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Studies of Thioiminocarbonates. I. The Formation and Decomposition of *O*-Alkyl *S*-Aryl Thioiminocarbonates in the Reaction of Aryl Thiocyanates with Alcohols in the Presence of the Cyanide Ion[1]

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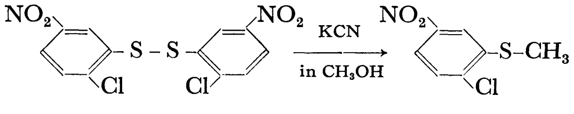
The reactions of aryl thiocyanates (I) with alcohol in the presence of cyanide ion were found to give alkyl aryl sulfides (III). The intermediate was isolated in the case of *p*-tolyl thiocyanate with methanol at 0°C and was determined to be *O*-methyl *S*-*p*-tolyl thioiminocarbonate (IIa) on the basis of NMR and IR spectral studies. The treatment of IIa with the cyanide ion afforded methyl *p*-tolyl sulfide (IIIa) in a high yield. When a mixture of an equimolecular amount of *O*-methyl *S*-*p*-tolyl thioiminocarbonate (IIa) and *O*-ethyl *S*-*p*-chlorophenyl thioiminocarbonate (IId) was treated with sodium cyanide in ethanol, all the anticipated sulfides——methyl *p*-tolyl sulfide (IIIa), *p*-tolyl sulfide (IIIb), methyl *p*-chlorophenyl sulfide (IIIc) and ethyl *p*-chlorophenyl sulfide (IIId)——were isolated. The mechanistic route, which involves the addition of alcohol to aryl thiocyanate, and the dissociation of the resulting *O*-alkyl *S*-aryl thioiminocarbonate (II) into aryl mercaptide ion and aryl cyanate, was proposed.

In the course of the work on the desulfurization of disulfides with the cyanide ion,[2] an interesting reaction was observed. When bis(2-chloro-5-nitrophenyl) disulfide was treated with potassium cyanide in methanol, methyl 2-chloro-5-nitrophenyl sulfide was isolated (Eq. (1)):



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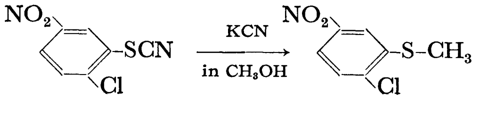

(2)

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[1] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

[2] To be published elsewhere.

Methyl 2-chloro-5-nitrophenyl sufide was also obtained in the reaction of 2-chloro-5-nitrophenyl thiocyanate with potassium cyanide under the same reaction conditions (Eq. (2)). The formation of alkyl aryl sulfide was ascribed to the reaction of aryl thiocyanate, which is the intermediate postulated for the desulfurization of diaryl disulfide by the cyanide ion.[2]

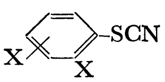
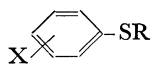
The present study was undertaken in order to clarify the reaction mechanism of the formation of sulfide and to isolate the intermediate formed when aryl thiocyanate is treated with alcohol in the presence of the cyanide ion.

Results and Discussion

Formation of Alkyl Aryl Sulfides in the Reaction of Aryl Thiocyanates with Alcohols in the Presence of the Cyanide Ion. When aryl thiocyanate was treated with alcohol in the presence of an equimolecular amount of sodium (or potassium) cyanide, alkyl aryl sulfide was easily obtained in a fairly good yield. The results are summarized in Table 1. In order to examine the general application of this novel reaction, we attempted to prepare benzyl and *n*-butyl aryl sulfide by the same procedure. However, sodium cyanide and potassium cyanide were only slightly soluble in these alcohols. This was overcome by using dimethyl sulfoxide as the solvent or by using tetraethylammonium cyanide as the cyanide-ion precursor in acetonitrile. Thus, benzyl *p*-tolyl sulfide was obtained in a 68% yield in the reaction of *p*-tolyl thiocyanate with benzyl alcohol in the presence of sodium cyanide in DMSO, and *n*-butyl *p*-tolyl sulfide was obtained in a 59% yield by using tetraethylammonium cyanide in a mixture of

TABLE 1. FORMATION OF ALKYL ARYL SULFIDES IN THE REACTION OF ARYL THIOCYANATES WITH ALCOHOLS IN THE PRESENCE OF CYANIDE ION

I III

Aryl thiocyanate  X	Alcohol[a] ROH R	Cyanide Ion	React. temp. (°C)	React. time (hr)	Product[b]  (%)
p-Me–N	Me	NaCN	60	3	50
o-Me	Me	NaCN	50	3	59
m-Me	Me	NaCN	50	3	50
p-Me	Me	NaCN	50	3	55
p-Me	Me	NaCN (2 eq. exess)	50	3	58
p-Me	Me	NaCN	0, 50[c]	0.5, 3[c]	66
p-Me	*n*-Bu	Et_4NCN (in CH_3CN)[d]	r.t.	21	59
p-Me	*n*-Bu	NaCN (in DMSO)[d]	r.t.	22	60
p-Me	Me	NaCN	50	24	78
p-Me	Bz[e]	NaCN (in DMSO)[d]	50	20	68
H	Me	NaCN	r.t.	3	51
o-Cl	Et	NaCN	r.t.	5	47
o-Cl	*n*-Pr	NaCN	50	4	29
o-Cl	*n*-Pr	NaCN (in DMSO)[d]	50	5	50
o-Cl	*i*-Pr	NaCN (in DMSO)[d]	50	5	34
m-Cl	Me	NaCN	r.t.	3	61
p-Cl	Me	NaCN	50	1	59
p-Br	Me	NaCN	r.t.	5	59
p-SCN	Me	NaCN (2 eq. exess)	50	4	37
o-NO_2	Me	NaCN	45	1	70
o-NO_2	Et	NaCN	50	2	36
m-NO_2	Me	NaCN	r.t.	0.5	66
m-NO_2	Et	NaCN	r.t.	1	50
p-NO_2	Me	NaCN	50	2	70
2-Cl-5-NO_2	Me	KCN	reflux	4	48
2-NO_2-4-Cl	Et	NaCN	50	4	27

a) Alcohol was used as solvent
b) Isolated yield
c) 0.5 hr at 0°C, then 3 hr at 50°C
d) Mixture of alcohol and DMSO or CH_3CN
e) Benzyl

Table 2. Formation of alkyl aryl sulfides in the reaction of *O*-alkyl *S*-aryl thioiminocarbonates with bases

II	Solvent	Base	React. temp. (°C)	React. time (hr)	Yield of Sulfide (%)
IIa	MeOH	NaCN	50	3	IIIa (55)
IIa	DMSO	NaCN	r.t.	5	IIIa (81)
IIb	EtOH	IR-45[a]	60	12	IIIb (53)
IIb	EtOH	b	reflux	7.5	c

a) Weak basic ion-exchange resin Amberlite IR-45 (OH-form)
b) Without base
c) 87% of starting material (IIb) was recovered unchanged.

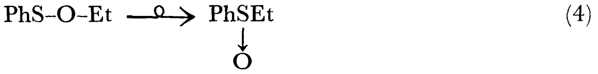
Table 3. Formation of alkyl aryl sulfides in the reaction of *O*-alkyl *S*-aryl thioiminocarbonates with cyanide ion

II	Cyanide Ion	Solvent	Reaction Condition		Yield of Sulfide	
			Temp. (°C)	Time (hr)	IIIa	IIb
IIa (0.05 mol)	NaCN (0.05 mol)	EtOH (200 m*l*)	50	3	67% (100)	0% (0)
IIb (0.05 mol)	NaCN (0.05 mol)	MeOH (200 m*l*)	50	3	7% (90)	64% (10)

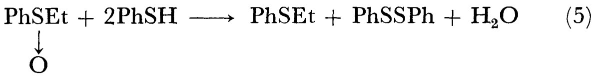
n-butyl alcohol (20 m*l*) and acetonitrile (50 m*l*).

Ross[3] reported the formation of ethyl phenyl sulfide in the reaction of phenyl thiocyanate and sodium ethoxide in ethanol; he proposed the following pathway:

$$2\mathrm{PhSCN} + 2\mathrm{EtONa} \longrightarrow \mathrm{PhSNa} + \mathrm{EtOCN} + \mathrm{PhS\text{-}O\text{-}Et} \qquad (3)$$



$$\mathrm{PhS\text{-}O\text{-}Et} \xrightarrow{\ \ } \underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{PhSEt}} \qquad (4)$$

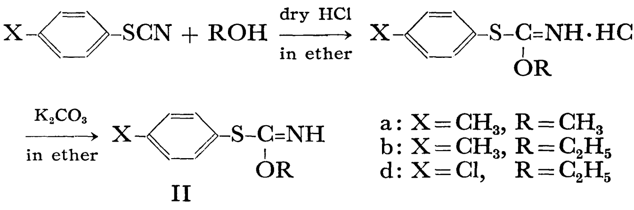


$$\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{PhSEt}} + 2\mathrm{PhSH} \longrightarrow \mathrm{PhSEt} + \mathrm{PhSSPh} + \mathrm{H_2O} \qquad (5)$$

However, he reported that ethyl phenyl sulfide was not obtained in the reaction of ethyl benzenesulfenate and thiophenol in ethanol containing sodium ethoxide. This result shows that sulfenate is not the intermediate. Recently, Mislow *et al.*[4] reported that methyl *p*-toluenesulfenate does not rearrange to methyl *p*-tolyl sulfoxide. Thus, there remains much doubt about the pathway in Eqs. (3)—(5).

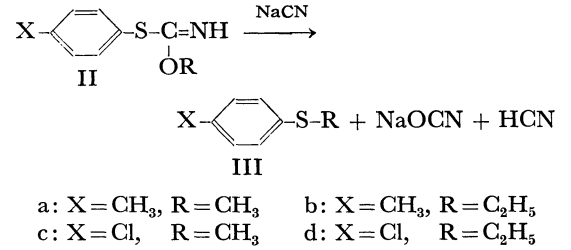
When *p*-tolyl thiocyanate was treated with sodium cyanide in methanol at 0°C, methyl *p*-tolyl sulfide (38%) and a pale yellow oil (2.1 g) were obtained. This oil showed a strong infrared band at 1634 cm^{-1} (C=N) and a weak band at 3360 cm^{-1} (NH), and the NMR peaks at τ 6.40 ($\mathrm{OCH_3}$) and at τ 3.45 (NH), in accordance with the expected formation of *O*-methyl *S*-*p*-tolyl thioiminocarbonate (IIa) as the intermediate.

The *O*-alkyl *S*-aryl thioiminocarbonates (II) were synthesized independently by the following procedure, similar to that reported by Knorr.[5] The results are reported in Table 5.



Scheme 1

Formation of Alkyl Aryl Sulfides from O-*Alkyl* S-*Aryl Thioiminocarbonates*. *O*-Alkyl *S*-aryl thioiminocarbonates (II) were treated with sodium cyanide in alcohol. In all the cases studied, alkyl aryl sulfide (III) was isolated in a fairly good yield. In DMSO, IIIa was obtained in an 81% yield, since the basicity of the cyanide ion and the nucleophilicity of the mercaptide ion were enhanced in dipolar aprotic solvents.[6] The results are reported in Table 2.



Scheme 2

The reaction of IIa with sodium cyanide in ethanol afforded IIIa exclusively, while the reaction of IIb in methanol gave a mixture of sulfides, which were shown by glc to be IIIb (64%) and IIIa (7%). These results show that the alkyl moiety of III was derived from that of II, not from the alcohol used as a solvent.

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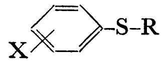
[3] J. Ross, *J. Amer. Chem. Soc.*, **56**, 727 (1934).

[4] E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966).

[5] A. Knorr, *Ber.*, **49**, 1735 (1916).

[6] A. J. Parker, "Advances in Organic Chemistry, Methods and Results," Vol. 5, ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1965), p.l.

Table 4. The analytical data and physical constants of alkyl aryl sulfides

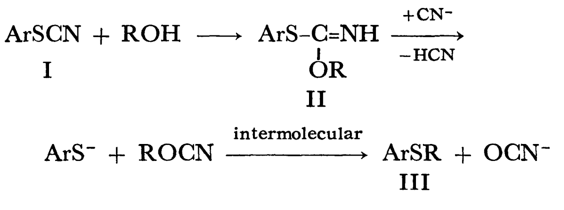


X	R	Mp (°C) (Bp °C/mmHg)	Analysis % Found (Calcd) C	H	N	S	Cl
p-Me_2N	Me	(115/3)	64.39 (64.42)	7.95 (7.83)	8.53 (8.37)	18.89 (19.17)	
p-CH_3	*n*-Bu	(142/27)	73.03 (73.30)	8.86 (8.95)		17.47 (17.75)	
p-CH_3	Bz	42—43	78.15 (78.45)	6.67 (6.58)		15.16 (14.96)	
o-Cl	Et	(123/18)	55.91 (55.64)	5.53 (5.25)		18.63 (18.57)	20.75 (20.53)
o-Cl	*n*-Pr	(135/18)	57.89 (57.90)	6.10 (5.94)		17.21 (17.17)	18.77 (18.99)
o-Cl	*i*-Pr	(130/22)	58.13 (57.90)	5.95 (5.94)		17.33 (17.17)	19.11 (18.99)
m-Cl	Et	(118/18)	55.39 (55.64)	5.16 (5.25)		18.36 (18.57)	20.82 (20.53)
o-NO_2	Me	60—61	49.73 (49.69)	4.10 (4.17)	8.38 (8.28)	18.97 (18.95)	
p-NO_2	Me	69—70	49.62 (49.69)	4.11 (4.17)	8.51 (8.28)	18.83 (18.95)	
2-Cl-5-NO_2	Me	97—99	40.98 (41.28)	2.87 (2.97)	6.92 (6.88)	15.83 (15.74)	17.39 (17.42)
2-NO_2-4-Cl	Et	95—96	44.41 (44.14)	3.64 (3.70)	6.53 (6.44)	15.01 (14.73)	16.46 (16.29)

This was also confirmed by the reaction of IIa with sodium cyanide in DMSO, which gave IIIa exclusively and in a high yield (Table 3).

Crossover Experiment with O-*Alkyl* S-*Aryl Thioiminocarbonates.* In order to find a clue to the mechanism of the formation of alkyl aryl sulfide (III) from *O*-alkyl *S*-aryl thioiminocarbonate (II), a crossover experiment using a mixture of *O*-methyl *S*-*p*-tolyl thioiminocarbonate (IIa) and *O*-ethyl *S*-*p*-chlorophenyl thioiminocarbonate (IId) was made. The mixture of IIa and IId was treated with sodium cyanide in ethanol, and the resulting mixture of sulfides was analyzed by glc. All four sulfides, *i.e.*, IIIa (23.8 mol%), IIIb (9.7 mol%), IIIc (22.8 mol%), and IIId (43.7 mol%), were found in the reaction mixture. Since IIa underwent no ester exchange with the ethanol used as the solvent, the ethyl moiety in IIIb is probably derived from that of IId.

On the basis of the observations presented earlier, we propose a following mechanism involving the dissociation of II into the aryl mercaptide ion and alkyl cyanate for the formation of sulfide:



$$\underset{\mathrm{I}}{\mathrm{ArSCN}} + \mathrm{ROH} \longrightarrow \underset{\mathrm{II}}{\mathrm{ArS{-}\underset{OR}{\underset{|}{C}}{=}NH}} \xrightarrow[-\mathrm{HCN}]{+\mathrm{CN}^-}$$

$$\mathrm{ArS^-} + \mathrm{ROCN} \xrightarrow{\text{intermolecular}} \underset{\mathrm{III}}{\mathrm{ArSR}} + \mathrm{OCN^-}$$

Scheme 3

Direct evidence for the existence of aryl mercaptide was obtained by the reaction of IIa with sodium cyanide in the presence of 2,4-dinitro-chlorobenzene, which is known to be a good mercaptide ion scavenger.[7] Thus the reaction of IIa (0.05 mol) with sodium cyanide (0.05 mol) in the presence of 2,4-dinitro-chlorobenzene (0.05 mol) in methanol afforded 2,4-dinitrophenyl *p*-tolyl sulfide in a 24% yield.

Kinetic studies of the formation and the decomposition of II will be reported in forthcoming papers.

Experimental

The melting points are uncorrected; the glc analyses were carried out with a Yanagimoto GCG-5DH chromatograph (Silicone DC-550, 190°) and with a Hitachi-Perkin-Elmer F-6D chromatograph (BDS-15 capillary column, 110°). The IR spectra were recorded on Nippon Bunko IR-S and DS-402G spectraphotometers. The NMR spectra were obtained on a Nihon-Denshi JNM 3H-60 spectrometer.

Reaction of Bis(2-chloro-5-nitrophenyl) Disulfide with Potassium Cyanide in Methanol. A solution of bis(2-chloro-5-nitrophenyl) disulfide (4.7 g, 0.0125 mol) and potassium cyanide (1 g, 0.0154 mol) in 200 m*l* of methanol was stirred for 4 hr under reflux. The precipitates were then removed by filtration, and water was added to the filtrate. The resulting yellow solid was separated by filtration; subsequent recrystallization from methanol gave 2 g of pale yellow needles (87%); mp 98—99°C; NMR ($CDCl_3$): τ 7.45 (SCH_3).

Found: C, 41.19; H, 2.90; N, 6.99; S, 15.76; Cl, 17.65%. Calcd for $C_7H_6NO_2SCl$: C, 41.28; H, 2.97; N, 6.88; S, 15.74; Cl, 17.42%.

Aryl Thiocyanates. Aryl thiocyanates (I) were prepared by the Sandmeyer reaction of the corresponding anilines.[8]

Formation of Alkyl Aryl Sulfides from Aryl Thiocyanates. General Procedure: Into a mixture of aryl thiocyanate (I, 0.05 mol) and alcohol (200 m*l*), powdered sodium cyanide

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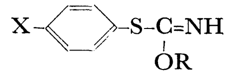
[7] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.*, **54**, 1985 (1932).

TABLE 5. PREPARATIONS AND PHYSICAL PROPERTIES *O*-ALKYL *S*-ARYL THIOIMINOCARBONATES



II	X	R	Yield (%)	BP °C/mmHg	Analysis C%	Found H%	(Calcd) N%
IIa	CH_3	CH_3	49	103—106/3	59.89	6.28	7.93
					(59.64)	(6.12)	(7.73)
IIb	CH_3	C_2H_5	52	112—114/3	61.60	6.81	7.30
					(61.50)	(6.71)	(7.17)
IId	Cl	C_2H_5	35	125—128/5	50.27	4.75	6.28
					(50.11)	(4.67)	(6.49)

TABLE 6. PROTON CHEMICAL SCHIFT τ OF *O*–ALKYL *S*–ARYL THIOIMINOCARBONATES
(Solvent: CCl_4; internal standard: TMS)

II	(CH_3-CH_2-O-)		(CH_3O-)	(C=NH)	(CH_3Ph)	(aromatic)
	CH_3-	-CH_2-				
IIa			6.40s	3.45s	7.75s	3.10m
IIb	8.72t	5.80q		3.20s	7.66s	2.72m
IId	8.74t	5.80q		3.18s		2.62m

TABLE 7. INFRARED FREQUENCIES (cm^{-1}) OF *O*-ALKYL *S*-ARYL THIOIMINOCARBONATES

II:	cm^{-1}								
IIa:	3360m,	2970m,	1634vs,	1433s,	1265vs,	1230vs,	1060vs,	930m,	813s
IIb:	3320m,	2980s,	1628vs,	1495m,	1260vs,	1228vs,	1060vs,	1015m,	810s
IId:	3350m,	3000m,	1636vs,	1482s,	1260vs,	1227vs,	1095s,	1013s,	823s

or potassium cyanide (0.05 mol) was stirred. After stirring had been continued for an appropriate period (see Table 1), the sodium (potassium) cyanate was removed by filtration. The filtrate and alcoholic washing were then combined, after which the usual work-up afforded alkyl aryl sulfide.

Preparation of O-*Alkyl* S-*Aryl Thioiminocarbonates. General Procedure*: Into a mixture of aryl thiocyanate (I, 0.134 mol) and absolute alcohol (0.134 mol), a stream of dry hydrogen chloride was introduced at 0°C. After the solution had been solidified, dry ether was added and the pale yellow solid of *O*-alkyl *S*-aryl thioiminocarbonate hydrochloride was pulverized and filtered. The dry hydrochloride was suspended in ether, and an aqueous solution of potassium carbonate was stirred in at 0°C. The ethereal layer was separated and dried with anhydrous sodium sulfate. Distillation *in vacuo* gave II as a transparent liquid. The physical constants and analytical data of II are reported in Table 5, Table 6, and Table 7.

Isolation of the Intermediate in the Reaction of p-*Tolyl Thiocyanate with Sodium Cyanide in Methanol.* Into a mixture of Ia (7.5 g, 0.05 mol) and absolute methanol (170 m*l*), powdered sodium cyanide (2.5 g, 0.05 mol) was stirred. After the stirring had been continued for 1 hr at 0°C, the solution was filtered. The filtrate was concentrated under reduced pressure, and the residue was extracted with ether. The ethereal solution was washed with a saturated aqueous solution of sodium chloride and dried with anhydrous sodium sulfate. Distillation under reduced pressure gave 2.6 g of IIIa (38%) and a pale yellow oil (2.1 g); IR: 3360 cm^{-1} (NH) and 1634 cm^{-1} (C=N).

NMR (TMS): τ 3.20 (aromatic), τ 3.40 (NH), τ 6.40 (OCH_3) and τ 7.83 (CH_3). This oil was identified as IIa.

Formation of Alkyl Aryl Sulfides from O-*Alkyl* S-*Aryl Thioiminocarbonates.* Into a solution of IIa (9.1 g, 0.05 mol) in absolute methanol (200 m*l*), powdered sodium cyanide (2.5 g, 0.05 mol) was added. After stirring had then been continued for 3 hr at 50°C, the precipitated sodium cyanate (1.6 g) was removed by filtration. The filtrate was concentrated under reduced pressure, and the residue was extracted with ether. The distillation of the dried ethereal solution gave IIIa in 55% yield; bp 100—102°C/20 mmHg (lit,[9] bp 104—105°C/20 mmHg). NMR (TMS): τ 3.33 (aromatic), τ 7.80 (S–CH_3) and τ 7.88 (CH_3).

In an analogous way, IIa in ethanol gave 4.6 g of IIIa, while IIb in methanol afforded IIIa and IIIb (90:10) by glc.

Crossover Experiment between O-*Methyl* S-p-*tolyl Thioiminocarbonate (IIa) and* O-*Ethyl* S-p-*Chlorophenyl Thioiminocarbonate (IIa).* Sodium cyanide (1.5 g, 0.03 mol) was added to a solution of IIa (2.7 g, 0.015 mol) and IId (3.2 g, 0.015 mol) in absolute ethanol (130 m*l*). After stirring for 3 hr at 50°C, the work-up gave an oil which was found by glc analysis to be a mixture of IIIa (23.8 mol%), IIIb (9.7 mol%), IIIc (22.8 mol%), and IIId (43.7 mol%).

Isolation of 2,4-Dinitrophenyl p-*Tolyl Sulfide.* Into a

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8) a) L. Gattermann and W. Haussknecht, *Ber.*, **23**, 738 (1890). b) G. Thurnauer, *ibid.*, **23**, 769 (1890). c) F. Challenger and A. D. Collins, *J. Chem. Soc.*, **125**, 1377 (1924). d) J. W. Dienske, *Rec. Trav. Chim. Pays-Bas*, **50**, 21 (1931). e) F. Challenger, C. Higginbottom, and A. Huntington, *J. Chem. Soc.*, **1930**, 26. f) A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896). g) K. Brand and H. W. Leyerzapf, *ibid.*, **70**, 284 (1937).

9) H. Gilman and N. J. Beaber, *J. Amer. Chem. Soc.*, **47**, 1449 (1925).

mixture of IIa (9.1 g, 0.05 mol) and 2,4-dinitro-chlorobenzene (10.1 g; 0.05 mol) in absolute methanol (200 m*l*), powdered sodium cyanide (2.5 g, 0.05 mol) was stirred. After stirring had been continued for 3 hr at 50°C, the solution was concentrated under reduced pressure; the residue was then recrystallized from ethanol to afford 3.5 g (24%) of 2,4-dinitrophenyl *p*-tolyl sulfide as yellow needles; mp 102—103°C (lit,[5] mp 103°C).

The authors wish to acknowledge the enthusiastic assistance of Mr. Masao Nishikuri in carrying out this work.