Reactions of Trichloroacetyl Isothiocyanate with Organic Azides

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Benzyl azide reacts with trichloroacetyl isothiocyanate to give **7a** in chloroform solution, and **11** in acetone solution. These 1,2,4-oxathiazolidines were characterized by ^{13}C nmr spectroscopy (Scheme 2), but could not be isolated since they deteriorated *via* the carbodiimide **8a** into the 1,2,4-thiadiazolidine **9a**. The oxathiazoline **6a** is assumed as an intermediate and was trapped by isocyanates and dicyclohexylcarbodiimide to give the 1,2,4-thiadiazolidines **10a,b** and **12** respectively. Isopropyl azide also reacts with trichloroacetyl isothiocyanate to give the labile oxathiazolidine **7b**, which decomposes to the carbodiimide **8b** and the 1,2,4-thiadiazolidine **9b**. In the case of diphenylmethyl azide, however, no evidence was obtained for the presence of the oxathiazolidine **7c** in the ^{1}H nmr spectra; only the carbodiimide **8c** was observed. A mechanistic rationalization is presented in Scheme 1.

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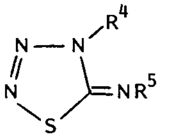
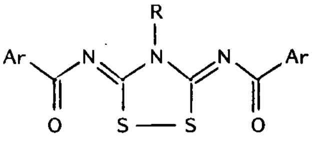
Alkyl azides react with isothiocyanates to give different heterocycles according to the nature of the isothiocyanate. The reactive arylsulfonyl isothiocyanates and picryl isothiocyanate combine with alkyl azides under mild reaction conditions to give isolable monoadducts; *i.e.* 4-alkyl-1,2,3,4-thiatriazolin-5-imines **1a** [1]. Phenyl isothiocyanate and its *p*-substituted derivatives react more sluggishly with alkyl azides and give the thiatriazolin-5-imines **1b** only as elusive intermediates which combine with a second molecule of isothiocyanate under extrusion of dinitrogen [2]. The mechanistic details of this second step have recently been elucidated [3].



1

a: R^5 = $ArSO_2$, Picryl
b: R^5 = $p\text{-}XC_6H_4$ (X = H, Me, Cl, NO_2)
c: R^5 = $p\text{-}XC_6H_4CO$ (X = H, Cl, NO_2)

Aroyl isothiocyanates, which are intermediate in reactivity between arylsulfonyl isothiocyanates and the usual aryl isothiocyanates, also fail to yield isolable thiatriazolin-5-imines **1c** when reacted with alkyl azides, but furnish the heterocycles **2** and **3** [4]. The reaction paths, leading to these products from the intermediate cycloadducts **1c**, have not been fully understood. Among the several possibilities to be considered, an anchimeric assistance of the carbonyl function during the elimination of dinitrogen (**1c** → **4**) is highly probable, and has already been suggested for the reactions of 5-amino-1,2,3,4-thiatriazole with acyl chlorides where **1c** (R^4 = H) is assumed as an intermediate [5]. In order to gain more insight into this aspect, the reactions of some alkyl azides with the strongly electrophilic trichloroacetyl isothiocyanate were investigated in detail and the results are described below.



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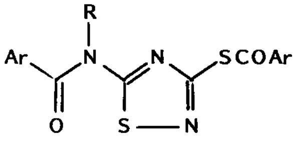

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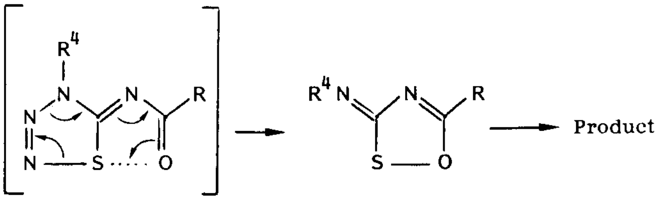


1c **4**

Results.

The reaction of benzyl azide with an equimolar amount of trichloroacetyl isothiocyanate in deuteriochloroform was followed by ^{1}H nmr spectroscopy (90 MHz) and the results are shown in Figure 1. Thus, three products are observed having methylene singlet absorptions at δ 4.98, δ 5.03 and 5.52 (equal intensity) and δ 5.38. The singlet at δ 5.38 is the major product peak at the early stage of the reaction and reaches a maximum concentration of 24% after 4 hours; it then decreases in intensity as the reaction progresses. A second product with δ 4.98 is also formed from the beginning of the reaction but remains at low concentration ($\leq$ 6%). The third product, with benzyl methylene absorptions at δ 5.03 and 5.52, appears only after an induction period of one hour when a considerable amount of the compound with δ 5.38 has already been formed. It constitutes the major product at the end of the reaction.

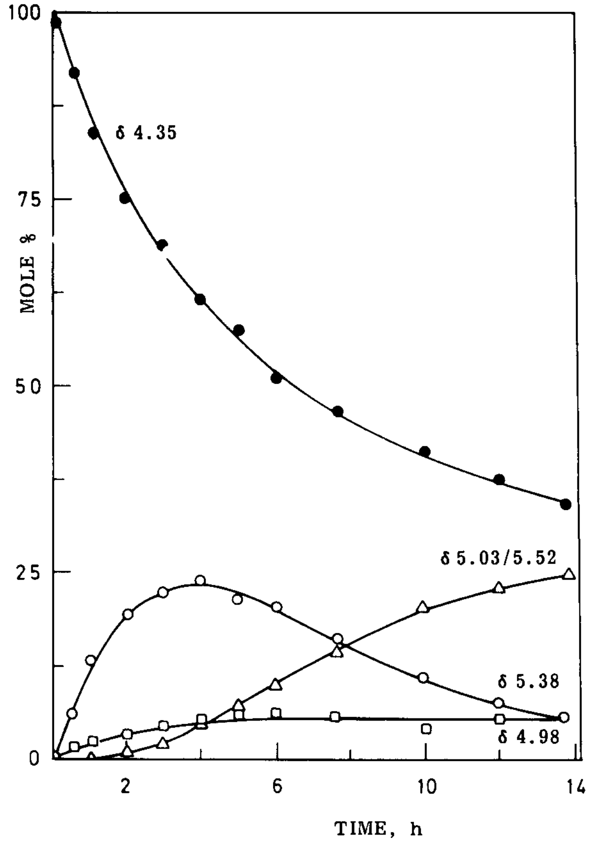


Figure 1. Reaction of benzyl azide (0.5 *M*) with an equimolar amount of trichloroacetyl isothiocyanate in deuteriochloroform at 30°. Relative concentrations of benzyl azide (•), **7a** (o), **8a** (□) and **9a** (△).

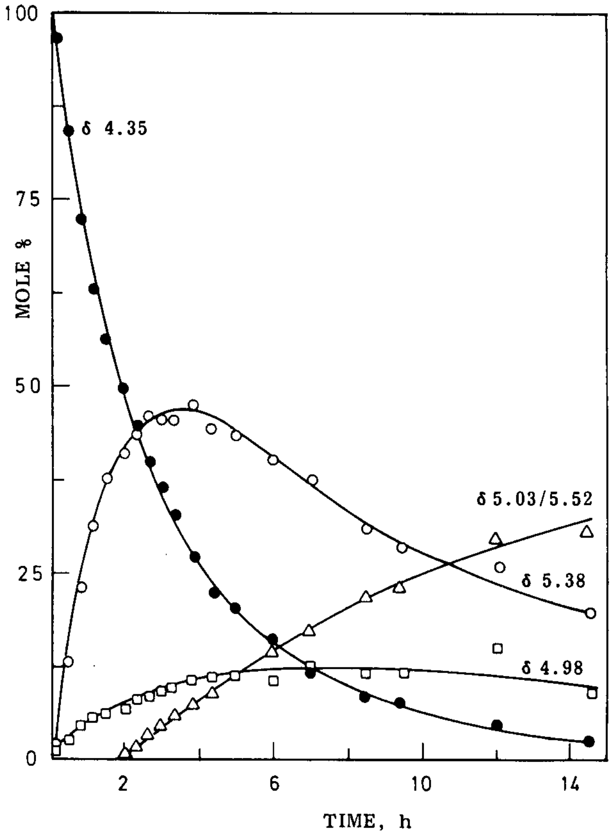


Figure 2. Reaction of benzyl azide (0.5 *M*) with two mole-equivalents of trichloroacetyl isothiocyanate in deuteriochloroform at 30°. Relative concentrations of benzyl azide (•), **7a** (o), **8a** (□) and **9a** (△).

When two equivalents of trichloroacetyl isothiocyanate were used, the same general trends were observed with the notable difference that the intermediate with δ 5.38 now reaches a maximum concentration of 48% after *ca.* 4 hours, and that benzyl azide (δ 4.35) is completely consumed at the end of the reaction (Figure 2). With a tenfold excess of isothiocyanate, the peak at δ 5.38 reaches a maximum concentration of 55% after 75 minutes.

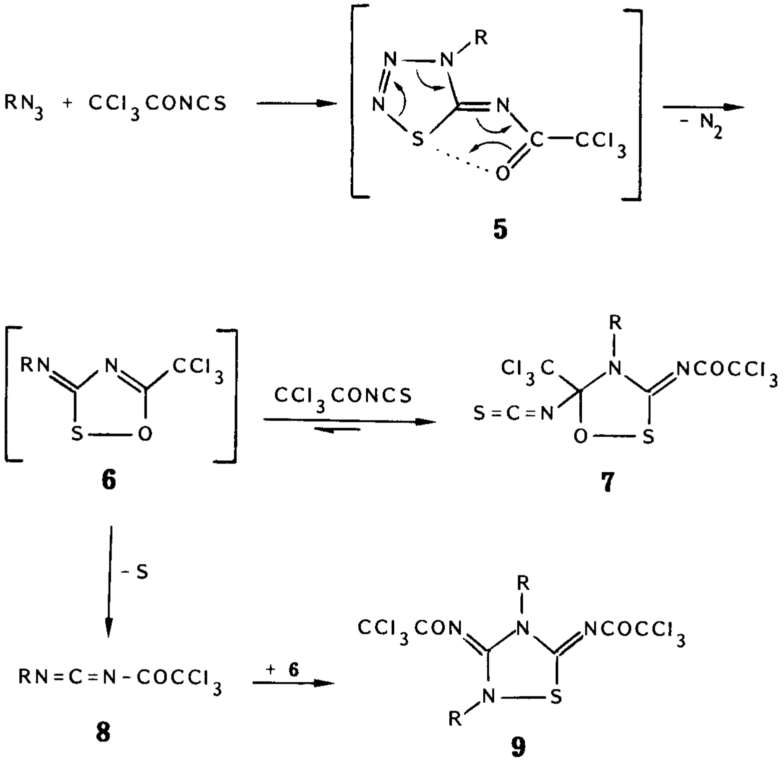
The product, resonating at δ 5.03 and 5.52, could be isolated when the reaction was carried out on a preparative scale, and was characterized as **9a** on the basis of spectral data and microanalysis (see Experimental). Similar compounds had been obtained during the decomposition of thiatriazolin-5-imines [6].

Several attempts were made to isolate the other products, but without success, so that the attribution of their structure relies on the interpretation of the spectra taken from the reaction mixtures in solution. In order to elucidate the structure of the important intermediate which resonates at δ 5.38, the reaction was carried out with a tenfold excess of isothiocyanate and analyzed after 40 minutes when nitrogen had evolved. The intermediate, present in about 50% yield, exhibits a methylene carbon absorption at δ 52.8 with a one-bond coupling constant $^1J_{CH}$ = 143 Hz. The position of the methylene hydrogen and carbon absorptions, as well as the $^1J_{CH}$ coupling constant, eliminate structure **6a** which is expected to resonate at δ_H 4.3-4.5 and δ_C 55-57 with $^1J_{CH}$ ~ 133-134 Hz [7]. The values, however, point to a benzyl group attached to an endocyclic nitrogen atom [7]. These, together with the other observed carbon resonances, indicate the presence of **7a**; the assignment of the resonances is shown in Scheme 2. Further corroboration of the structure is provided by the mass spectrum, which shows a peak at m/z 511 (0.3%) for the molecular ion with the expected isotope distribution for six chlorine atoms.

The structure of the minor component, absorbing at δ 4.98, is uncertain but may correspond to the carbodiimide **8a**. A similar compound, *N*-benzyl-*N'*-tosylcarbodiimide, gives a benzyl methylene absorption in the same region of the ^{1}H nmr spectrum (δ 4.7) [6].

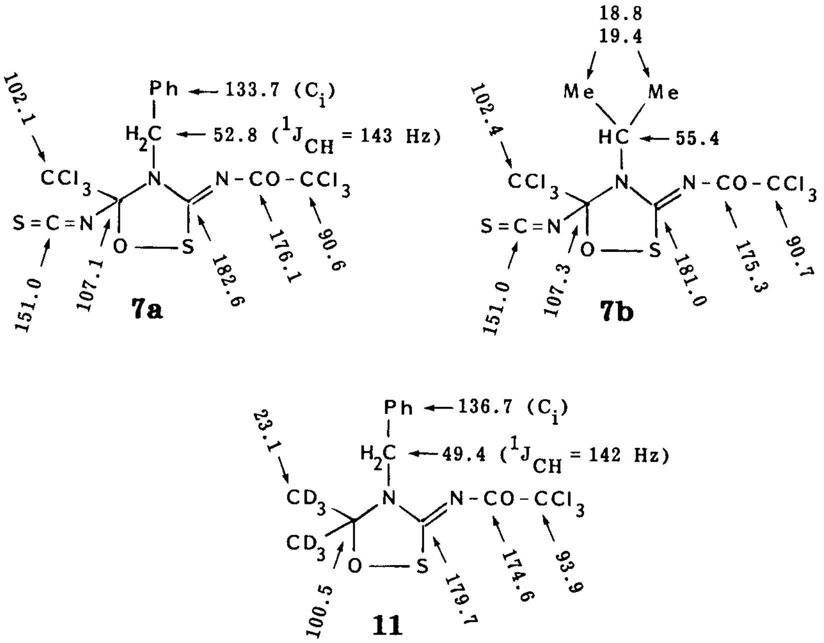
The reaction of isopropyl azide with an equimolar amount of trichloroacetyl isothiocyanate in deuteriochloroform was also monitored by ^{1}H nmr spectroscopy and showed methine septet absorptions at δ 4.3, 4.7 (x 2) and

Scheme 1



a: R = $PhCH_2$, b: R = Me_2CH, c: R = Ph_2CH

Scheme 2



5.2 (Figure 3). One of the septets at δ 4.7 corresponds to an intermediate which achieves a maximum concentration of 30% after 60 minutes, while the septets at δ 4.3 and 5.2 only appear after an induction period and represent the end-products of the reaction. We have checked that the amount of nitrogen evolved after one hour corresponds to the decrease of azide concentration, thus eliminating structure **5b** for the intermediate.

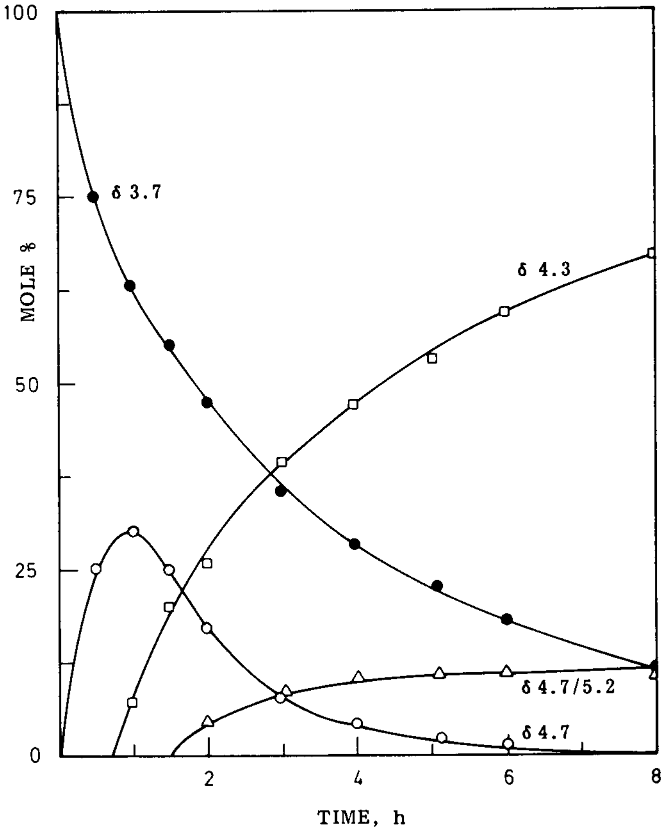
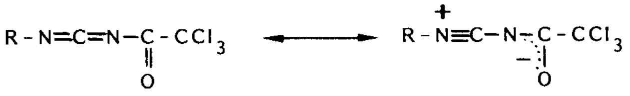


Figure 3. Reaction of isopropyl azide (0.5 *M*) with an equimolar amount of trichloroacetyl isothiocyanate at 40°. Relative concentrations of isopropyl azide (•), **7b** (o), **8b** (□) and **9b** (△).

When ten equivalents of isothiocyanate were used, the intermediate reached a concentration of 70% after 50 minutes and was analyzed by ^{13}C nmr spectroscopy. The data, shown in Scheme 2, are in consonance with structure **7b**. The end-products were isolated and identified as the carbodiimide **8b** (δ 4.3) and the thiadiazolidine **9b** (δ 4.7 and 5.2).

Diphenylmethyl azide is less reactive than the other azides towards trichloroacetyl isothiocyanate and requires heating at 60° in chloroform solution. The ^1H nmr spectra, recorded during the reaction, revealed the presence of only one product with a methine singlet absorption at δ 6.20, corresponding to the carbodiimide **8c**.

A comment on the unusual spectral properties of the carbodiimides **8b,c** is in order. They were found to absorb at higher frequency in the ir spectra (2260 and 2230 cm^{-1} respectively) and at higher field for the N=C=N carbon atom in the ^{13}C nmr spectra (δ 114 and 119 respectively) compared with aliphatic and aromatic carbodiimides. The latter show ir absorptions at 2120-2150 cm^{-1} [8] and ^{13}C nmr resonances at δ 140 [9]. In fact, **8b,c** absorb at positions similar to those of nitriles, suggesting a strong contribution of the canonical structure **8'** to the resonance stabilization of the carbodiimide. *N*-Ethoxycarbonyl-*N'*-isopropylcarbodiimide was prepared and showed also the expected shifts in the ir (2200 cm^{-1}) and ^{13}C nmr spectra (δ 124 for N=C=N). Finally, we have ascertained that the structure attribution of **8b,c** is correct by hydrolyzing them into the corresponding ureas.



8 **8'**

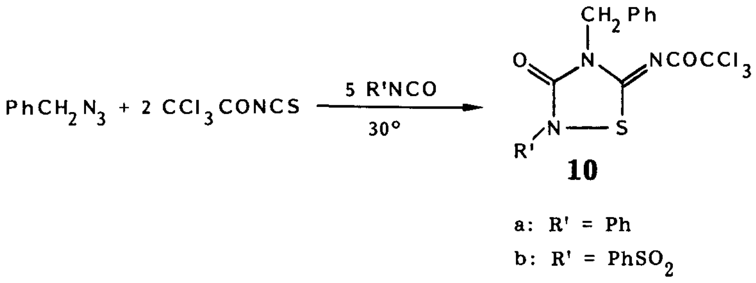
Mechanism.

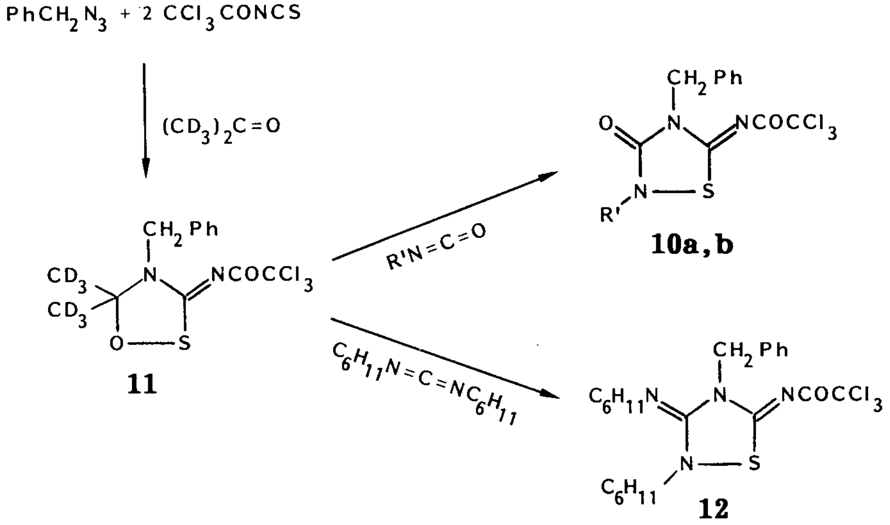
With these results we can formulate the reaction course shown in Scheme 1. The C=S monoadduct **5** is assumed as primary intermediate which decomposes spontaneously with anchimeric assistance of the carbonyl function, thus preventing its detection in the ^1H nmr spectra. The resulting oxathiazoline **6** possesses a thioimidate function capable of undergoing cycloaddition - ring opening reactions with electrophilic unsaturated systems [10]. The reaction with the acyl isothiocyanate would yield **7**, whereas reaction with the carbodiimide **8** (the decomposition product of **6**) would give **9**. As expected, these cycloaddition - ring opening reactions are more pronounced for the strongly nucleophilic, and less hindered benzyl derivative **6a**, and completely inhibited for the diphenylmethyl derivative **6c** which yields only **8c** as detectable product. In the case of the isopropyl derivative **6b**, the adduct **7b** is formed easily, but **9b** remains at low concentration.

The 1,2,4-oxathiazolidin-3-imines **7a** and **7b** are unstable due to their weak S-O bonds. A similar compound has been isolated recently under exceptionally favorable conditions, but even then it deteriorated to a thiadiazolidine derivative similar to **9** [11]. Our failure to isolate **7a** and **7b** is understood if we assume that these compounds are in equilibrium with a small amount of **6a,b**, not detectable by nmr, and decompose *via* the pathway **7** → **6** → **8** → **9** during the reactions or work up procedures.

Trapping Experiments.

The 1,2,4-oxathiazoline **6** constitutes the key intermediate in the reaction Scheme 1, but has not been detected by nmr spectroscopy. Since it is assumed to react as a masked





1,3-dipole [10] in the formation of **7** and **9**, we have carried out a series of trapping experiments using isocyanates as co-reagents. Thus, when the reaction of benzyl azide with two mole-equivalents of trichloroacetyl isothiocyanate was conducted in the presence of a fivefold excess of phenyl isocyanate at 30°, the ^{1}H nmr spectra (deuteriochloroform) were devoid of absorptions corresponding to **7a**, **8a** and **9a**, but showed a methylene resonance at δ 5.30 for **10a**. Phenylsulfonyl isocyanate gave similar results and produced **10b** (δ 5.10) as the sole reaction product.

Acetone as solvent is also an efficient trap for **6a**. Indeed, when benzyl azide was allowed to react with trichloroacetyl isothiocyanate in acetone at 30°, one mole-equivalent of nitrogen was collected and a single product was formed in over 95% yield according to the ^{1}H nmr spectrum (δ 5.0). A ^{13}C nmr analysis of the solution indicated that the oxathiazolidine **11** is present (see Scheme 2). This adduct remained stable in acetone solution at 0°, but our attempts at isolation resulted in the formation of **9a**.

When an acetone solution of **11** was treated with a fivefold excess of phenyl isocyanate at 60°, **10a** was formed (35%) in addition to **9a**. Under similar conditions, phenylsulfonyl isocyanate and *N,N'*-dicyclohexylcarbodiimide gave single products corresponding to **10b** and **12** respectively. These results are rationalized by assuming that **11** is unstable and equilibrates with **6a**, which is trapped by the heterocumulene.

EXPERIMENTAL

Trichloroacetyl Isothiocyanate.

This compound was prepared following the literature procedure [12]; ^{13}C nmr (deuteriochloroform): δ 92.3 (CCl$_3$), 150.1 (NCS), 156.4 (CO).

4-Benzyl-5-isothiocyanato-3-trichloroacetylimino-5-trichloromethyl-1,2,4-oxathiazolidine (**7a**).

A solution of benzyl azide (17 mg, 0.5 *M*) and 10 equivalents of trichloroacetyl isothiocyanate (255 mg) in deuteriochloroform (0.25 ml) was thermostatized at 30° for 40 minutes, while nitrogen evolved. The sample was analyzed by ^{1}H nmr (one major singlet at δ 5.38), ^{13}C nmr spectroscopy (see Scheme 2) and ms (M$^{+\cdot}$ at m/z 511, 0.3%). Note: Attempts to isolate this product resulted in the formation of **9a** (*vide infra*).

4-Isopropyl-5-isothiocyanato-3-trichloroacetylimino-5-trichloromethyl-1,2,4-oxathiazolidine (**7b**).

A solution of isopropyl azide (11 mg) and 10 equivalents of trichloroacetyl isothiocyanate (255 mg) in deuteriochloroform (0.25 ml) was thermostatized at 40° for 50 minutes, while nitrogen evolution occurred. The sample was cooled to 0° and analyzed by ^{1}H nmr (doublets at δ 1.65 and 1.75, septet at δ 4.7, 70%) and ^{13}C nmr spectroscopy (see Scheme 2).

3,5-Bis(trichloroacetylimino)-2,4-dibenzyl-1,2,4-thiadiazolidine (**9a**).

A solution of benzyl azide (1 g, 7.5 mmoles) and trichloroacetyl isothiocyanate (1.71 g, 7.5 mmoles) in dry dichloromethane (15 ml) was stirred at room temperature for 3 days. Ether (15 ml) was added and the precipitate was filtered off in 41% yield (0.9 g), mp 205° (ether-dichloromethane, 1:1); ir (potassium bromide): 1650 (s, CO), 1565 cm^{-1} (s, C = N); ^{1}H nmr (250 MHz, deuteriochloroform): δ 5.0 and 5.5 (two s, 4H, two CH_2), 7.3-7.45 and 7.7-7.8 (two m, 10H, two Ph); ^{13}C nmr (deuteriochloroform): δ 51.2 and 53.1 (two CH_2), 92.5 and 95.7 (two CCl_3), 128.9-130.3, 132.0 and 133.4 (Ph C-atoms), 154.1 (C-3), 165.6 (CON at position 3), 173.0 (C-5), 174.7 (CON at position 5).

Anal. Calcd. for $C_{20}H_{14}Cl_6N_4O_2S$ (mol wt 587): C, 40.91; H, 2.40. Found: C, 40.67; H, 2.34.

Reaction of Isopropyl Azide with Trichloroacetyl Isothiocyanate.

A solution of isopropyl azide (0.42 g, 4.1 mmoles) and trichloroacetyl isothiocyanate (1.02 g, 4.1 mmoles) in dry dichloromethane (10 ml) was stirred overnight at 40°. The solvent was removed and the residue was triturated with ether to give a precipitate.

3,5-Bis(trichloroacetylimino)-2,4-diisopropyl-1,2,4-thiadiazolidine (**9b**).

This compound was obtained in 11% yield (115 mg), mp 212° (ether-dichloromethane, 1:1); ir (potassium bromide): 1660 (s, CO), 1550 cm^{-1} (s, C = N); ^{1}H nmr (250 MHz, deuteriochloroform): δ 1.55 and 1.7 (two d, 12H, four Me), 4.7 and 5.2 (two sept., 2H, two CH); ^{13}C nmr (deuteriochloroform): δ 19.1, 21.9, 52.5 and 54.8 (two $CHMe_2$), 92.6 and 95.9 (two CCl_3), 154.7 (C-3), 164.8 (CON at position 3), 172.5 (C-5), 174.4 (CON at position 5).

Anal. Calcd. for $C_{12}H_{14}Cl_6N_4O_2S$ (mol wt 491): C, 29.35; H, 2.87. Found: C, 29.35; H, 2.77.

N-Isopropyl-*N'*-trichloroacetylcarbodiimide (**8b**).

This compound was obtained as an impure oil by evaporation of the ether filtrate; ir (neat): 2250 cm^{-1} (s); ^{1}H nmr (deuteriochloroform): δ 1.5 (d, 6H, two Me), 4.3 (sept, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 23.5 and 49.9 ($CHMe_2$), 93.5 (CCl_3), 113.8 (N = C = N), 169.2 (CO).

N-Isopropyl-*N'*-trichloroacetylurea.

This compound was obtained by dissolving the oil **8b** in acetone (10 ml), containing 1 ml of water. After stirring at room temperature for 3 days, the solvent was changed for ether, dried over sodium sulfate and evaporated, yield 54% (545 mg), mp 132° (ether); ir (potassium bromide): 3335 (m, NH), 1725 with shoulder at 1710 cm^{-1} (s, CO); ^{1}H nmr (deuteriochloroform): δ 1.2 (d, 6H, two Me), 3.95 (sept, 1H, CH), 7.7 and 9.1 (two br, 2H, two NH); ^{13}C nmr (deuteriochloroform): δ 22.5 and 42.8 ($CHMe_2$), 91.7 (CCl_3), 150.7 (NCON), 162.1 (NCOC).

Anal. Calcd. for $C_6H_9Cl_3N_2O_2$ (mol wt 247.5): C, 29.12; H, 3.66. Found: C, 29.22; H, 3.60.

Reaction of Diphenylmethyl Azide with Trichloroacetyl Isothiocyanate.

A solution of diphenylmethyl azide (1.04 g, 5 mmoles) and trichloroacetyl isothiocyanate (1.02 g, 5 mmoles) in dry chloroform (5 ml) was stirred overnight at 60°. After removal of the solvent, the oil was analyzed by ir (2230 cm^{-1}, s) and ^{1}H nmr spectroscopy (δ 6.2) and was estimated to contain 70% of the carbodiimide **8c**. The oil was refluxed overnight in wet acetone, and then chromatographed on silica gel with ether-petroleum ether (2:1) as the eluent.

N-Diphenylmethyl-*N'*-trichloroacetylurea.

This compound was obtained in 55% yield (1.03 g), mp 135° (ether-petroleum ether, 1:1.5), ir (potassium bromide): 3300 and 3340 (s, NH), 1720 cm^{-1} (s, CO); ^{1}H nmr (250 MHz, deuteriochloroform): δ 6.18 (d, 1H, CH), 7.2-7.4 (m, 10H, two Ph), 8.7 (d, 1H, NH), 9.35 (br s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 58.3 (CH), 91.5 (CCl_3), 127.2, 127.8, 128.9 and 140.7 (Ph C-atoms), 150.9 (N-CO-N), 162.4 (N-*C*O-C).

Anal. Calcd. for $C_{16}H_{13}Cl_3N_2O_2$ (mol wt 371.6): C, 51.71; H, 3.53. Found: C, 51.93; H, 3.46.

4-Benzyl-2-phenyl-5-trichloroacetylimino-1,2,4-thiadiazolidin-3-one (**10a**).

A solution containing benzyl azide (195 mg, 1.47 mmoles), trichloroacetyl isothiocyanate (1.5 g, 7.35 mmoles) and phenyl isocyanate (0.95 g, 7.35 mmoles) in carbon tetrachloride (3 ml) was stirred at room temperature for 2 hours. After addition of pentane, the precipitated **10a** was collected in 51% yield (325 mg), mp 119° (ether); ir (potassium bromide): 1715 (s), 1610 (s), 1510 cm^{-1} (s); ^{1}H nmr (250 MHz, deuteriochloroform): δ 5.30 (s, 2H, CH_2), 7.3-7.8 (m, 10H, two Ph); ^{13}C nmr (deuteriochloroform): δ 49.2 (CH_2), 92.9 (CCl_3), 123.8, 127.7-130.1, 134.3 and 135.1 (Ph C-atoms), 150.3 (C-3), 172.4 (C-5), 174.5 (CO).

Anal. Calcd. for $C_{17}H_{12}Cl_3N_3O_2S$ (mol wt 429): C, 47.63; H, 2.82. Found: C, 47.65; H, 2.91.

4-Benzyl-2-phenylsulfonyl-5-trichloroacetylimino-1,2,4-thiadiazolidin-3-one (**10b**).

A solution containing benzyl azide (195 mg, 1.47 mmoles), trichloroacetyl isothiocyanate (0.6 g, 2.9 mmoles) and phenylsulfonyl isocyanate (1.33 g, 7.35 mmoles) in dry carbon tetrachloride (3 ml) was stirred at room temperature for 3 hours. The precipitated **10b** was filtered off in 79% yield (570 mg), mp 193° (ether-dichloromethane, 1:1); ir (potassium bromide): 1740 (s), 1615 (m), 1510 cm^{-1} (s); ^{1}H nmr (250 MHz, deuteriochloroform): δ 5.10 (s, 2H, CH_2), 7.2-8.2 (five m, 10H, two Ph); ^{13}C nmr (deuteriochloroform): δ 49.2 (CH_2), 92.0 (CCl_3), 128.7-129.9, 133.4, 135.3 and 136.5 (Ph C-atoms), 148.6 (C-3), 174.0 (C-5), 175.6 (CO).

Anal. Calcd. for $C_{17}H_{12}Cl_3N_3O_4S_2$ (mol wt 493): C, 41.44; H, 2.45. Found: C, 41.39; H, 2.48.

4-Benzyl-5,5-dimethyl-d_6-3-trichloroacetylimino-1,2,4-oxathiazolidine (**11**).

A solution of benzyl azide (33 mg, 0.5 *M*) and two equivalents of trichloroacetyl isothiocyanate (102 mg) in deuterated acetone (0.5 ml) was thermostatized at 30° for 2 hours, while nitrogen evolution was observed. The sample was analyzed by ^{1}H nmr (singlet at δ 5.0, >95%) and ^{13}C nmr spectroscopy (see Scheme 2). Notes: (i) Attempts to isolate this compound resulted in the formation of **9a**.

(ii) When a 1 molar solution of benzyl azide and trichloroacetyl isothiocyanate in deuterated acetone was first allowed to stand at 30° for 3 hours, and then treated with five equivalents of phenyl isocyanate at 60°, the ^{1}H nmr spectrum showed the presence of **10a** and **9a** in 35% and 17% respectively after 9 hours.

(iii) When a 0.5 molar solution of benzyl azide and trichloroacetyl isothiocyanate in deuterated acetone was first allowed to stand at 30° for 3 hours, and then treated with five equivalents of phenylsulfonyl isocyanate at 60°, the ^{1}H nmr spectrum showed the presence of a single product **10b** in 55% after 3 hours.

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-trichloroacetylimino-1,2,4-thiadiazolidine (**12**).

A solution of benzyl azide (1 g, 7.5 mmoles) and trichloroacetyl isothiocyanate (1.71 g, 7.5 mmoles) in acetone (7 ml) was stirred at 30° for 3 hours. Then, five equivalents of *N,N'*-dicyclohexylcarbodiimide (7.68 g) were added and the whole was stirred at 60° for 7 hours. The solvent and excess of carbodiimide were distilled off under reduced pressure, and the residue was chromatographed on silica gel with ether-petroleum ether (1:1) as the eluent. The resulting oil was crystallized from ether at $-20°$ to give **12** in 10% yield (400 mg, not uptimized), mp 141° (ether); ir (potassium bromide): 1670 (s), 1625 (m), 1520 cm^{-1} (s); ^{1}H nmr (250 MHz, deuteriochloroform): δ 1.0-2.0, 3.4-3.6 and 3.65-3.85 (three m, 22H, two cyclohexyl), 5.24 (s, 2H, benzyl CH_2), 7.2-7.7 (two m, 5H, Ph); ^{13}C nmr (deuteriochloroform): δ 24.5, 25.0, 25.8, 31.4, 35.0, 55.2 and 59.0 (cyclohexyl C-atoms), 49.0 (benzyl CH_2), 94.1 (CCl_3), 128.0, 128.1, 129.8 and 135.7 (Ph C-atoms), 141.9 (C-3), 173.2 (C-5), 174.1 (CO).

Anal. Calcd. for $C_{23}H_{29}Cl_3N_4OS$ (mol wt 515.9): C, 53.54; H, 5.67. Found: C, 53.27; H, 5.53.

Kinetics.

The nmr tubes containing the azide (0.5 *M*) and trichloroacetyl isothiocyanate in deuteriochloroform were placed in a thermostat at the appropriate temperature (30° or 40° $\pm 0.1°$). At several time intervals the nmr tubes were analyzed by ^{1}H nmr spectroscopy (90 MHz). The concentrations of the products were followed by integration of the benzyl methylene or isopropyl methine absorptions in the spectra and the results are plotted in Figures 1-3.

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