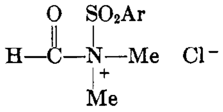
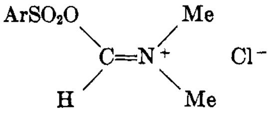
When p-toluenesulfonyl chloride was refluxed with DMF, the tetramethylformamidinium p-toluenesulfonate (I, R = H; Ar = p-$CH_3C_6H_5$) was isolated along with appreciable quantities of dimethylamine hydrochloride; rigorous exclusion of water did not retard formation of the latter.

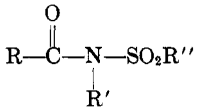
Hall[3] proposed the formation of either II or III to


$\mathrm{H{-}\overset{O}{\overset{\|}{C}}{-}\underset{Me}{\overset{SO_2Ar}{N^+}}{-}Me\ \ Cl^-}$

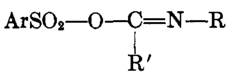
II


III

account for the fact that benzenesulfonyl chloride gave rise to conducting solutions in DMF at room temperature. Mixed imides of the type IV are known,[4] but the


$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\underset{R'}{N}{-}SO_2R''}$

IV


$\mathrm{ArSO_2{-}O{-}\underset{R'}{C}{=}N{-}R}$

V

quaternary ammonium salts such as II are not.[5] Isolation of I would appear to implicate III as a reasonable intermediate. The latter is analogous to the complex presumed to form on addition of thionyl chloride to a dialkylamide[6]; treatment of the complex with an amine leads to the corresponding amidine.[7] Although amides are now known to undergo oxygen protonation in acid solution,[8] there is no assurance that the relative basicities of oxygen and nitrogen would be preserved with respect to other electrophiles. On the other hand, support for III as a likely sulfonylation intermediate can be found from several sources. The mild dehydration of amides to nitriles with benzenesulfonyl chloride[9] must proceed *via* the unstable imidosulfonate (V, R = H); treatment of N-monoalkylamides with this same reagent, in fact, does give an isolable imidosulfonate in some cases.[10] Furthermore, the reaction of α-chlorimines with salts of carboxylic acids to give diacyl amines[11] must certainly involve rearrangement of an intermediate imido ester. At the same time, the reaction of α-chlorimines with the silver salt of benzenesulfonic acid has been shown to produce material identical with that obtained from the Neber rearrangement of the corresponding oxime benzenesulfonate[12]; this product has been identified as the imido ester V.

When dimethylacetamide was substituted for DMF, the principal crystalline product obtained was dimethylamine hydrochloride, although traces of the expected tetramethylacetamidinium arenesulfonate (I, R = CH_3) could be detected in the infrared and n.m.r. spectra. When tetramethylurea (TMU) was employed instead of DMF, only the N,N-dimethylsulfonamides were obtained in quantity together with small amounts of dimethylamine hydroarenesulfonates and dimethylamine hydrochloride. The second NH_2 group in TMU might be expected to enhance the basicity of nitrogen relative to that of oxygen on the grounds of both electronic and statistical considerations. In this case an intermediate analogous to II would appear more likely and is indeed implicated by the nearly exclusive formation of the sulfonamides.

Although amidines and their hydrochloride salts have been prepared in great numbers,[13] only three preparations of quaternary amidinium salts have been reported.[1,14-16] One of these[15] describes the action of phosgene on DMF, a reaction analogous to the one reported here.

Experimental

Tetramethylformamidinium Benzenesulfonate.—A mixture of 128 ml. (1 mole) of benzenesulfonyl chloride and 500 ml. of DMF was allowed to stand for 2 hr. at room temperature, followed by 4 hr. of gentle refluxing. On slow cooling, large prismatic colorless crystals formed. Though these were exceedingly hygroscopic in this form, recrystallization from DMF or MeOH gave a nearly quantitative yield (240 g.) of tetramethylformamidinium benzenesulfonate, m.p. 132.5–133.0°.

Anal. Calcd. for $C_{11}H_{18}N_2O_3S$: C, 51.1; H, 7.02; N, 10.8; S, 12.4. Found: C, 50.6, 50.9; H, 7.1, 7.1; N, 10.7, 10.8; S, 12.0, 11.8.

Tetramethylformamidinium p-Toluenesulfonate.—A mixture of 100 g. (0.524 mole) of p-toluenesulfonyl chloride and 200 ml. of DMF was handled as above. On cooling in ice–water some dimethylamine hydrochloride crystallized and was removed by filtering. The mother liquor was then diluted with twice the volume of acetone and chilled in an ice bath. The tetramethylformamidinium p-toluenesulfonate crystallized in long needles; recrystallization from DMF gave 108 g. (79%) of material with m.p. 140° which contained traces of dimethylamine hydrochloride.

Anal. Calcd. for $C_{12}H_{20}N_2O_3S$: C, 53.2; H, 7.42; N, 10.3. Found: C, 52.8, 52.8; H, 7.5, 7.6; N, 10.5, 10.7.

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(3) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2717 (1956).

(4) P. Oxley and F. W. Short, *J. Chem. Soc.*, 382 (1947).

(5) Salts of the type $R'CON^+R_3$ have been prepared by F. Klages and E. Zange [*Ann.*, **607**, 35 (1957)] and were shown to be unstable.

(6) H. H. Bosshard, R. Mory, M. Schmidt, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

(7) H. Eilingfeld, M. Seefelder, and H. Weidinger, *Angew. Chem., Intern. Ed. Engl.*, 45 (1961).

(8) A. R. Katritzky and R. A. Y. Jones, *Chem. Ind.* (London), 722 (1961); A. R. Katritzky and R. E. Reavill, *ibid.*, 753 (1963), and other papers in this series.

(9) For example, see P. Oxley, *et al.*, *J. Chem. Soc.*, 763 (1946); C. R. Stephens, E. J. Bianco, and F. J. Pilgrim, *J. Am. Chem. Soc.*, **77**, 1701 (1955).

(10) P. Oxley, D. A. Peak, and W. F. Short, *J. Chem. Soc.*, 1618 (1948); R. J. W. Crewlyn, *ibid.*, 1641 (1961).

(11) O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, **48**, 379 (1915).

(12) M. Kuhara, K. Matsumiya, and N. Matsunami, *Mem. Coll. Sci. Univ. Kyoto*, **1**, 25, 105 (1914); *Chem. Abstr.*, **9**, 1613 (1915). For a discussion of the mechanism of the Neber rearrangement, see C. O'Brien, *Chem. Rev.*, **64**, 81 (1964).

(13) R. L. Shriner and F. W. Neumann, *ibid.*, **35**, 351 (1954).

(14) A. Vilsmeir and A. Haack, *Ber.*, **60**, 119 (1927).

(15) Z. Arnold, *Chem. Listy*, **52**, 478 (1958); *Chem. Abstr.*, **53**, 4120*i* (1959). Z. Arnold, *Collection Czech. Chem. Commun.*, **24**, 760 (1959); *Chem. Abstr.*, **53**, 12168*b* (1959). *Cf.* W. König and R. Regners, *Ber.*, **63**, 2823 (1930).

(16) Note Added in Proof.—Since this writing another method for the preparation of the tetramethylformamidinium system has been reported: H. Bredereck, F. Effenberger, and G. Simchen, *ibid.*, **98**, 1078 (1965).

The Reaction of Arylamines with Diethylthiocarbamoyl Chloride. A New Synthesis of Aryl Isothiocyanates

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Received February 5, 1965

The general synthesis of isothiocyanates from primary amines and thiophosgene is rendered undesirable by the toxicity and unavailability of the thiophosgene. The alternate synthetic approach, based on the reaction of primary amines with carbon disulfide with further

TABLE I

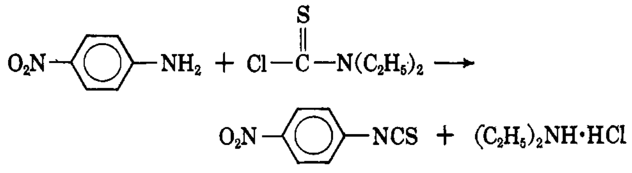
ARYLISOTHIOCYANATES (RNCS)

R	pK_a of starting amine	Yield of RNCS, %	Yield of $(C_2H_5)_2NH \cdot HCl$, %	Solvent	Reaction time, hr.	M.p., °C.	Lit. m.p., °C.	Recrystn. solvent
o-$O_2NC_6H_4$	−0.28[a]	21[b]	69	Chlorobenzene	1.5	67–70	73–74[c]	Acetone
p-$O_2NC_6H_4$	0.98[a]	60	~100	Benzene	1	108–110	112[d]	Acetone
		52	~100	Toluene	3	110–112		
p-NCC_6H_4	1.74[e]	50	78.5	Ethylene dichloride	1	119–120	122[f]	n-Hexane
p-$CH_3COC_6H_4$	2.29[g]	48.5	78.9	Ethylene dichloride	1	75–76	76[f]	n-Hexane–cyclohexane[h]
p-$C_2H_5OOCC_6H_4$	2.38[a]	79.5	98.1	Toluene	2	51–53[i] 123–127[k]	98[j]	Ethyl acetate
o-ClC_6H_4	2.62[a]	65	94.5	Chlorobenzene	1	92–93[l]	...	...

[a] H. C. Brown, D. H. McDaniel, and O. Hafler, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955; p. 590. [b] The actual yield is higher, substantial losses occurring on recrystallization. [c] F. Arndt and B. Rosenau, *Ber.*, **50**, 1255 (1917). [d] D. W. Browne and G. M. Dyson, *J. Chem. Soc.*, 3299 (1931). [e] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, **81**, 4226 (1959). [f] G. M. Dyson, H. J. George, and R. F. Hunter, *J. Chem. Soc.*, 439 (1927). [g] A. V. Willi and W. Meier, *Helv. Chim. Acta*, **39**, 318 (1956). [h] A 1:1 mixture. [i] *Anal.* Calcd. for $C_{10}H_9NO_2S$: N, 6.76. Found: N, 7.10. The n.m.r. spectrum of this compound in CCl_4 showed a characteristic *para*-substituted benzene derivative pattern at 7.62 p.p.m., a quartet at 4.33 p.p.m. for the methylene group attached to the oxygen, and a triplet at 1.38 p.p.m. (relative to TMS) for the methyl group with an area of 4:2:3. [j] This melting point, reported by R. G. Dubenko and P. S. Pel'kis [*Ukr. Khim. Zh.*, **27**, 669 (1961); *Chem. Abstr.*, **56**, 8607 (1962)] may be a typographical error as recrystallization from ethyl acetate did not increase the observed melting point. [k] Boiling point at 0.1 mm. [l] Boiling point at 1.0 mm.; J. N. Baxter, J. Cymerman-Craig, M. Moyle, and R. A. White [*J. Chem. Soc.*, 659 (1956)] reported b.p. 91° (1.5 mm.).

transformation of the resultant dithiocarbamate,[1] is not applicable to aromatic amines having electron-withdrawing substituents. p-Nitroaniline, for example, does not give the corresponding dithiocarbamate.[2]

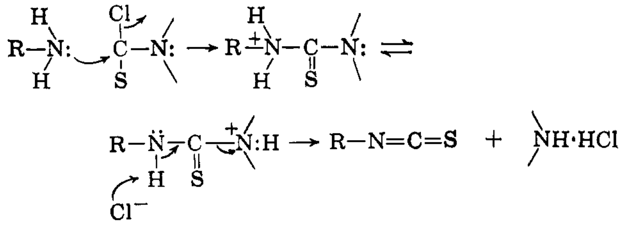
We wish to report a general, one-step synthesis of aryl isothiocyanates. The procedure followed was to heat the aromatic amine with N,N-diethylthiocarbamoyl chloride in an inert solvent. Thus p-nitroaniline gave p-nitrophenyl isothiocyanate (I) and diethylamine hydrochloride.



I

Isothiocyanates prepared by this method are listed in Table I. Although no attempts were made to obtain maximum yields, higher yields were observed with decreasing amine acidity. The limiting pK_a value operative was 4.6, as evidenced by the trace amounts of phenyl isothiocyanate formed from aniline under the reaction conditions.

An SN2 mechanism may be operative: arylamine attack on the thiocarbamoyl group, proton transfer, and diethylamine hydrochloride elimination.



Experimental[3]

Starting Materials.—The aniline derivatives were commercially obtained. The N,N-diethylthiocarbamoyl chloride (Pennsalt Chemical Co.) was redistilled.

General Procedure.—A solution or suspension of the aniline derivative (0.1 mole) and N,N-diethylthiocarbamoyl chloride (0.105 mole) in solvent (300 ml.) was refluxed for the indicated time period and allowed to cool, and the precipitated diethylamine hydrochloride was removed by filtration. The solvent was removed; the product was purified as indicated in Table I.

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(1) For a recent review on the synthesis and reactions of isothiocyanates, see S. J. Assony, "Organic Sulfur Compounds," Vol. I, Pergamon Press Inc., New York, N. Y., 1961, p. 326.

(2) See ref. 1, p. 328.

(3) Boiling points and melting points are uncorrected. Microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; infrared and n.m.r. spectra were determined on a Perkin-Elmer Model 21 and a Varian A-60 spectrometer, respectively.

A New Reaction between Cyclohexanecarbonyl Chloride and Phenyl Isocyanate

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Received December 22, 1964

The analogy between reactions of ketenes and those of isocyanates has been generally recognized for a long time.[1] Aside from reactions with compounds bearing active hydrogen, both ketenes and isocyanates dimerize, trimerize, and homopolymerize. In view of this similarity, it was of interest to examine some reactions between ketenes and isocyanates.

Staudinger and co-workers[2] were the first to note that diphenylketene reacted with phenyl isocyanate. They obtained a 20% yield of a product, **1**, formulated as N-phenyldiphenylmalonimide, after 5 hr. at 220°. Aniline converted the imide into the dianilide of diphenylmalonic acid. Staudinger also reported[3] that

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(1) H. Staudinger and R. Endle, *Ber.*, **50**, 1042 (1917).

(2) H. Staudinger, O. Göhring, and M. Schöller, *ibid.*, **47**, 40 (1914).

(3) H. Staudinger, F. Felix, and E. Geiger, *Helv. Chim. Acta*, **8**, 314 (1925).