Sulfurization of Isocyanides[1]

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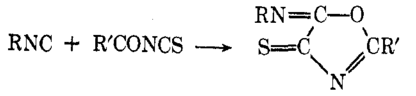
Both direct combination with elemental sulfur and reversible transfer of sulfur from an isothiocyanate transformed each of nine aryl isocyanides into the corresponding isothiocyanate. An equimolar mixture of phenyl isocyanide and phenyl isothiocyanate reacted with water in the presence of acid to form thiooxanilide in low yield.

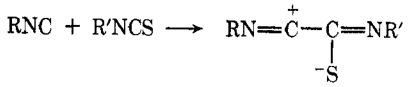
Sulfur transformed carbon monoxide in the presence of sodium acetate into carbon oxysulfide[2] and an isocyanide into an isothiocyanate.[3] Known for over a century this carbenoid reaction of an isocyanide has received little attention. The isocyano carbon also combined with selenium[3c] but failed to combine with either oxygen (without a catalyst)[4] or tellurium.[3c] Apparently these are reactions at nucleophilic isocyano carbon, $RN\overset{+}{\equiv}C{:}^{-}$.[5] A similar addition of sulfur to nucleophilic carbenes has been reported for diamino carbenes, $(R_2N)_2C{:}$[6a] and considered for diphenyl carbene, $(C_6H_5)_2C{:}$;[6b] however, an explanation for the formation of a thioketone based on initial dissociation of a tetraaminoethylene into a diaminocarbene followed by addition to sulfur[6a] has been challenged and replaced with one which calls for an initial attack on the π-electron system of the tetraaminoethylene.[6c]

$$(R_2N)_2C{=}C(NR_2)_2 \overset{?}{\rightleftharpoons} (R_2N)_2C{:}$$

$$(R_2N)_2C{=}C(NR_2)_2 \xrightarrow{S} (R_2N)_2C{=}S$$

A nucleophilic attack by an isocyano carbon may occur in the [4 + 1] addition of an isocyanide to an acyl isothiocyanate,[7] and a similar, but previously unknown, attack by isocyano carbon upon a monofunctional isothiocyanate would be expected to lead initially to a zwitterionic adduct. A comparable adduct of a diamino carbene has been obtained from the dimer, a tetraaminoethylene, and phenyl isothiocyanate.[8]





$$RNC + R'NCS \longrightarrow RN{=}\overset{+}{C}{-}\underset{\substack{|\\ {}^{-}S}}{C}{=}NR'$$

$$(R_2N)_2C{=}C(NR_2)_2 + C_6H_5NCS \longrightarrow (R_2N)_2\overset{+}{C}{-}C({=}NC_6H_5)\overset{-}{S}$$

Results

Aryl isocyanides, **1–9** were transformed into isothiocyanates **10–18** by heating each in benzene with sulfur, the preferred reagent, or with phenyl isothiocyanate (Scheme I) (Tables I and II). For three different systems a reversible transfer of sulfur from an isothiocyanate to an isocyanide was demonstrated (Table III).

SCHEME I

$$\underset{\mathbf{1\text{–}9}}{ArNC} + S \longrightarrow \underset{\mathbf{10\text{–}18}}{ArNCS}$$

$$ArNC + Ar'NCS \rightleftharpoons ArNCS + Ar'NC$$

Ar								
$CH_3OC_6H_4$			$O_2NC_6H_4$		$(CH_3O)_2C_6H_3$			C_6H_5–C_6H_4
o-	*m*-	*p*-	*m*-	*p*-	2,4-	2,5-	3,4-	*o*-
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
10	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**

TABLE I

ISOTHIOCYANATES FROM ISOCYANIDES AND SULFUR[a]

Isocyanides, ArNC			Isothiocyanates, ArNCS		
No.	mmol	Gc rt, min	No.	Yield, %	Gc rt, min
1	1.353	6.2	**10**	87.3[b]	12.8
2	1.353	4.2	**11**	44.2	10.8
3	1.353	5.5	**12**	65.0	14.0
4	1.014	4.2	**13**	76.2	8.2
5	1.014	4.0	**14**	79.6	8.5
6	1.000	8.8	**15**	77.5	16.8
7	1.227	4.2	**16**	83.6	7.4
8	1.000	1.9	**17**	82.8	3.2
9	0.894	6.2	**18**	97.6	10.8

[a] See Experimental Section for gc details; rt, retention time. [b] This value corresponds to 72.5% recovery of **1** and 87.3% yield of **10**. A duplicate experiment gave 78.5% recovery of **1** and 84.9% yield of **10**.

No interaction between **6** and **12** in benzene at room temperature could be detected after 64 hr and **12** was quantitatively recovered. Under similar conditions sulfur also failed to transform **6** into **15**. In refluxing methylene chloride, bp 39°, there was no interaction between **6** and **12** but a trace of **15** was produced after 64 hr from the combination of **6** and sulfur.

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[1] Financial support was received from NASA Grant No. NGR 14-012-004.

[2] V. P. Savin, P. V. Naumkin, G. E. Semenova, and S. Ya. Kazakova, *Khim. Prom (Moscow)*, **44**, 550 (1968); *Chem. Abstr.*, **69**, 78824r (1968).

[3] (a) W. Weith, *Chem. Ber.*, **6**, 210 (1873). (b) J. U. Nef, *Justus Liebigs Ann. Chem.*, **280**, 291 (1894). (c) M. Lipp, F. Dallacker, and I. Meier zu Köcker [*Monatsh. Chem.*, **90**, 41 (1959)] reported thermal sulfurization of isocyanides in the presence of amines to produce thioureas. An intermediate isothiocyanate was assumed. In a similar reaction with selenium, an intermediate isoselenocyanate was apparently transformed into a selenourea. (d) Y. Kowaoka [*J. Soc. Chem. Ind., Jap.*, **43**, 151 (1940); *Chem. Abstr.*, **34**, 6487 (1940)] treated phenyl isocyanide with sulfur and carbon disulfide at 151° for 4 hr at pressures up to 200 psi. A solid black mass containing a trace of mercaptobenzothiazole, the only identified product, confirms the earlier report[3a] that trace quantities of phenyl isothiocyanate may be formed from phenyl isocyanide and sulfur.

[4] S. Otsuka and M. Tatsuno, Japanese Patent 70 19,884 (1970); *Chem. Abstr.*, **73**, 98442a (1970).

[5] I. Ugi, "Isonitrile Chemistry," Academic Press, New York, N. Y., 1971, p 66.

[6] (a) H.-W. Wanzlick and B. König, *Chem. Ber.*, **97**, 3513 (1964). (b) N. Latif and I. Fathy [*J. Org. Chem.*, **27**, 1634 (1962)] suggested the intermediate formation of a thiocarbonyl compound by the reaction between a carbene and sulfur in the overall transformation of a diazoalkane and sulfur into a tetrasubstituted ethylene sulfide. (c) D. M. Lemal in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, pp 701–748.

[7] (a) R. Neidlein, *Angew. Chem.*, **76**, 500 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 446 (1964); *Chem. Ber.*, **97**, 3476 (1964); *Arch. Pharm. (Weinheim)*, **298**, 124 (1965). (b) J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 3831 (1965); H. Schenk, *ibid.*, **99**, 1258 (1966).

[8] H. E. Winberg and D. D. Coffman, *J. Amer. Chem. Soc.*, **87**, 2776 (1965).

TABLE II

ISOTHIOCYANATES FROM ISOCYANIDES AND PHENYL ISOTHIOCYANATE[a]

Isocyanides, ArNC		Isothiocyanates, ArNCS	
No.	mmol	No.	Yield, %
1	1.000	**10**	46.1
2	1.128	**11**	34.0[b]
3	1.209	**12**	55.7[b-d]
4	1.014	**13**	52.5
5	1.014	**14**	26.5[e,f]
6	0.614	**15**	66.8[b]
7	1.227	**16**	65.6
8	1.000	**17**	36.4

[a] See Experimental Section for gc details and Table I for each retention time. Amount of phenyl isothiocyanate was equimolar with **1**, **3**, **4**, **5**, and **8**; in a molar excess of 40% with **2** and 20% with **6**; and in a molar deficiency of 8% with **7**. The presence of phenyl isothiocyanate was detected during the work-up of each reaction mixture by gc and tlc. In the reaction with **6** it was recovered in 62.0% (0.459 mmol). [b] Based on amount isolated from a column chromatographic fraction. Gc analysis was abandoned because of tailing. [c] By ir and tlc *m*-anisidine and its *N*-formyl derivative were detected. [d] Reaction time 90 hr. [e] Determined by a gc comparison of a column chromatographic fraction with authentic data. [f] In a duplicate run a 34% yield of **14** was determined by gc analysis of a concentrated product mixture in chloroform. The higher yield is attributed to further reaction at the gc temperature of 190°.

TABLE III

REVERSIBLE TRANSFER OF SULFUR FROM AN ISOTHIOCYANATE TO AN ISOCYANIDE

$$\text{ArNC} + \text{Ar'NCS} \rightleftharpoons \text{ArNCS} + \text{Ar'NC}$$

Mixture composition obtained from an initial equimolar mixture of starting materials, ArNC and Ar'NCS			
ArNC, %[a]	Ar'NCS, %[a]	ArNCS, %[a]	Ar'NC, %[a]
4, 45.0[b]	**12**, 43.2[b]	**13**, 2.2[c]	**3**, trace[d]
3, 29.6[b,e]	**13**, 30.6[f]	**12**, 2.0[f]	**4**, *e*
5, 43.3[b]	**12**, 42.4[b]	**14**, 2.7[c]	**3**, trace[d]
3, 42.1[b]	**14**, 47.2[b]	**12**, 1.1[f]	**5**, none
6, 37.1[f]	**12**, 43.4[f]	**15**, 4.6[f]	**3**, 4.1[f]
3, 44.4[b]	**15**, 44.9[b]	**12**, 3.0[f]	**6**, 1.5[b]
6, 32.8[c]	**12**, 34.9[c]	**15**, 8.1[c]	**3**, 7.2[c]
3, 38.8[c]	**15**, 36.2[c]	**12**, 4.4[c]	**6**, 3.0[c]

[a] Proportion of reaction mixture. Unaccounted for material is assumed to be polymeric. [b] From weight of material isolated by column chromatography. [c] The amount was determined by gc analysis of the concentrated reaction mixture. The differences for mixtures of **6**, **12**, **15**, and **3** are attributed to further reaction at the temperature, 170°, of the gc analysis. [d] Detected by tlc and by odor, identified by comparison with authentic data. [e] The *N*-formyl derivatives of *p*-anisidine and of *m*-nitroaniline were detected by tlc and identified by comparison with authentic values. [f] From gc analysis of a column chromatographic fraction and comparison with authentic data.

p-Methoxyphenyl isothiocyanate (**12**) transformed *m*- and *p*-nitrophenyl and 2,4-dimethoxyphenyl isocyanides (**4**, **5**, and **6**) into the corresponding isothiocyanates **13** and **14** in moderate yields and **15** in higher yield (Table III). Similar reactions with phenyl isothiocyanate (Table II) also revealed higher reactivity in **6** when compared with a nitrophenyl isocyanide (**4** or **5**).

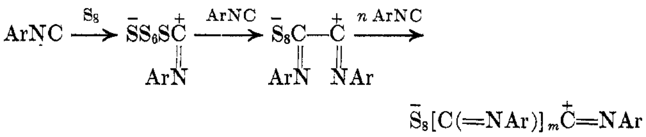
Phenyl isothiocyanate and 2,4-dimethoxyphenyl isothiocyanate (**15**) were each more efficient than a nitrophenyl isothiocyanate (**13** or **14**) in transferring sulfur to *p*-methoxyphenyl isocyanide (**3**).

In very low yield an equimolar mixture of phenyl isocyanide and phenyl isothiocyanate interacted with water on a silica gel column to give thiooxanilide.

Discussion

When heated with sulfur, ethyl and phenyl isocyanides were converted into isothiocyanates; however, no more than a trace amount of unisolated phenyl isothiocyanate was found and a percentage yield of ethyl isothiocyanate was not reported.[3a,b] Without isolation, other isothiocyanates have probably been formed by this reaction; *e.g.*, a thiourea from an isocyanide, sulfur, and an amine probably came from an intermediate isothiocyanate.[3c] Heating phenyl isocyanide, sulfur, and carbon disulfide under pressure gave a solid black mass,[3d] perhaps polymeric.

Identification of a polymer of an aryl isocyanide has not been reported; however, both a bis anil of 4-azanaphthquinone-1,2 which is an orange-red trimer[9] and a bis anil of indigo which is a blue-black tetramer[10] are obtained from phenyl isocyanide. Just as α,α addition, generally initiated by a nucleophilic isocyano carbon, describes many of its other chemical reactions, α,α self-addition, with the formation of only carbon to carbon bonds, would result in the polymerization of an isocyanide.[11] By combining with an isocyano carbon, sulfur could conceivably catalyze polymerization and, at the same time, produce an isothiocyanate.[12] A nucleophilic attack by isocyano carbon upon sulfur is assumed.



$$\text{Ar}\underset{\cdot\cdot}{\text{N}}\text{C} \xrightarrow{\text{S}_8} \bar{\text{S}}\text{S}_6\text{S}\overset{+}{\underset{\underset{\text{ArN}}{\|}}{\text{C}}} \xrightarrow{\text{ArNC}} \bar{\text{S}}_8\underset{\underset{\text{ArN}}{\|}}{\text{C}}-\overset{+}{\underset{\underset{\text{NAr}}{\|}}{\text{C}}} \xrightarrow{n\,\text{ArNC}} \bar{\text{S}}_8[\text{C}(=\text{NAr})]_m\overset{+}{\text{C}}=\text{NAr}$$

$$(\text{ArNC})_x\text{S}_8 \longrightarrow \text{ArNCS} + [(\text{ArNC})_{(x-1)} + \text{S}_7]$$

Three dimethoxyphenyl and two nitrophenyl isocyanides are transformed by sulfur into corresponding isothiocyanates in excellent yields, but the results are scattered for the reaction with the three isomeric methoxyphenyl isocyanides (Table I). Inductive substituent effects appear to influence these reactions, as expected in the absence of resonance interaction between the isocyano group and another ring substituent.[13] Possibly an ortho-substituent effect is needed to account for consistently high yields of **10**, **15**, **16**, and **18**. Intramolecular interaction between an *o*-methoxy or an *o*-phenyl substituent and the cationic center in the suggested intermediate adduct could

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(9) M. Passerini and T. Bonciana, *Gazz. Chim. Ital.*, **61**, 959 (1931).

(10) C. Grundmann, *Chem. Ber.*, **91**, 1380 (1958).

(11) T. Saegusa, Y. Ito, and S. Kobayashi [*Tetrahedron Lett.*, 521 (1967)] described a polymer of cyclohexyl isocyanide. F. Millich and R. G. Sinclair [*J. Polym. Sci.*, *Part A-1*, **6**, 1417 (1968); *Part C*, **22**, 33 (1968)] reported heterogeneous polymerization of alkyl isocyanides in the presence of a strong acid and a free-radical source. Liquid samples of isocyanides on long storage in amber bottles at room temperature also polymerized. An explanation for a poly-α-phenylethyl isonitrile with repeating imino units was based, in part, on chain propagation by a α,α self-addition to isocyano carbon and detection of the repeating imino group by ir absorption at 1625 cm^{-1} and uv absorption below 220 nm.

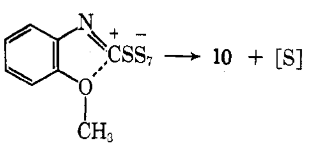
(12) T. G. Levi [*Gazz. Chim. Ital.*, **61**, 619 (1931)] reported polysulfides of aryl isothiocyanates, from which an aryl isothiocyanate may dissociate.

$$\text{C}_6\text{H}_5\text{NHC}(=\text{S})\bar{\text{S}}\overset{+}{\text{N}}\text{H}_4 + \text{S}_2\text{Cl}_2 \longrightarrow (\text{C}_6\text{H}_5\text{NC})_2\text{S}_8$$

$$(\text{C}_6\text{H}_5\text{NC})_2\text{S}_8 \xrightarrow[\text{KCN}]{\text{C}_2\text{H}_5\text{OH}} \text{C}_6\text{H}_5\text{NCS} + \text{NH}_4\text{SCN}$$

(13) P. v. R. Schleyer and A. Allerhand, *J. Amer. Chem. Soc.*, **84**, 1322 (1962); **85**, 866 (1963). L. L. Ferstandig, *ibid.*, **84**, 3553 (1962). Reference 5, pp 1–7.

improve the yield of product and decrease the amount of polymer formed. A similar effect might be expected for *o*-nitrophenyl isocyanide, but our efforts to prepare this unknown compound were unsuccessful.



Apart from an interest in the reaction mechanism for the reversible transfer of sulfur from an isothiocyanate to an isocyanide, application to organic synthesis will be limited. There is not only the problem of separating a product from the four-component reaction mixture but also the occurrence of competitive reactions which partially consume both isocyanides and isothiocyanates. These have not been investigated; nevertheless it is assumed that polymerization accounts for a tarry material collected at the top of the chromatographic column in the work-up of each reaction mixture. Trace amounts of formanilides can be attributed to hydration of isocyanides, perhaps by trace amounts of water in the reaction mixture, but more likely by water from the silica column.

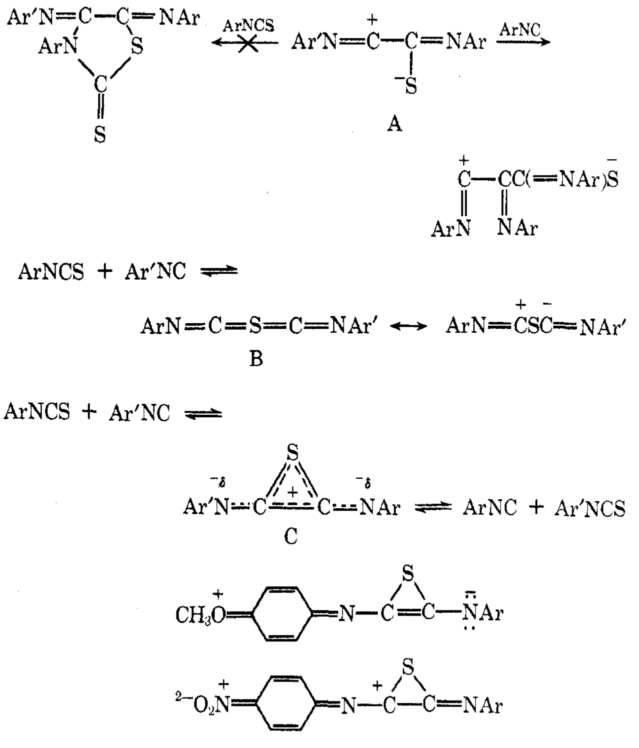
Product separation was fortuitously simplified when phenyl isothiocyanate was the sulfurization reagent. Apparently phenyl isocyanide was rapidly polymerized since no more than trace quantities were detected in any of the reaction mixtures. While this has undoubtedly brought about an increase in the yield of product isothiocyanate, thereby enhancing value in preparative work, sulfur is the reagent of choice for the sulfurization of an isocyanide.

As revealed (Table II) by recovery of starting material, *o*-methoxyphenyl and 2,5-dimethoxyphenyl isocyanides (**1** and **7**) appear to be the least reactive of the isocyanides studied in the presence of phenyl isothiocyanate while *m*-methoxyphenyl and 2,4-dimethoxyphenyl isocyanides (**2** and **6**) appear to be the most reactive. Since unrecovered **1** and **2** are mostly consumed in an unidentified reaction(s), **6** has been judged to be the most efficient of the isocyanides studied in capturing sulfur from phenyl isothiocyanate. *p*-Nitrophenyl isocyanide (**5**) appears to be the least efficient. Similarly **6** is more effective than either *m*- or *p*-nitrophenyl isocyanide (**4** or **5**) in taking sulfur from *p*-methoxyphenyl isothiocyanate (**12**); however, it must also participate more extensively in other reactions to account for total amount consumed (Table III).

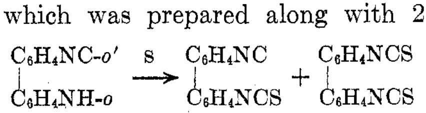
The transfer of sulfur to the isocyanide **3** from the isothiocyanates **13**, **14**, or **15** produced isothiocyanate **12** in yields of 10, 36, and 59%, respectively (Table III). Corresponding limits on competitive but uninvestigated consumption of starting material, including polymerization, were 38, 10, and 6%. Clearly the 2,4-dimethoxyphenyl group makes both the isocyanide **6** and also the isothiocyanate **15** the most productive of each kind for the sulfur transfer, perhaps as a result of inhibiting side reactions. A side reaction which is significant for its absence in all isocyanide–isothiocyanate systems in this study is the dipolar addition of an isothiocyanate to an assumed zwitterionic 1:1 adduct. In contrast the zwitterion $(R_2N)_2C^+$—C(=NC_6H_5)S^- readily combined with an isothiocyanate and other 1,3 dipolariphiles.[8] Of course an isothiocyanate may be a poor competitor with an isocyanide for a dipolariphile such as adduct A.

For the formation of an adduct, a nucleophilic attack by isocyano carbon upon isothiocyanato carbon was expected but has not been differentiated from an attack on sulfur. The latter might give initially a tetracovalent sulfur derivative B.[14] Both A and B are electron-localized forms of adduct C in which lower reactivity may be attributed to resonance. Electron donation, *e.g.*, by an *o*- or *p*-methoxyphenyl group, would tend to stabilize the cationic charge in C. While electron withdrawal, *e.g.*, by an *o*- or *p*-nitrophenyl group, would tend to stabilize the anionic center in C, such resonance interaction would favor an attack by isocyano carbon leading to polymerization (Scheme II).

SCHEME II



An unsuccessful attempt was made to detect an intramolecular "adduct" from 2-isocyano-2′-isothiocyanatobiphenyl which was prepared along with 2,2′-diisothiocyanatobiphenyl from 2,2′-diisocyanobiphenyl and sulfur.



$$\begin{matrix} C_6H_4NC\text{-}o' \\ | \\ C_6H_4NH\text{-}o \end{matrix} \xrightarrow{S} \begin{matrix} C_6H_4NC \\ | \\ C_6H_4NCS \end{matrix} + \begin{matrix} C_6H_4NCS \\ | \\ C_6H_4NCS \end{matrix}$$

On the other hand a low yield of thiooxanilide was obtained by passing a mixture of phenyl isocyanide and phenyl isothiocyanate over a silica gel column.[15] Addition of water to an intermediate zwitterion C (Ar = Ar′ = C_6H_5) would account for the product. In a similar manner a solid obtained in trace quantity from 2,4-dimethoxyphenyl isocyanide and 2,4-dimethoxyphenyl isothiocyanate may be the corresponding tetramethoxythiooxanilide; however, the tentative identi-

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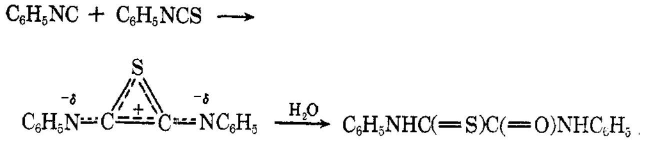
[14] M. Takaku, S. Mitamura, and H. Nozaki [*Tetrahedron Lett.*, 3651 (1969)] generated $(CH_3)_2N)_2C^+SC^-HCO_2CH_3$. M. Carmack, I. W. Stapleton, and R. Y. Yen [*Org. Prep. Proced.*, **1**, 255 (1969)] discuss and refer to hetero, tetravalent, sulfur intermediates.

[15] We are indebted to Dr. J. de Jong for first observing this reaction.

fication, supported by the mass spectrum, M^+ 376, and mp 230°, for the yellow solid needs to be confirmed. Further investigation in this area is planned.



$C_6H_5NC + C_6H_5NCS \longrightarrow$

$C_6H_5\overset{-\delta}{N}{\cdots}C{\cdots}C{\cdots}\overset{-\delta}{N}C_6H_5 \xrightarrow{H_2O} C_6H_5NHC(=S)C(=O)NHC_6H_5$

Experimental Section

Instrumental data were obtained from a Barber-Colman Model 5320 flame ionization gas chromatograph with an attached Sargent recorder equipped with an integrator, a Perkin-Elmer Model 237B grating infrared spectrophotometer, a Hitachi-Coleman Model 124 spectrophotometer, a Varian A-60A spectrometer, and a Perkin-Elmer Model 270 gas chromatograph and attached mass spectrometer. Elemental analyses were obtained from Micro-tech Laboratories, Chicago, Ill. For gc analyses the gas chromatograph was equipped with a stainless steel column, 8 ft by 0.25 in., of 5% GE, XE60 on Chromosorb G, 60-80 AW DMGS (Nuclear Chicago); nitrogen was the carrier gas. J. T. Baker silica gel powder, 60–200 mesh, in a column, 12 in. by 1 in., was the adsorbent in column chromatography. Hexane–benzene mixtures, with the ratio progressing from 1:0 to 0:1, eluted the column. Separation by tlc was achieved on strips of ChromAR sheet-500.

Sulfurization of 1 to 2 mmol of each isocyanide **1–9** by either elemental sulfur (1.0 to 1.5 molar excess) or phenyl isothiocyanate was carried out in a solution of 25 ml of anhydrous benzene at reflux temperature for 64 hr. Yields were based on recovered isocyanide and were determined by gc analysis of the concentrated reaction mixture in chloroform. The identity and amount of each component in a reaction mixture were determined by comparison with gc analysis of a standard solution of the authentic material. In addition each component of a reaction mixture was also identified by comparing ir and tlc absorption with authentic data and by mixture melting point wherever possible. Each gc analysis was carried out under a carrier gas pressure of 18–20 psi. The retention times (Table I) were obtained at a column temperature of 132° for **1**, **2**, **3**, **10**, **11**, and **12**; 190° for **4**, **5**, **7**, **13**, **14**, and **16**; 170° for **6** and **15**; 212° for **8** and **17**; and 175° for **9** and **18**. Phenyl isocyanide was occasionally detected by gc analysis of reaction mixtures described in Table II. It was more often detected by odor. Results are found in Tables I and II.

The reaction mixture of four components obtained by the reversible transfer of sulfur from an isothiocyanate to an isocyanide was analyzed for the forward and reverse reaction in three systems. Conditions for the reaction are identical with the ones described above. Reaction mixture composition was determined by gc and column chromatography. Results are found in Table III.

Preparation of Isocyanides. 3,4-Dimethoxyphenyl Isocyanide.—A mixture of 15.3 g (100 mmol) of 3,4-dimethoxyaniline in 125 ml of formic acid (88%) was heated under reflux for 2 hr. After vacuum distillation had removed excess formic acid and the residue had been treated with ice–water, organic material was extracted with chloroform, washed separately with dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water, and dried over magnesium sulfate. Filtration and then removal of solvent left 10.0 g (55%) of 3,4-dimethoxyformanilide as a colorless solid, mp 87–88°, which was recrystallized from a mixture of chloroform and ether.

A solution of 9.0 g (50 mmol) of 3,4-dimethoxyformanilide in 300 ml of methylene chloride and 25 ml of triethylamine in a 500-ml, three-necked, round-bottomed flask equipped with a condenser, a mechanical stirrer, and a condenser cooled by Dry Ice in acetone was cooled in an ice bath and stirred while phosgene gas was introduced through the Dry Ice–acetone cooled condenser until 110 drops were added. Stirring was continued for 1 hr and then ~100 ml of water was added to the reaction mixture. The organic layer was separated, washed with about 200 ml of water, dried over magnesium sulfate, and concentrated by evaporation. The residue was slurried with silica gel and chromatographed by a column, 10 in. by 1.5 in., of silica. Elution with 800 ml of a mixture of benzene–hexane (1:1) removed 6.5 g (79.7%) of 3,4-dimethoxyphenyl isocyanide **8**, mp 48°, as colorless crystals. An analytical sample was obtained by rechromatographing the crude product. Elution with hexane–benzene gave **8** as a colorless crystalline solid: mp 49–50°; ir ($CHCl_3$) 2128 cm^{-1} (NC); nmr ($CDCl_3$) δ 3.84 (s, 6 H, OCH_3), 6.7–7.1 (m, 3 H, aromatic); uv ($CHCl_3$) 254 nm (log ϵ 4.12), 285 (3.69), 292 (3.67); mass spectrum (70 eV) *m/e* 163 (M^+), 148, 120, 102, 93, 92. *Anal.* Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.59; N, 8.65. Other isocyanides were known.

Preparation of Isothiocyanates. 2,4-Dimethoxyphenyl Isothiocyanate.—To an ice-cooled solution of 4.1 g (20 mmol) of *N*,*N'*-dicyclohexylcarbodiimide in 10 ml of carbon disulfide and 4 ml of pyridine a solution of 3.06 g (20 mmol) of 2,4-dimethoxyaniline in 8 ml of pyridine was added dropwise with stirring. After the mixture stirred overnight, ether was added, and a precipitate of dicyclohexylthiourea was removed by filtration. After concentration the filtrate was taken up in chloroform and washed consecutively with water, dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water. After the mixture dried over magnesium sulfate, removal of solvent left a liquid which solidified and was purified chromatographically from a silica gel column. It was eluted immediately by 400 ml of a mixture of benzene–hexane (1:3) and isolated after removal of solvent as 3.05 g (78.2% yield) of a colorless solid: mp 52–53° (after several recrystallizations from hexane an analytical sample, mp 53–53.5°, was obtained); ir ($CHCl_3$) 2128–2041 cm^{-1} (NCS); uv ($CHCl_3$) 274 nm (log ϵ 4.05), 301 (4.06); nmr ($CDCl_3$) δ 3.83 and 3.90 (2 s, 6 H, OCH_3), 6.3–7.2 (m, 3 H, aromatic); mass spectrum (70 ev) *m/e* 195 (M^+), 180, 163, 152, 137, 120. *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.39; H, 4.65; N, 7.18; S, 16.40. Found: C, 55.24; H, 4.54; N, 7.06; S, 16.48.

The other isothiocyanates were each prepared by the same method or were commercially available. Previously reported[16] as an oil, 3,4-dimethoxyphenyl isothiocyanate was obtained as a colorless solid: mp 48–48.5°; nmr ($CDCl_3$) δ 3.83 (s, 6 H, OCH_3) 6.7–6.8 (m, 3 H, aromatic). *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.39; H, 4.65; N, 7.18; S, 16.40. Found: C, 55.49; H, 4.69; N, 7.07; S, 16.15.

Thiooxanilide was obtained by placing an equimolar mixture of phenyl isocyanide and phenyl isothiocyanate (20.0 mmol each) on a silica gel column. After elution of phenyl isothiocyanate by 500 ml of hexane and then phenyl isocyanide by a mixture of 400 ml of hexane–benzene (3:1), it was eluted from the column by a mixture of 400 ml of hexane-benzene (1:1) and isolated in trace amount as yellow needles, mp and mmp 142–144°,[17] *m/e* 256 (M^+).

A mixture of 204.0 mg (1.0 mmol) of 2,2'-diisocyanobiphenyl[18] and 32.0 mg (1.0 mmol) of sulfur in 25 ml of benzene was heated at reflux for 64 hr. The concentrated product mixture was chromatographed from a silica gel column, 12 in. by 1 in. After sulfur was eluted with 200 ml of hexane, further elution with 300 ml of hexane removed **2,2'-diisothiocyanatobiphenyl** as a colorless semisolid, 18.0 mg, mp 33–36°, 15.4% yield. When the concentrated product mixture was analyzed by gc at a column temperature of 190° the diisothiocyanate, retention time 28.0 min, was found in 14.9% yield, ir ($CHCl_3$) 2128–2041 cm^{-1} (NCS). *Anal.* Calcd for $C_{14}H_8N_2S_2$: C, 62.69; H, 3.01; N, 10.44; S, 23.86. Found: C, 62.59; H, 3.19; N, 10.64; S, 24.09.

Further elution of the column with 600 ml of hexane–benzene (3:1) gave 55.0 mg of **2-isocyano-2'-isothiocyanatobiphenyl** as a light pink semisolid, 53.4% yield. Rechromatographic separation gave an analytical sample as a light pink semisolid. Gc analysis, *vide supra*, gave the product, retention time 19.4 min, in 36.7% yield (presumably some of the isocyanide polymerized at 190°): ir ($CHCl_3$) 2128 (NC), 2128–2041 cm^{-1} (NCS). *Anal.* Calcd for $C_{14}H_8N_2OS$: C, 71.18; H, 3.41; N, 11.86; S, 13.55. Found: C, 71.46; H, 3.63; N, 11.58; S, 13.59.

Further elution of the column with 400 ml of benzene–hexane (1:1) gave unreacted 2,2'-diisocyanobiphenyl, 115.0 mg, retention time 10.0 min, 56.4%, identified by comparison with identical tlc and ir data. Yields are based on the recovered starting material.

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[16] G. M. Dyson, H. J. George, and R. F. Hunter, *J. Chem. Soc.*, 436 (1927).

[17] B. Milligan and J. M. Swan, *ibid.*, 2969 (1959).

[18] Unpublished preparation by Dr. J. de Jong.

A repeat sulfurization of 2,2′-diisocyanobiphenyl with a 6 molar excess of sulfur gave 2,2′-diisothiocyanatobiphenyl found in 67.2% yield by isolation from a silica gel column and 87.5% yield by gc (apparently there was additional reaction at 190°). The 2-isocyano-2′-isothiocyanatobiphenyl was found in 10.2% yield by isolation from a silica gel column and was not detected by gc analysis of the product mixture. There was no recovered starting material.

Registry No.—**8,** 33904-01-7; 3,4-dimethoxyformanilide, 33904-02-8; 2,4-dimethoxyphenyl isothiocyanate, 33904-03-9; 3,4-dimethoxyphenyl isothiocyanate, 33904-04-0; 2,2′-diisothiocyanatobiphenyl, 33904-05-1; 2-isocyano-2′-isothiocyanatobiphenyl, 33904-06-2.

Reactions of Dimethylsulfonium Cyclopentadienylide with Electrophiles and Dienophiles

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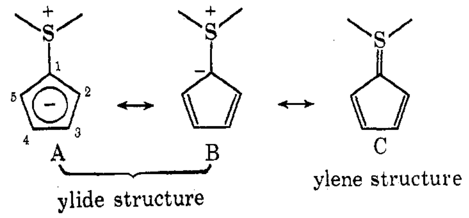
The reactions of dimethylsulfonium cyclopentadienylide (I) with electrophiles and dienophiles have been attempted. Electrophiles such as acetyl chloride, benzenesulfonic acid anhydride, Vilsmeier reagent, and triethyloxonium fluoroborate react with I to give acetyl-, benzenesulfonyl-, diformyl-, and ethyl-substituted derivatives of I, respectively. Dienophiles such as diethyl acetylenedicarboxylate, tetracyanoethylene, and chloranil react with I to afford the respective Michael addition products of I. From these reaction behaviors, an aromatic character of the five-membered ring in I has been discussed.

Dimethylsulfonium cyclopentadienylide (I) is considered to be the resonance hybrid of ylide structures A, B, and ylene structure C. Although I was first synthesized by Behringer[1] in 1965, no reactions of I have been reported so far except diazo coupling.[1] It was suggested in our previous communication[2] that the ylide structures predominantly contribute to the resonance hybrid of sulfonium and phosphonium cyclopentadienylide on the basis of theoretical consideration of their electronic spectra. In our other communications[3,4] the reaction of triphenylphosphonium cyclopentadienylide (II) with electrophiles and dienophiles were reported and it was found that electrophilic substitutions and Michael additions took place at the 2 position of the five-membered ring in II without cleavage of the C–P bond. In this paper we describe the reactions of I with electrophiles and dienophiles, and discuss which resonance structure (A, B, or C) plays an important role in the reaction.



Results and Discussion

Preparation of I.—Though I was prepared by Behringer, *et al.*,[1] in 1965, their procedure afforded I in only a few per cent yield. We used *N,N*-dimethylformamide as a solvent, and kept low temperature during the reaction. This improved procedure afforded I in considerably better yield (15–20%).

Reactions of I with Electrophiles.—The treatment of I with acetyl chloride, benzenesulfonic acid anhydride, Vilsmeier reagent, and triethyloxonium fluoroborate yielded 2-acetyl (III), 2-benzenesulfonyl (IV), 2,5-diformyl (V), and 2-ethyl (VI) derivatives of I, respectively. In the ir spectra of III and V, the carbonyl stretching vibrations were found at 1580 and 1630 cm^{-1} respectively. These shifts to lower wave numbers are attributed to the delocalization of the negative charge of the five-membered ring to the carbonyl oxygen atom. Since the delocalization of the negative charge generally stabilizes the five-membered ring, the derivatives whose substituents have electron-withdrawing nature, such as acetyl, benzenesulfonyl, and formyl, are more stable than I and the ethyl is less stable[5] than I. The position of substitution was determined by the nmr spectrum of each derivative of I. The signal for five-membered ring protons of I appears as an AA′BB′-type multiplet centered at τ 3.8 (4 H) and the exact chemical shifts and the coupling constants were obtained by simulating the spectrum.[6] The part in the lower field of the signal is assigned to the protons at 2,5 positions and the part in the higher field to the protons at 3,4 positions, as similarly in the case of II. The nmr spectrum of III exhibited three multiplets of equal area (1 H) centered at τ 3.0 (doublet of doublets, J = 3,8, 2.3 Hz), 3.5 (doublet of doublets, J = 3.8, 2.3 Hz), and 3.9 (t, J = 3.8 Hz), which are assigned to cyclopentadienyl ring protons. Among these three peaks, one is nearly in the same position as that in I and the other two peaks shift downfield from the cyclopentadienyl ring proton in I. This is well interpreted if the acetyl group is attached to the 2 position[7] of I; *i.e.*, two electron-withdrawing substituents (dimethylsulfonium and acetyl) make two

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[1] H. Behringer and F. Scheidl, *Tetrahedron Lett.*, **No. 22**, 1757 (1965).

[2] Z. Yoshida, K. Iwata, and S. Yoneda, *ibid.*, 1519 (1971); K. Iwata, S. Yoneda, and Z. Yoshida, *J. Amer. Chem. Soc.*, **93**, 6745 (1971).

[3] Z. Yoshida, S. Yoneda, H. Hashimoto, and Y. Murata, *Tetrahedron Lett.*, 1523 (1971).

[4] Z. Yoshida, S. Yoneda, Y. Murata, and H. Hashimoto, *ibid.*, 1527 (1971).

[5] VI decomposes within 2 or 3 days under nitrogen atmosphere, whereas I does not decompose for about 1 month even in the air.

[6] Z. Yoshida, S. Yoneda, and M. Hazama, *Chem. Commun.*, 716 (1971).

[7] Rationalization of 2 substitution was discussed in the previous publications.[3,8] Lloyd[9] also mentioned the substitution of the 2 position of the cyclopentadienyl ring of II.

[8] Z. Yoshida, S. Yoneda, and Y. Murata, unpublished (to be submitted to *J. Org. Chem.*).

[9] D. Lloyd and M. I. C. Singer, *Chem. Ind.* (*London*), 786 (1971).