The Photolytically Induced Interconversions of Benzyl Thiocyanates and Isothiocyanates

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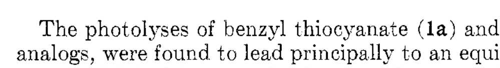
The photolyses of benzyl thiocyanate (**1a**) and isothiocyanate (**2a**), as well as some of their para-substituted analogs, were found to lead principally to an equilibrium mixture of the two isomers. The equilibrium position was established in several solvents. Rates of photoisomerization were measured. Evidence is presented for the source of several by-products of the reactions.

In the past we[3] and others[4] have devoted considerable effort to the elucidation of the mechanisms of thermally induced thiocyanate–isothiocyanate isomerizations. We now describe some of the few known isomerizations of these compounds which are induced photolytically.[5]

The benzyl thiocyanates were chosen as first objects of study owing to their sluggish uncatalyzed thermal isomerizations[6] and the resultant extensive decomposition prevalent at the required elevated temperatures. It was felt that their photoisomerizations might contrast this and proceed under considerably milder conditions. This indeed proved to be so, as benzyl thiocyanate (**1a**) in an oxygen-free acetonitrile solution at 25° isomerized in 1 hr to a mixture largely composed of isothiocyanate **2a** when irradiated with a medium-pressure Hanovia lamp. Since it was apparent from control studies on **2a** that the isomerization was a reversible one, it was undertaken to clarify some aspects of the equilibration process.


1 2

a, R = H
b, R = CH_3
c, R = OCH_3
d, R = Cl
e, R = CF_3

Initial efforts centered on investigation of the photoequilibrium position as a function of solvent dielectric. As the equilibrium position of some reversible thermal thiocyanate–isothiocyanate isomerizations had shown a clear influence of this type,[7] we were curious to see if it existed in the photoequilibrium. In actuality, solutions 0.002–0.01 *M* in **1a** or **2a** afforded upon irradiation photoequilibria which varied only from SCN:NCS = 4:96 (cyclohexane) to SCN:NCS = 1:99 (acetonitrile) in the solvents *n*-hexane, cyclohexane, dioxane, and acetonitrile. These ratios were verified as stationary states in each solvent by approach from either isomer. From 0.01 *M* solutions, the photoequilibrium was attained in 3–21 hr from pure **1a** and in 4–10 hr from pure **2a**, depending on the solvent utilized. Photoequilibrium was reached considerably faster (<1 hr) when 0.002 *M* solutions were used.

In a further exploration of possible influences on the photoequilibrium position, photolyses of the various para-substituted isomers, **1b–e** and **2b–e**, were effected in an attempt to ascertain whether any internal electronic influences were involved. For 0.01 *M* cyclohexane solutions of these compounds, however, the photoequilibrium position in every case was SCN:NCS = 4:96, within estimated error limits.

The rates of isomerization for all of these compounds were measured, since we had some evidence from our studies of the equilibrium positions that the attainment of photoequilibrium did not occur in identical time spans. The data from these measurements, made by gc and derived from the initial slopes of concentration *vs.* time plots, are given in Table I.

TABLE I

RATES OF PHOTOISOMERIZATION BY CYCLOHEXANE SOLUTIONS OF BENZYL THIOCYANATES AND ISOTHIOCYANATES

Para substituent	Concn, *M*	RSCN, $k \times 10^4$ sec^{-1}	RNCS,[a] $k \times 10^6$ sec^{-1}
H	0.002	12.8 ± 3.2	3.3 ± 2.0
	0.01	1.1 ± 0.1	2.1 ± 1.4
CH_3O		3.6 ± 0.8	9.2 ± 0.6
CH_3		3.7 ± 0.8	6.2 ± 2.0
Cl		2.5 ± 0.6	
CF_3		2.3 ± 0.2	

[a] The generally greater error limits given for the isothiocyanates reflect the difficulties in accurately determining the small amounts of thiocyanate generated during the photolyses of the isothiocyanates.

The lack of important electronic influences deducible from these experiments is in accord with the earlier work of Mazzucato, *et al.*,[5] in which homolytic scission of the substrates **1a** and **2a** was indicated by detection of the fluorescence emission of benzyl radical during the isomerization. The principal difference in our findings is the equilibrium position for **1a** and **2a** (the earlier report gave SCN:NCS = 70:30) and the discovery on our part of several by-products of the reaction. When the product mixtures from irradiations of **1a** and **2a** in cyclohexane were subjected to careful gc and mass

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[1] Taken in part from the Ph.D. thesis of T. E. Parks, Brown University 1971.

[2] Alfred P. Sloan Fellow, 1973–1975.

[3] See, for example, L. A. Spurlock, R. K. Porter, and W. G. Cox, *J. Org. Chem.*, **37**, 1162 (1972), and references cited therein.

[4] For recent reviews see (a) L. A. Spurlock and T. E. Parks in "Mechanisms of Reactions of Sulfur Compounds," Vol. 3, N. Kharasch, Ed., Intra-Science Research Foundation, Santa Monica, Calif., 1970, p 161; (b) A. Fava in "Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Oxford, 1966, p 85. See also (c) A. Fava, *et al.*, *J. Amer. Chem. Soc.*, **87**, 1045 (1965); (d) A. Ceccon, A. Fava, and I. Papa, *Chim. Ind.* (*Milan*), **51**, 53 (1969).

[5] The single earlier report of this type of isomerization [U. Mazzucato, G. Beggiato, and G. Favaro, *Tetrahedron Lett.*, 5455 (1966)] is substantially at odds with our own findings. Possible reasons for this discrepancy will presently be discussed.

[6] (a) L. A. Spurlock and R. G. Fayter, Jr., *J. Org. Chem.*, **34**, 4035 (1969); (b) P. A. S. Smith and D. W. Emerson, *J. Amer. Chem. Soc.*, **82**, 3076 (1960).

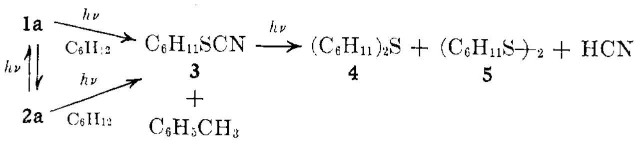
[7] The furfuryl isomers show this effect most clearly. See ref 6a.

spectral analyses, three other products were identified—dicyclohexyl sulfide (**4**), dicyclohexyl disulfide (**5**), and toluene. The relative amount of **4** in the product mixture was time dependent and varied from 5% after 4 hr of irradiation to 56% after 36 hr. It was more difficult to accurately analyze for **5** and toluene but it was apparent that their proportions also showed an increase with time of irradiation. No bibenzyl was detected.

As cyclohexyl thiocyanate (**3**) was the suspected precursor of **4** and **5**, despite its absence from the product mixtures, photolysis of an authentic sample of this compound was conducted under conditions identical with those used for the benzyl substrates. This procedure did indeed rapidly afford **4** and **5**. In addition, hydrogen cyanide was evolved, and, when reexaminations of the photolysis mixtures from **1a** and **2a** were undertaken, hydrogen cyanide was also discovered in both samples. This observation allowed a possible explanation for the wide disparity between our photoequilibrium and that of Mazzucato, *et al.* Our recheck of their reported analytical procedure showed that there was no means of distinguishing between **1a** and hydrogen cyanide by their methods. Since they seemingly were unaware of the presence of the latter in the products, this seems a likely reason for the contradiction.[8]

The overall reaction shown in Scheme I is most explicable as initiated by light-induced homolytic cleavages of the C–S and C–N bonds in the benzyl thiocyanates and isothiocyanates, respectively. Isomerization then results from simple recombination of the benzyl and thiocyanate radicals generated in this fashion.[9] The by-products can be viewed as the results of attack on solvent by the energetic intermediates, probably after they have diffused from the solvent cage in which they were generated.

SCHEME I



It was further interesting to note that cyclohexyl thiocyanate (**3**), unlike its benzyl counterparts, underwent no discernible photoisomerization to isothiocyanate (cyclohexyl radical formation), but rather gave products from cyclohexylthienyl radical. Whether this failure to isomerize reflects the lesser stability of cyclohexyl radical relative to benzyl radicals, or an intramolecular photosensitization by the benzene rings in the benzyl substrates,[10] is not determinable from these results. Whatever the case, however, it is certain that photoisomerization is not a general process for simple, primary, and secondary alkyl thiocyanates and isothiocyanates.

Experimental Section[11]

Benzyl Thiocyanates (1).—All thiocyanates utilized, except the commercially available benzyl derivative, were prepared from the corresponding chlorides or bromides. These precursors were readily available from treatment of the requisite alcohol with concentrated hydrochloric acid or triphenylphosphine dibromide. A typical procedure is that used for synthesis of *p*-trifluoromethylbenzyl thiocyanate (**1e**).

To 6.0 g (0.025 mol) of *p*-trifluoromethylbenzyl bromide in 35 ml of anhydrous acetone was added 4.85 g (0.05 mol) of dry potassium thiocyanate. This mixture was heated at reflux for 18 hr, diluted with 300 ml of water, and extracted three times with 25-ml aliquots of ethyl ether. Combination of the ether extracts was followed by water washing, drying, and solvent evaporation. Distillation of the residue gave 4.77 g (88%) of **1e**: bp 72–74° (0.13 mm); ir (neat) 2147, 1618, 1415, 1320, 1250, 1170–1110, 1065, 1018, 844, 755, 740 cm^{-1}; nmr τ 5.87 (s, 2 H), 2.45 (A_2B_2, 4 H); mass spectrum *m/e* (rel intensity) 217 (4.0), 160 (8.9), 159 (100), 109 (18).

Anal. Calcd for $C_9H_6F_3NS$: C, 49.76; H, 2.78; F, 26.24; N, 6.45. Found: C, 49.70; H, 2.82; F, 26.37; N, 6.42.

The presence of 1.4% *p*-trifluoromethylbenzyl isothiocyanate (**2e**) in the product from the above reaction allowed determination of the nmr spectrum of this isomer. The only difference between the spectra of **1e** and isothiocyanate **2e** was in the methylene protons, where a singlet occurred at τ 5.24 in **2e**. *p*-Chlorobenzyl isothiocyanate (**2d**), occurring to the extent of 4.0% in the product of an exactly analogous preparation of **1d**, showed methylene protons at τ 5.32 in its nmr spectrum.

The remaining benzyl thiocyanates examined in this study, along with their boiling points and important infrared and nmr absorptions, are given in Table II.

TABLE II

PHYSICAL PROPERTIES OF BENZYL THIOCYANATES AND ISOTHIOCYANATES PHOTOLYZED

Compd	Bp, °C (mm)	Lit. bp, °C (mm)	Ir, ν_{max}, cm^{-1}	Nmr, τ Phenyl	–CH_2–	*p*-CH_3
2a	82–85 (0.65)	126–128 (14)[a]	2090	2.70 (s)	5.40 (s)	
1b	85–86 (0.10)	148–150 (14)[b]	2140	3.00 (s)	6.00 (s)	7.70 (s)
2b	85–87 (0.12)	94 (1.0)[c]	2080	3.00 (s)	5.50 (s)	7.70 (s)
1c	107–110 (0.15)	109 (0.5)[d]	2140	3.15 (A_2B_2)	6.03 (s)	6.32 (s)
2c	108–110 (0.15)	160 (2)[c]	2080	3.15 (A_2B_2)	5.51 (s)	6.32 (s)
1d	90–91 (0.05)	Mp 17[e]	2145	2.82 (s)	6.00 (s)	

[a] D. Martin, E. Beyer, and H. Gross, East German Patent 43,996 (Dec 15, 1965); *Chem. Abstr.*, **65**, 3746*h* (1966). [b] J. von Braun, W. May, and R. Michaelis, *Justus Liebigs Ann. Chem.*, **490**, 189 (1931). [c] K. Antos, A. Stullerova, V. Knoppova, and P. Kristian, *Chem. Zvesti*, **19**, 353 (1965). [d] J. Nosek and V. Janousek, *Chem. Zvesti*, **7**, 676 (1953). [e] C. L. Jackson and A. W. Field, *Amer. Chem. J.*, **2**, 91 (1880).

Benzyl Isothiocyanates (2).—The procedure utilizing carbon disulfide, ethyl chloroformate, and potassium hydroxide as described by Spurlock and Cox[3] afforded the benzyl isothiocyanates listed in Table II in yields varying from 65 to 82%. The crude products from the reaction were purified by elution from a silica gel column (20:1 silica gel to crude isothiocyanate) with pentane. The fractions shown by their infrared spectra to be free of carbonyl-containing impurities were combined and distilled. Gc analyses of the distilled products indicated them to be >99.5% pure isothiocyanate.

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(8) An alternative explanation may lie in their use of a low-pressure Hanovia lamp as compared to our medium-pressure lamp. This appears less likely considering the transparency of **1a** [λ_{max} 260 nm (ϵ 470)] and **2a** [λ_{max} 250 nm (ϵ 1520)] at wavelengths >280 nm.

(9) The direction of the concentration effect on isomerization rate suggests that a radical-chain reaction is unlikely.

(10) Several examples of intramolecular photosensitization are known. See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, p 14.

(11) Infrared spectra were determined on either a Perkin-Elmer Model 237 or 247 grating infrared spectrometer using sodium chloride optics. Nmr determinations were carried out on a Varian Associates A-60A spectrometer; approximately 20% solutions in CCl_4 were employed with tetramethylsilane as the internal standard. Mass spectra were determined at 70 eV on a Hitachi Perkin-Elmer RMU-6D instrument. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del. Practical grade cyclohexane was stirred with concentrated sulfuric acid, the acid was removed, and the remaining cyclohexane was extracted three times with water. This procedure was repeated until the sulfuric acid layer remained colorless after stirring for 24 hr. The recovered cyclohexane was dried and distilled from sodium through a 20-in. Vigreux column. An identical procedure was used for purification of *n*-hexane. Reagent grade acetonitrile was distilled from anhydrous magnesium sulfate. Dioxane was purified by the method of Fieser; see L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955, pp 284–285.

Photolytic Procedures.—The apparatus used in these studies consisted of a Vycor filtered 450-W medium-pressure Hanovia mercury arc lamp placed in a water-cooled quartz jacket fitted with a 45/50 male joint. This assembly was placed in a 700-ml glass finger with a 45/50 female joint. The quartz jacket was of sufficient depth to permit the lamp to be below the surface of 500 ml of liquid contained in the glass finger. The glass portion of the apparatus had a gas inlet tube and a 24/40 side arm to which a water-cooled condenser was attached. All solvents were purified prior to their use.[11] In a typical photolysis, sufficient thiocyanate or isothiocyanate starting material was diluted to 500 ml in solvent to afford the desired concentration. This solution was placed in the glass portion of the apparatus, the lamp assembly was inserted, and argon gas was passed through the solution for a minimum of 1 hr before the lamp was turned on. During argon gas flushing and photolysis the solution was magnetically stirred. At intervals after lamp ignition, aliquots (10 ml for gc analysis and 40 ml for nmr) were removed, the solvent was evaporated, and the residue was analyzed by gc and mass spectrum. Gc was used to analyze the products from the photolyses of **1a**, **2a**, and **3**. On a 2 ft × 0.125 in. 15% diethylene glycol succinate on Chromosorb W column at 150° with a helium carrier gas flow of 75 ml/min, **1a** and **2a** showed retention times of 5.5 and 3.5 min, respectively. In the remaining benzyl systems, nmr analysis was accomplished by comparing the relative peak areas for the benzyl methylene protons of the thiocyanates and isothiocyanates within a given sample. The relative peak areas were measured by integration on the nmr and these results were compared with the relative areas measured with a planimeter. These methods were mutually consistent.

Dicyclohexyl Sulfide (4).—To 1.67 g (0.011 mol) of cyclohexanethiol in 15 ml of anhydrous nitrogen-flushed pyridine was added 2.87 g (0.011 mol) of cyclohexyl *p*-toluenesulfonate. The reaction mixture was heated at reflux for 24 hr, cooled, and poured into 100 ml of water. The water solution was extracted three times with 20-ml portions of ether. The ether extracts were combined and washed successively with water, 10% hydrochloric acid solution, and saturated sodium bicarbonate solution. Drying of the resultant ether solution followed by solvent removal afforded 2.4 g of a crude product. Gas chromatographic analysis of this mixture using conditions identical with those used for analysis of the photolysis products from **1a** and **2a** indicated a component with a retention time of 0.80 min. Gc collection of this material afforded dicyclohexyl sulfide: mass spectrum *m/e* (rel intensity) 198 (17), 117 (94), 115 (16), 83 (100), 82 (54), 81 (21), 67 (37), 55 (70), 41 (40), 39 (20).

The mass spectrum and gc retention time of **4** were identical with those shown by the by-product from the photolyses of **1a** and **2a**.

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Registry No.—**1a**, 3012-37-1; **1b**, 18991-39-4; **1c**, 19927-28-7; **1d**, 2082-64-6; **1e**, 41499-20-1; **2a**, 622-78-6; **2b**, 3694-46-0; **2c**, 3694-57-3; **2d**, 3694-45-9; **2e**, 41499-21-2; **4**, 7133-46-2; *p*-trifluoromethylbenzyl bromide, 402-49-3.

Perfluorovinyl Isocyanates

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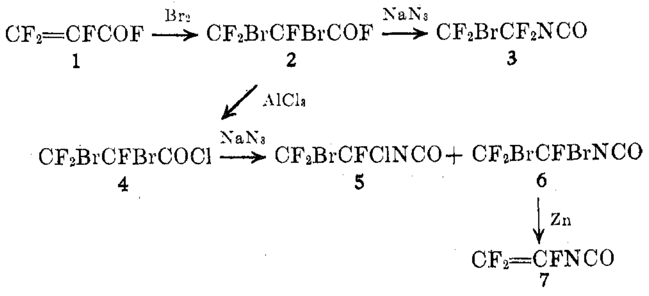
Two new polymerizable monomers, trifluorovinyl isocyanate (**7**) and 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate (**18**), were prepared by dehalogenation of dichloro- (and dibromo-) trifluoroethyl isocyanates (**6** and **13**) and 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate (**17**), respectively. The isocyanates **6** and **13** were prepared by the Curtius reaction from the corresponding propionyl chlorides (**4** and **11**) which were in turn prepared by halogenation of trifluoroacryloyl fluoride (**1**) and replacement of the acyl fluorine with chlorine from $AlCl_3$. The isocyanate **17** was prepared in one step by reaction of 1,3-chloropentafluoroacetone imine with oxalyl chloride. Hexafluoroacetone imine and dichlorotetrafluoroacetone imine also gave α-chloro isocyanates with oxalyl chloride. The new vinyl isocyanates, **7** and **18**, add nucleophiles to the isocyanate group in preference to the carbon–carbon double bond.

Although many perfluoroalkyl isocyanates are known,[1] trifluorovinyl isocyanate and other perfluoro isocyanates with α,β double bonds have not been reported previously. Such isocyanates would be expected to polymerize easily and could be used to prepare perfluorinated polymers containing isocyanate groups.

We have prepared trifluorovinyl isocyanate (**7**) in several steps from trifluoroacyloyl fluoride (**1**)[2] (Scheme I). Reaction of **1** with sodium azide to give **7** directly by means of the Curtius reaction failed and gave instead an unidentified, highly explosive material. This explosive material probably resulted from an attack of azide ion on the β-carbon atom of **1**, since it is known that nucleophiles preferentially replace the vinylic β-fluorine atoms of **1** instead of the acyl fluoride.[3]

Scheme I



To circumvent this problem, the double bond was protected by bromination, with the idea that it could be regenerated after the isocyanate was formed by the Curtius reaction. The dibromopropionyl fluoride **2** reacted smoothly with sodium azide, but the major product was the monobromo isocyanate **3**. The sodium fluoride formed in the reaction had apparently replaced the α bromine with fluorine in either the intermediate dibromopropionyl azide or in the expected dibromo isocyanate **6**. It seems most likely that the halogen exchange occurs with **6**, since it could be

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[1] W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969.

[2] R. E. Banks, J. M. Birchall, T. Clarke, R. M. Haszeldine, M. J. Stevenson, and H. Iserson, *J. Chem. Soc. C*, 266 (1968).

[3] Y. A. Cheburkov and M. D. Bargamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 833 (1967).