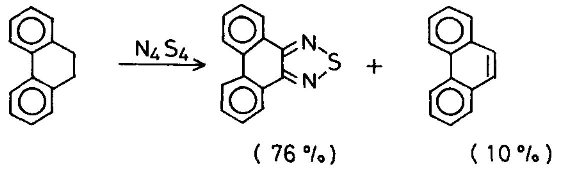


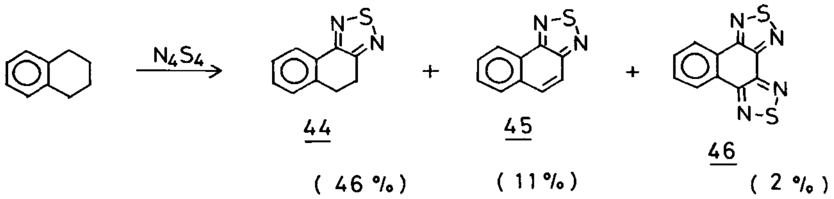
IV. REACTIONS WITH ARYL ETHANE DERIVATIVES

N_4S_4 reacts with ethylarenes such as ethylbenzene, ethylnaphthalene, and diphenylethane to afford 1,2,5-thiadiazoles.[50,51] A small amount of the corresponding amino-1,2,5-thiadiazole is formed in the reaction with ethylbenzene.[47] Though the yields are poor, the reaction is interesting because of the simple starting materials.



Tetrahydronaphthalene and 9, 10-dihydrophenanthrene also react with N_4S_4 under thermal and photochemical conditions to give 1,2,5-thiadiazole-condensed aromatic compounds.[52] The reaction is suggested to be initiated by a free radical from N_4S_4 which abstracts a hydrogen from a benzylic position, thus bringing about the following sequence of events.

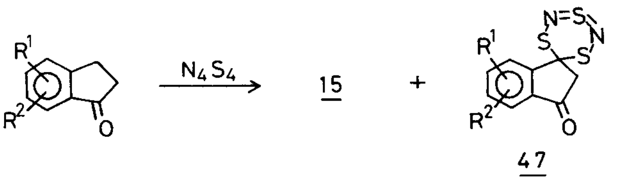




$\underline{44} \xrightarrow{N_4S_4} \underline{45} + \underline{46}$

(31%) (6%)

Indanones react with N_4S_4 in refluxing toluene to give indenothiadiazoles (**15**) in low yields.[53] A small amount of the red-colored novel compound (**47**) is also isolated.



47

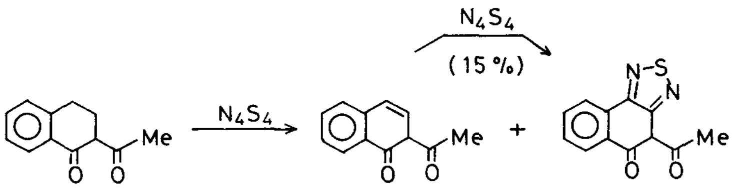
TABLE IX

Reaction with indanones

Indanone		Products Yield (%)	
R^1	R^2	15	47
H	H	9	1
4-CH_3	7-CH_3	1	–
5-CH_3	6-CH_3	3	+

Though 1-tetralone does not react with N_4S_4 in toluene at reflux, 2-acetyl-1-tetralone gives the 3,4-dehydro derivative **48** and the expected thiadiazolotetralone **49**.[53]

Reaction of **48** with N_4S_4 in refluxing toluene gives **49**.[53]

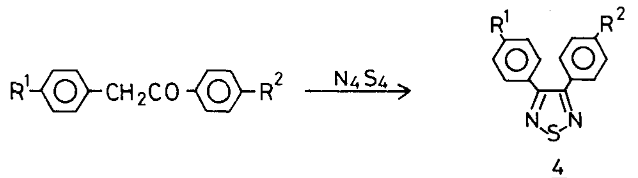


48 (22%) 49 (1%)

V. REACTIONS WITH METHYLENE KETONES

V.1. Reactions with Benzyl Ketones[54]

The reaction with desoxybenzoins give 3,4-diaryl-1,2,5-thiadiazoles (**4**) in the yields summarized in Table X. The yield is influenced by the nature and the position of the substituents. Electron-withdrawing groups in 4- and/or 4′-position raise the yield while electron-donating groups decrease it.



4

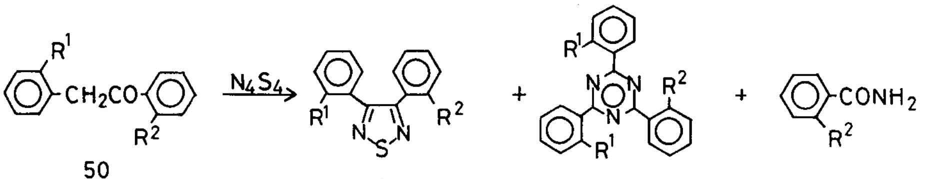
The size of the substituent in the 2- and/or 2′-position controls the reaction. In the reaction with 2-methyl-, 2-chloro- and 2-nitrodesoxybenzoin, the expected 1,2,5-thiadiazoles (**4**) are obtained in 3–18 % yield and unreacted desoxybenzoins are recovered, although the N_4S_4 is completely consumed. This is because the initial attack of N_4S_4 on the benzylic positions is obstructed by the steric hindrance of the ortho-substituent.

TABLE X

Preparation of 4

R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
H	H	42	H	CH_3	32
Cl	H	30	CH_3	Cl	49
H	Cl	39	Cl	CH_3	44
NO_2	H	41	Cl	Cl	60
CH_3	H	47	CH_3	CH_3	28

The desoxybenzoins are completely consumed in their reactions with N_4S_4, but the yields of 1,2,5-thiadiazoles are low and amides **52** are formed, too. The ring closure of the intermediate of yet unknown structure might be interrupted and subsequent C—C bond cleavage give **52**. Since the chloro group is smaller than the methyl and the bromo group, the ring closure is not interrupted and the corresponding 1,2,5-thiadiazole (**4**) is obtained in 46 % yield in the reaction with 2′-chlorodesoxybenzoin.



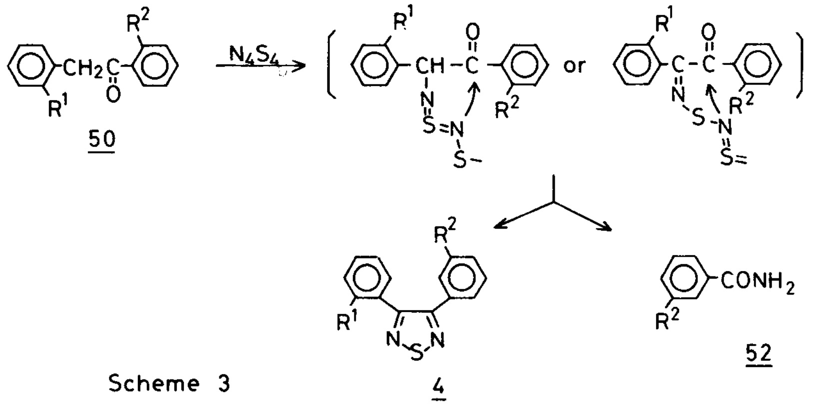
50 4 51 52

A radical mechanism has been suggested for the reaction of N_4S_4 with 9,10-dihydrophenanthrene.[52] Introduction of air during the reaction of N_4S_4 with desoxybenzoin decreases the yield of **4a**. Furthermore, addition of *m*-dinitrobenzene which is known as a radical anion scavenger, decreases the yield, thus suggesting a radical anion mechanism for the reaction of N_4S_4 with desoxybenzoins.

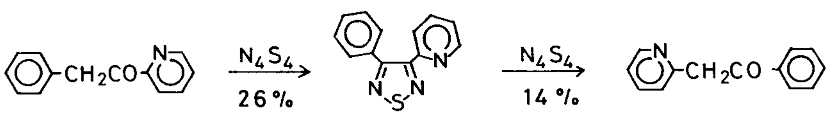
TABLE XI

Reaction with 50

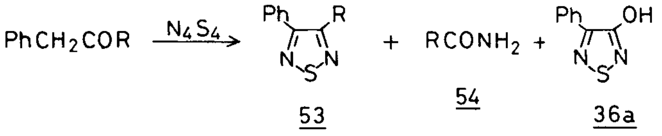
R^1	R^2	Products Yield (%)			Recovered
		4	51	52	50
CH_3	H	11	–	–	60
Cl	H	18	–	–	56
NO	H	18	–	–	25
H	CH_3	12	3	14	–
H	Cl	46	+	–	–
H	Br	18	4	15	–



Scheme 3



Pyridyl-1,2,5-thiadiazole can be prepared from both ketones. 3-Methyl-, 3-propyl-, 3-isopropyl-, 3-butyl-, and 3-benzyl-4-phenyl-1,2,5-thiadiazoles are obtained in practical yields, as shown in Table XII. Curiously, 3-ethyl-4-phenyl-1,2,5-thiadiazole cannot be obtained by this method. The amides **54** are formed in the reactions with benzyl isopropyl ketone and benzyl butyl ketone. Compound **36a** is isolated in the reaction with dibenzyl ketone in 14 % yield.

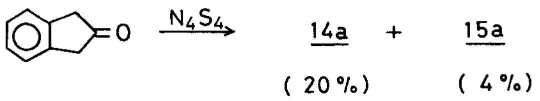


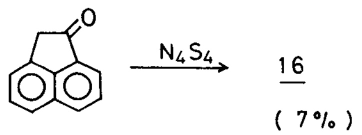
The reactions with cyclic benzyl ketones such as 2-indanone and acenaphthenone give the corresponding 1,2,5-thiadiazoles **14a** and **16**.

TABLE XII

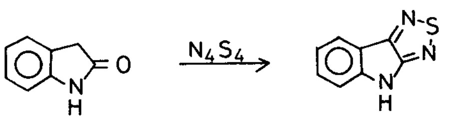
Reaction with alkyl benzyl ketones

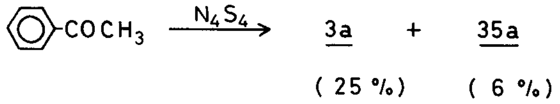
R	Products Yield (%)		
	53	54	36a
CH_3	47	–	–
C_3H_7	20	–	–
C_3H_7	19	9	–
C_4H_9	30	20	–
$PhCH_2$	32	–	14





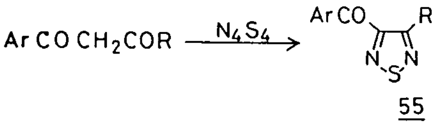
N-Methyl-phenylacetamide does not react with N_4S_4 in refluxing toluene. Interestingly, oxindole gives the corresponding 1,2,5-thiadiazole in poor yield with recovery of oxindole in 63 % yield. Acetophenone does not react with N_4S_4 in toluene or xylene at reflux, but, when heated with N_4S_4 at 100—110 °C under a nitrogen atmosphere it gives 1,2,5-thiadiazoles (**3a** and **35a**).[55]





V.2. Reactions with 1,3-Diketones[56]

Diaroylmethanes and aroylacetones give the corresponding 1,2,5-thiadiazoloketones (**55**) in yields shown in Table XIII. In the reaction with asymmetrical diaroylmethanes, the expected two isomeric 1,2,5-thiadiazoles are obtained. Aryl-1,2,5-thiadiazoloketones are formed as the sole products in the reactions with aroylacetones. Introduction of a trifluoromethyl group in place of a methyl group raises the yield and 3-aroyl-4-trifluoromethyl-1,2,5-thiadiazoles can be prepared in practical yields.



Cyclic 1,3-diketones also give the expected 1,2,5-thiadiazoloindanones.

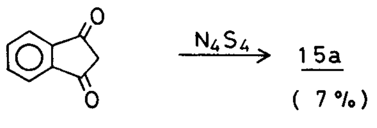
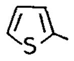


TABLE XIII

Preparation of 55

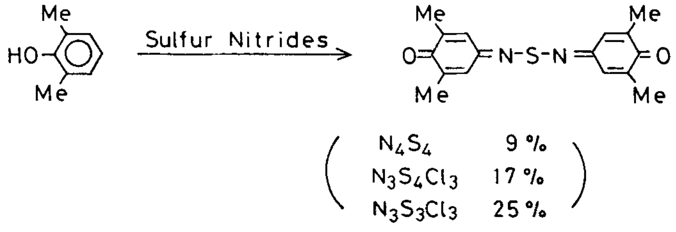
Ar	R	Yield (%)
Ph	Ph	40
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	34
p-Cl C_6H_4	p-Cl C_6H_4	44
p-Cl C_6H_4	Ph	9
Ph	p-Cl C_6H_4	17
Ph	CH_3	12
Ph	CF_3	50
	CF_3	40

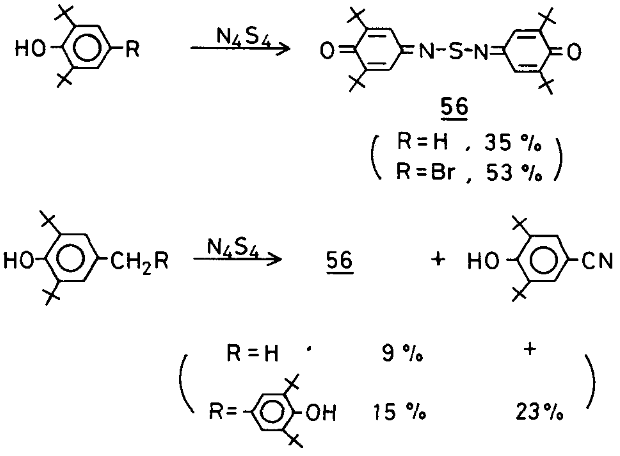
Ethyl benzoylacetate gives **5a**.[57]

$$PhCOCH_2CO_2Et \xrightarrow{N_4S_4} \underline{5a} \quad (36\%)$$

VI. REACTIONS WITH PHENOLS

2,6-Xylenol[17] reacts slowly with N_4S_4, more rapidly with $N_3S_4Cl_3$, and much more readily with $N_3S_3Cl_3$ giving *N*,*N*′-thiobis-(2,6-dimethyl-1,4-benzoquinoneimine) in yields proportional to the order of reactivity of the sulfur nitrides. 2,6-Di-*t*-butylphenol reacts smoothly with N_4S_4 in refluxing toluene to afford **56**.[57] In the reaction with 4-bromo-2,6-di-*t*-butylphenol, bromine is eliminated and **56** is obtained in a higher yield. A C—C bond is cleaved in the reaction with 2,6-di-*t*-butyl-4-alkylphenols and 2,6-di-*t*-butyl-4-cyanophenol and **56** are obtained.





Contrary to the above mentioned cases 4-methyl-, 4-isopropyl- and 4-*t*-butylphenol give the corresponding 2,1,3-benzothiadiazoles.[58]

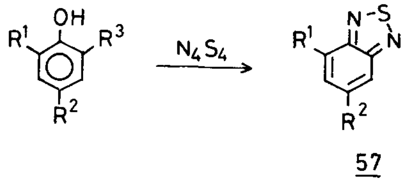


TABLE XIV

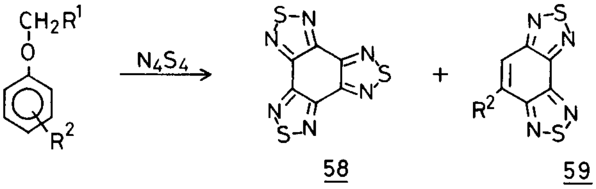
Preparation of 57

R¹	R²	R³	Yield (%) 57
H	Me	H	27
H	iso-Pr	H	41
H	t-Bu	H	47
Me	Me	H	31
t-Bu	Me	H	34
iso-Pr	t-Bu	H	72
t-Bu	t-Bu	H	68
t-Bu	t-Bu	t-Bu	52
t-Bu	t-Bu	F	63
t-Bu	t-Bu	Cl	50
t-Bu	t-Bu	Br	43
t-Bu	t-Bu	I	86

TABLE XV
Reaction with alkoxybenzenes

R^1	R^2	Products Yield (%) 58	59
H	H	1.9	0.7
H	o-CH_3O	0.7	0.4
H	m-CH_3O	—	0.4
Ph	H	4.5	4.3

The novel reaction of N_4S_4 with anisole, dimethoxybenzenes, and benzyl phenyl ether have been reported to give benzotris-(**58**) and benzobis-1,2,5-thiadiazole (**59**).[59]



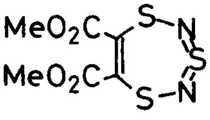
REFERENCES

1. M. Gregory, *J. Pharm.*, **21**, 315 (1835); *ibid.*, **22**, 301 (1835). For the preparation of N_4S_4, see: M. Becke-Goehring, *Inorg. Synth.*, **6**, 123 (1960), and, M. Villena-Blanco and W. L. Jolly, *ibid.*, **9**, 98 (1967).
2. B. D. Sharma and J. Donohue, *J. Acta. Cryst.*, **16**, 891 (1963).
3. E. J. Louis, A. G. McDiarmid, A. F. Garito, and A. J. Heeger, *J. Chem. Soc. Chem. Comm.*, 426 (1976).
4. C. W. Allen, *J. Chem. Educ.*, **44**, 38 (1967).
5. M. Becke-Goehring, *Angew. Chem.*, **73**, 589 (1961); *Sulfur Inst. J.*, 2 (1966).
6. O. Glemser, *Angew. Chem. Internat. Edit.*, **2**, 530 (1963).
7. Y. Sasaki and F. P. Olsen, *J. Chem. Soc. Chem. Comm.*, 1424 (1969).
8. Idem., *Can. J. Chem.*, **49**, 271 (1971).
9. V. Bertini and P. Pino, *Angew. Chem.*, **77**, 262 (1965).
10. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
11. V. Bertini and P. Pino, *Angew. Chem.*, **78**, 493 (1966).
12. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
13. R. Schenk, *Ann.*, **290**, 171 (1896).
14. S. Mataka, K. Takahashi, S. Ishi-i, and M. Tashiro, *J. Chem. Soc. Perkin Trans.* **I**, 2905 (1979).
15. H. Garcia-Fernandez, *Bull. Soc. Chim.* **Fr.**, 3647 (1967).
16. M. Tashiro and S. Mataka, *Chem. Lett.*, 627 (1976).
17. D. H. R. Barton and W. A. Bubb, *J. Chem. Soc. Perkin Trans.* **I**, 916 (1977).
18. M. Tashiro and S. Mataka, *Heterocycles*, **4**, 1243 (1976).
19. S. T. A. K. Daley and C. W. Rees, *Tetrahedron Lett.*, 1759 (1981).
20. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
21. E. Fluck, *Z. Anorg. Allg. Chem.*, **312**, 195 (1961).
22. S. Mataka, S. Ishi-i, and M. Tashiro, *Rep. Res. Inst. Ind. Sci.*, Kyushu University, **73**, 39 (1982).
23. S. Mataka, S. Ishi-i, and M. Tashiro, *J. Org. Chem.*, **43**, 3730 (1978).
24. J. Weiss and H. Piechaczek, *Z. Naturforsch.*, *B*, **18**, 1139 (1963).
25. S. Mataka, K. Takahashi, H. Yamamoto, and M. Tashiro, *J. Chem. Soc. Perkin Trans.* **I**, 2417 (1980).
26. I. Ruppert, V. Bastian, and R. Appel, Chem. Ber., **107**, 3426 (1974).
27. H. W. Roesky and M. Dietl, *Angew. Chem.*, **85**, 453 (1973).
28. D. Haenssgen and W. Roelle, *J. Organomet. Chem.*, **56**, C14 (1973).

29. H. W. Roesky and H. Wiezer, *Angew. Chem.*, **85**, 722 (1973).
30. Idem. *ibid.*, **87**, 254 (1975).
31. H. W. Roesky, G. Holtschneider, H. Wiezer, and B. Krebs, *Chem. Ber.*, **109**, 1358 (1976).
32. H. W. Roesky and A. Hamza, *Angew. Chem.*, **88**, 226 (1976).
33. E. Fluck, M. Becke-Goehring, and G. Z. Dehoust, *Z. Anorg. Allg. Chem.*, **312**, 60 (1970).
34. E. M. Holt and S. L. Holt, *J. Chem. Soc. Chem. Comm.*, 1704 (1970).
35. M. Becke-Goehring and D. Schläfer, *Z. Anorg. Allg. Chem.*, 356, 234 (1968).
36. R. Gleiter, *J. Chem. Soc.* **A**, 3174 (1970).
37. M. R. Brinkman and C. W. Allen, *J. Am. Chem. Soc.*, **94**, 1550 (1972).
38. W. L. Mock and I. Mehrotra, *J. Chem. Soc. Chem. Comm.*, 123 (1976).
39. A. M. Griffin and G. M. Sheldrick, *Acta Cryst.*, **B31**, 895 (1975).
40. R. R. Adkins and A. G. Turner, *Inorg. Chim. Acta*, **25**, 233 (1977).
41. W. Bludssus and R. Mews, *J. Chem. Soc. Chem. Comm.*, 123 (1977).
42. R. Appel, M. Montenarh, and I. Ruppert, *Chem. Ber.*, **108**, 582 (1977).
43. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
44. M. Tashiro, S. Mataka, and K. Takahashi, *Heterocycles*, **6**, 933 (1977).
45. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
46. *Idem.*, *Heterocycles*, **20**, 2047 (1983).
47. S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, **16**, 1009 (1979).
48. A. D. Josey, "Abstracts of the 15th National Meeting of the American Chemical Society", San Francisco, California, 1968, p. 14.
49. W. Bludssus and R. Mews, *J. Chem. Soc. Chem. Comm.*, 35 (1979).
50. V. Bertini and P. Pino, *Angew. Chem.*, **77**, 262 (1965).
51. V. Bertini and A. De Munno, *Gazz. Chim. Ital.*, **97**, 1614 (1967).
52. V. Bertini, A. De Munno, and A. Marraccini, *J. Org. Chem.*, **37**, 2587 (1972).
53. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
54. S. Mataka, A. Hosoki, K. Takahashi, and M. Tashiro, *Synthesis*, 524 (1979); *J. Heterocycl. Chem.*, **17**, 1681 (1980).
55. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
56. S. Mataka, A. Hosoki, K. Takahashi, and M. Tahsiro, *Synthesis*, 976 (1982).
57. S. Mataka, K. Takahashi, and M. Tashiro, unpublished.
58. S. Mataka, K. Takahashi, S. Shiwaku, and M. Tashiro, *J. Chem. Soc. Chem. Commun.*, 1136 (1983).
59. S. Mataka, K. Takahashi, and M. Tashiro, *J. Heterocycl. Chem.*, **14**, 963 (1977).

Note Added in Proof

Very recently, X-ray analyses were carried out by C. W. Rees et al.[1] on some of the minor products of the reaction of N_4S_4 with dimethyl acetylenedicarboxylate, diphenylacetylene, and phenylacetylene. The results revealed that the previous assignments are incorrect and the products contain novel ring systems, as shown below. The reaction products with DMAD, **41** (R = CO_2Me) and **43**, are a planar 10π electron aromatic trithiadiazepine and trithiatriazepine, respectively. The 1:1-adduct (37) of N_2S_2 with diphenylacetylene is a thermally stable 1,4,2,6-dithiadiazine. The deep violet compound **34a** obtained in the reaction with phenylacetylene has an interesting bicyclic structure. The 1,2,5-thiadiazole and 1,3,2-dithiazole rings are coplanar and the interannular S...N separation of 2.695 Å suggests a small interaction between two atoms.



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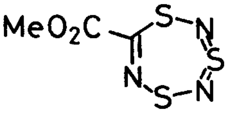
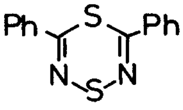
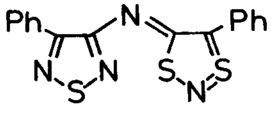


43



37



34a

Reference

1. S. T. A. K. Daley, C. W. Rees and D. J. Williams, *J. Chem. Soc. Chem. Com.*, **55**, 57 (1984).