Table I. Rate Constant Ratios and Derived Data for Cl_2/DMB/Fluorinated Benzenes[a]

Ar	k_4/k_6, mol L^{-1}	k_5/k_6	k_3/k_2, mol L^{-1}	k_3,[b] L mol^{-1} s^{-1}
PhH	19.6 ± 9.3	22.4 ± 6.6	2.7 ± 0.2	6.0×10^9
PhF	8.0 ± 4.4	11.8 ± 3.0	1.9 ± 0.4	3.8×10^9
PhF_2	9.1 ± 3.9	7.8 ± 1.8	1.0 ± 0.2	2.0×10^9

[a] Uncertainties are 95% confidence intervals. [b] For benzene k_3 was taken from ref 3; for PhF and PhF_2, k_3 was calculated by using $k_2 = 2.0 \times 10^9$ L mol^{-1} s^{-1}.[3]

and primary alkyl radicals. All experiments were done at dimethylbutane/Cl_2 ratios >10. The aromatic complexing solvents were fluorobenzene (PhF), 1,4-difluorobenzene (PhF_2), 1,3,5-trifluorobenzene (PhF_3), and hexafluorobenzene (PhF_6). The effect of the aromatic compound on the selectivity decreased in the order PhH > PhF > PhF_2 > PhF_3 and had disappeared completely in the case of PhF_6. Figure 1 shows the variation in molar selectivity [3°-Cl]/[1°-Cl] with dimethylbutane concentration.

According to Scheme I, the overall molar selectivity for dimethylbutane is given by eq 1.

$$S^m = \frac{k_1[Cl^\bullet] + k_5[ArHCl^\bullet]}{k_2[Cl^\bullet] + k_6[ArHCl^\bullet]} \quad (1)$$

When the nonobservable concentrations of $Cl^\bullet$ and $(ArHCl)^\bullet$ are eliminated, eq 2 is obtained. When [ArH]

$$S^m = \frac{k_1(k_4 + (k_5 + k_6)[DMB]) + k_3k_5[ArH]}{k_2(k_4 + (k_5 + k_6)[DMB]) + k_3k_6[ArH]} \quad (2)$$

= 0 (absence of complexing solvent) then $S^m = k_1/k_2$, i.e., the selectivity in noncomplexing solvents. However as [DMB] → 0, eq 2 does not reduce to the selectivity of the complex (k_5/k_6) but instead to a more complicated function. Rearranging eq 2 somewhat, we obtain eq 3 in which S^m is expressed in terms of the two reactant concentrations [ArH] and [DMB] and four combinations of rate constants.

$$S^m = \{(k_1/k_2)((k_4/k_6) + (1 + (k_5/k_6)) \times [DMB]) + (k_5/k_6)(k_3/k_2)[ArH]\}/\{((k_4/k_6) + (1 + (k_5/k_6))[DMB]) + (k_3/k_2)[ArH]\} \quad (3)$$

We obtained values k_5/k_6 (the selectivity of the complex), k_3/k_2, and k_4/k_6 by a multiple regression procedure (Table I) in which k_1/k_2 (the selectivity of uncomplexed $Cl^\bullet$) was set equal to 0.66.[3] For benzene, the results are in good agreement with those we reported previously.[3] Convergence of the regression analysis was obtained for PhF and PhF_2, but not for PhF_3. The data for PhF_3 show similar trends to those obtained with the less fluorinated benzenes, but the quality of the data is poor; at low [PhF_3] the molar selectivity changes very little, while at high [PhF_3] a minor impurity in the PhF_3 interfered with the analysis of the alkyl chlorides. Consequently, we were not able to quantitate the trend of decreasing selectivity of the complex (k_5/k_6) beyond difluorobenzene.

The trend that the overall selectivity falls in the series PhH > PhF .... PhF_6 can be interpreted to result from the combination of several factors. Both the rate constant for forming the complex (k_3) and the intrinsic selectivity (k_5/k_6) decrease in this series. These effects may be ascribed to the electron-attracting tendency of the fluorine substituents. Complex formation (k_3) becomes increasingly less competitive with the attack of $Cl^\bullet$ on DMB because $Cl^\bullet$ is a rather electrophilic species. Correspondingly, the stabilization of the complexes is reduced by fluorine substitution, and this makes the complex less selective; i.e. the activation energy for hydrogen abstraction by the complex is reduced as originally argued by Walling.[1b] It may thus be presumed that both k_5 and k_6 increase with increasing fluorination of the aromatic component. Finally, if k_6 increases, it must follow that k_4, the dissociation of the complex, grows rapidly with increasing fluorination. None of these effects should be the result of steric hindrance, given the similar covalent radii of fluorine and hydrogen. To summarize, the lower selectivity for chlorination of 2,3-dimethylbutane in the presence of increasingly fluorinated benzenes results from a combination of three factors: lower rate of complex formation; higher rate of complex dissociation; and lower intrinsic selectivity of the complex.

Experimental Section

Procedures for sample preparation and VPC analysis were described recently.[4] The fluorinated benzenes were available commercially (Aldrich); they were used as received, after first checking their purities by VPC Only 1,3,5-trifluorobenzene had purity <99.5%; its purity was between 98% and 99% (two different lots). A list of the reactant concentrations and observed selectivities (Table II) is available from N.J.B.

The multiple regression analysis was based on a group of subroutines (MLREGR) written by R. A. LaBudde and modified by R. J. LeRoy and J. E. Grabenstetter. A driver program written by C. L. Forber of our laboratory was used to convert the observed quantities [DMB], [ArH], and S into the form required by MLREGR. This involved obtaining the analytical forms of the partial derivatives $\delta S^m/\delta(k_4/k_6)$, $\delta S^m/\delta(k_5/k_6)$, and $\delta S^m/\delta(k_3/k_2)$. Values of these partial derivatives were obtained from trial values of the rate constant ratios. The program was run iteratively so that the "best" values of the rate constant ratios were those that minimized the partial derivatives.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and C. L. Forber for assistance with the multiple regression analysis.

Registry No. 2,4-Dimethylbutane, 79-29-8; fluorobenzene, 462-06-6; 1,4-diflurobenzene, 540-36-3; 1,3,5-trifluorobenzene, 372-38-3; hexafluorobenzene, 392-56-3.

(4) Bunce, N. J.; Cheung, H. K. Y.; Langshaw, J.-A. *J. Org. Chem.* **1986**, *51*, 5421.

Studies on the Reactivity of Carbon Monosulfide toward Amines and Thiols[1]

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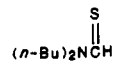
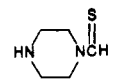
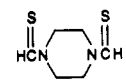
Carbon monosulfide, CS, is a highly reactive gaseous species which in the absence of reaction partners rapidly polymerizes to a brown-black polymer.[3,4] CS has been known for almost a century, but due to the transient nature of CS it has mainly been subjected only to spectroscopic

(1) Carbon Monosulfide Chemistry in Solution. 4. For 3, see ref 10. For 5, see ref 9b.
(2) (a) Kansas State University. (b) Aarhus University.
(3) Klabunde, K. J.; Kramer, M. P.; Senning, A.; Moltzen, E. K. *J. Am. Chem. Soc.* **1984**, *106*, 263.
(4) (a) Dewar, J.; Jones, H. O. *Proc. R. Soc. London, Ser. A* **1910**, *83*, 408, 526; **1911**, *85*, 574. (b) Steudel, R. *Z. Naturforsch.* **1966**, *21b*, 1106. (c) Richardson, R. J.; Powell, H. T.; Kelley, J. D. *J. Phys. Chem.* **1973**, *77*, 2601. (d) Breckenridge; W. H.; Bida, G. T.; Kolln, W. S. *J. Phys. Chem.* **1979**, *83*, 1150.

0022-3263/87/1952-1156$01.50/0

Table I. Results of Reactions between Amines and CS

amine	product	yield,[a] %
$PhNH_2$	PhNHCHNPh (2)	2.0 or 6.0[b]
$PhCH_2NH_2$	$PhCH_2NHC(=S)H$ (3)	1.3
$t\text{-}C_8H_{17}NH_2$	$t\text{-}C_8H_{17}NHC(=S)H$ (4)	0.5
	 (5)	49
$(n\text{-}Bu)_2NH$	 (6)	14
	 (7)	30
	 (8)	40

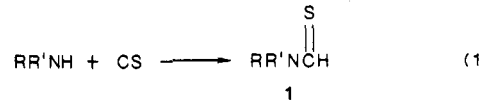
[a] Based on amount of starting amine. [b] Depending on reaction conditions.

investigations.[5] However, when considering that CS is isoelectronic with versatile building blocks such as carbon monoxide[6] and isocyanides,[7] it becomes obvious that CS has a large potential as a synthon in organic and organometallic synthesis, both in the synthesis of thiocarbonyl-containing compounds and in a broader sense as a source of a C_1 building block. Within the last decade CS has become available in multigram quantities by decomposition of CS_2 vapor in a high-voltage AC discharge[3,8] and a more systematic investigation of the chemistry of CS has thus become possible.

Our efforts in this area have as their main goal to give an overall picture of the reactivity of CS and to determine the scope of the application of CS as a synthetic reagent. Our earlier work has demonstrated that CS inserts into halogen–halogen,[8] sulfur–halogen,[3,9] and hydrogen–halogen[8] bonds, adds to aminoacetylenes,[10] and displaces nitrogen in diazo compounds[11a,b] while a number of substrate types are inert to CS under the applied reaction conditions.[11] Especially the reactions of CS with sulfenyl chlorides turned out to be versatile synthetic pathways to a number of so far inaccessible compounds.

Although the chemistry of CS begins to show similarities with that of electron-rich carbenes[12] as well as isocyanides,[7] the results obtained so far do not give a clear picture of the reactivity of CS; e.g., sulfenyl chlorides are electrophilic systems while aminoacetylenes are nucleophilic systems, but CS reacts readily with both types of compounds. In order to gain a better understanding of the reactivity of CS as well as to extend the known chemistry of CS, the present study of reactions of CS with amines and thiols, respectively, was carried out.

The reactions of CS with amines gave mainly the expected thioformamides, **1**, according to eq 1. Since our



$$RR'NH + CS \longrightarrow RR'NCH \quad (1)$$

1

primary interest was in reactivity comparisons, a series of amines were treated with CS and throughout the experiments we attempted to keep the CS/(>NH group) molar ratio constant. Temperature and solvent optimization were not attempted so the yields in Table I should be considered as minima. Furthermore, the two methods used, A and B, gave different CS yields, 70% for A but only 10–20% for B, where a cold trap for CS_2 collections was used; see Experimental Section.

Besides the reactions mentioned in Table I, attempted reactions were performed with *p*-nitroaniline, diisopropylamine, *N*-methylaniline, diphenylamine, pyridine, and triethylamine, all of which, however, failed to react with CS under the applied reaction conditions.

The main product in the reaction with aniline was *N*,*N*′-diphenylformamidine (**2**) while the reaction with piperazine yielded a mixture of *N*-thioformylpiperazine (**7**) and *N*,*N*′-bis(thioformyl)piperazine (**8**).

Two factors seem to affect the reactivity of CS toward amines, the basicity of the amine and the steric hindrance of the >NH group.

The steric influence becomes obvious when the product yields from secondary amines are considered. Morpholine reacts most efficiently with CS.[14] This can be concluded from both the high yield of the insertion product **5** and from the complete absence of polymeric CS which immediately forms in the absence of a suitable reaction partner. A similar high reactivity was observed in the reaction with piperazine. The two products, **7** and **8**, which were unknown compounds prior to this work, were obtained in yields comparable to the yield of **5** and again there was no significant formation of $(CS)_n$. The formation of either **7** or **8** can obviously be controlled by varying the CS/piperazine molar ratio. With di-*n*-butylamine the yield of insertion product **6** was significantly lower and formation of $(CS)_n$ was observed from the start of the reaction. Finally, the reaction with diisopropylamine did not give any insertion product at all. Since the basicities of these amines are comparable,[16] the very different reactivities toward CS must be due to different degrees of steric hindrance around the >NH group.

In addition, the basicities of the amines apparently have an effect on reactivity. The primary systems benzylamine

(5) For reviews, see: (a) Gattow, G.; Behrendt W. In *Topics in Sulfur Chemistry*, Senning, A., Ed.; Georg Thieme Publishers: Stuttgart, 1977; Vol. 2, p 197 ff. (b) *Gmelin Handbuch der Anorganischen Chemie*; Koschel, D., Ed.; Springer-Verlag: Berlin, 1977; Vol. D4, p 7 ff.

(6) See, e.g.,: Holliday, A. K.; Hughes, G.; Walker, S. M. In *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Ed.; Pergamon Press: Oxford, 1973; Vol. 1, p 1225 ff.

(7) (a) Saegusa, T.; Ito, Y. In *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York, 1971; p 65 ff. (b) Periasamy, M. P.; Walborsky, H. M. *Org. Prep. Proc. Int.* **1979**, *11*, 295.

(8) Klabunde, K. J.; White, C. M.; Efner, H. F. *Inorg. Chem.* **1974**, *13*, 1778.

(9) (a) Moltzen, E. K.; Senning, A.; Kramer, M. P.; Klabunde, K. J. *J. Org. Chem.* **1984**, *49*, 3854. (b) Moltzen, E. K.; Jensen, B.; Senning, A. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 609. (c) Moltzen, E. K.; Senning, A. *Sulfur Lett.* **1986**, *4*, 97. (d) Moltzen, E. K.; Jensen, B.; Senning, A. *Sulfur Lett.* **1986**, *4*, 203.

(10) Krebs, A.; Guntner, A.; Senning, A.; Moltzen, E. K.; Klabunde, K. J.; Kramer, M. P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 729.

(11) (a) White, C. M. Master of Arts Thesis, University of North Dakota, 1974. (b) Moltzen, E. K. Cand. Scient. Thesis, Aarhus University, 1985. (c) Kramer, M. P. Ph.D. Thesis, Kansas State University, 1986.

(12) See, e.g.: Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; p 409 ff.

(13) Moltzen, E. K.; Senning, A.; Hazell, R. G.; Lund, H. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 593.

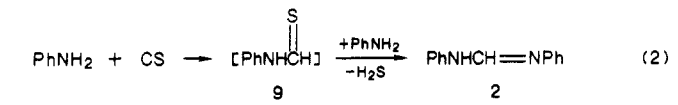
(14) This reaction has been reported earlier (ref 15), but the method applied in those reports is not likely to be feasible in synthetic scale reactions.

(15) (a) Fjeldstad, P. E.; Undheim, K. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 375. (b) Skramstad, J.; Chaudry, M. S.; Garvang, A. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 509.

(16) See, e.g.: Bohme, D. K., In *The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1982; p 750 ff.

and *tert*-octylamine both reacted very sluggishly with CS, giving the thioformamides **3** and **4**, respectively. The low yields seem to reflect the fact that primary amines generally are less basic than secondary amines.[16] The reactions with aromatic amines emphasize the same trend. Diphenylamine, having both a sterically hindered >NH group and low basicity, gave no product. Aniline reacted with CS, giving **2** in low yield while the reaction of *N*-methylaniline, possessing greater basicity than aniline but more steric hindrance of the >NH group, gave no adduct.

The formation of **2** from the reaction of aniline with CS is obviously a result of a secondary reaction between the initially formed thioformanilide, **9**, and aniline according to eq 2. This reaction sequence is in accordance with the



(2)

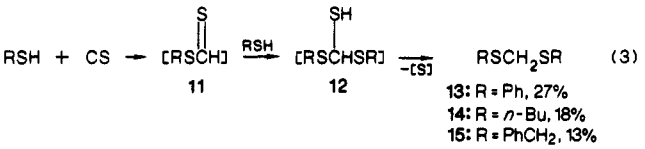
known fact[17] that thioamides react with amines, giving the H_2S salt of the corresponding amidines, and could be further substantiated by treatment of an authentic sample of **9** with excess aniline which gave **2** in 84% yield. The spontaneous loss of H_2S must be due to the low basicity of the nitrogen atoms in **2** (H_2S was a product in the reaction and was detected by smell, but not determined quantitatively).

Interestingly, aliphatic amines did not give secondary reactions as aniline did. The attack of amine on the electrophilic thiocarbonyl group of the product thioamide apparently needs to be facilitated by a directly attached aromatic substituent, thereby increasing the electrophilic character of the thiocarbonyl group.

Since the preparation of thioformamides via CS is of synthetic interest, it would be desirable to increase the yield in the reactions with primary amines. Copper compounds such as CuCl and Cu_2O are known to catalyze a variety of reactions with isocyanides via the formation of a copper–isocyanide complex which is the reactive species.[7a] Considering that CS is isoelectronic with isocyanides, we had reason to assume that these copper compounds also would catalyze the insertion of CS into the N–H bond of amines. This turned out not to be the case. By treatment of benzylamine with CS in the presence of CuCl or Cu_2O, the formation of **3** was completely depressed. Instead a small amount of *N*,*N*′-dibenzylthiourea (**10**) was formed, most probably originating from the reaction of amine with CS_2, as shown by treatment of benzylamine with CS_2 in toluene in the presence of catalytic amounts of CuCl which gave **3** in a yield comparable to the yield of **3** from the CS reaction.

Evidently, the insertion of CS into the N–H bond cannot be catalyzed in the same manner as the corresponding reactions with isocyanides. That CS does form adducts with the copper compounds can be seen from the effect on the polymerization of CS. Usually polymeric CS is formed on the walls throughout the vacuum line. With CuCl or Cu_2O present, all the CS was trapped in the reaction mixture and in the reaction with CuCl the formation of $(CS)_n$ was very rapid even at −78 °C. In the reaction with Cu_2O, the effect was more pronounced. At low temperature, no formation of $(CS)_n$ could be observed, but when warmed to room temperature the reaction mixture rapidly turned black and a large amount of $(CS)_n$ could be obtained. Obviously CS coordinates to the copper, but the polymerization reaction must be highly favored[18] compared to the reaction with the amine since no thioformamide was formed.

Treatment of thiols with CS resulted mainly in the formation of bis(alkylthio)methanes, **13**–**15**, possibly according to eq 3. CS and thiol are possible sulfur abstractors in the final step.



(3)

In the reaction with thiophenol no further products could be isolated, but with the aliphatic thiols small amounts of the corresponding trialkyl orthotrithioformates, **16** and **17** could be isolated.

$(RS)_3CH$
16: R = *n*-Bu
17: R = $PhCH_2$

The formation of secondary products from these reactions is not surprising. Most compounds containing the thioformyl group as the initially formed dithioformates, **11**, are known to be notoriously unstable,[19] with a few exceptions such as thioformamides, thioformates, and their vinylogues. When thioformyl compounds, RC(S)H, are formed in the absence of suitable reaction partners, they usually react rapidly to form trimers and oligomers.[19] In the reactions of thiols with CS, however, none of these product types were found.

The formation of the intermediate **11** is supported by the isolation of small amounts of orthotrithioformates **16** and **17** in the reactions with phenylmethanethiol and butanethiol, respectively. When one considers the fact that orthotrithioformates can be prepared by treatment of formates with thiols,[20] it becomes very likely that the same type of reaction can occur with **11** which is much more reactive than a formate. The formation of **16** and **17** from **11** might also occur via the intermediate **12**.

The reaction with thiophenol gives a slightly better yield than the reactions with aliphatic thiols, but the difference is far less pronounced than in the reactions with amines. It is obvious that steric factors are of minor importance and the differences are most likely due to electronic factors. These are, however, not as important as in the amine reactions probably because of the softer, more polarizable character of sulfur compared to nitrogen.

The addition of catalytic amounts of CuCl did not influence the reactions with thiols. The same products were obtained in the same yields as without catalyst and the only observed difference was the above-mentioned effect on the polymerization of CS.

Methanol is completely inert to CS under the applied reaction conditions[11a] and can in fact be used as solvent for CS reactions.[13]

The observed reactivities suggest that CS is a weak electrophile since both amines and thiols can be considered as nucleophilic systems and since the most nucleophilic amines react most readily. This suggestion is also supported by the earlier reported reactivity of CS toward electron-rich acetylenes, and the analogy with isocyanides

(17) Gautier, J. A.; Miocque, M.; Farnoux, C. C. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; John Wiley & Sons: London, 1975; p 303.

(18) The catalytic effect of metal compounds on the polymerization of gas-phase CS has been described. See ref 4d.

(19) For a recent listing of the relevant literature, see: Vedejs, E.; Perry, D. A.; Wilde, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2985.

(20) (a) Schonberg, A.; Praefcke, K. *Chem. Ber.* **1966**, *99*, 2371. (b) Engler, R.; Gattow, G.; Drager, M. *Z. Anorg. Allg. Chem.* **1972**, *390*, 64 and references herein.

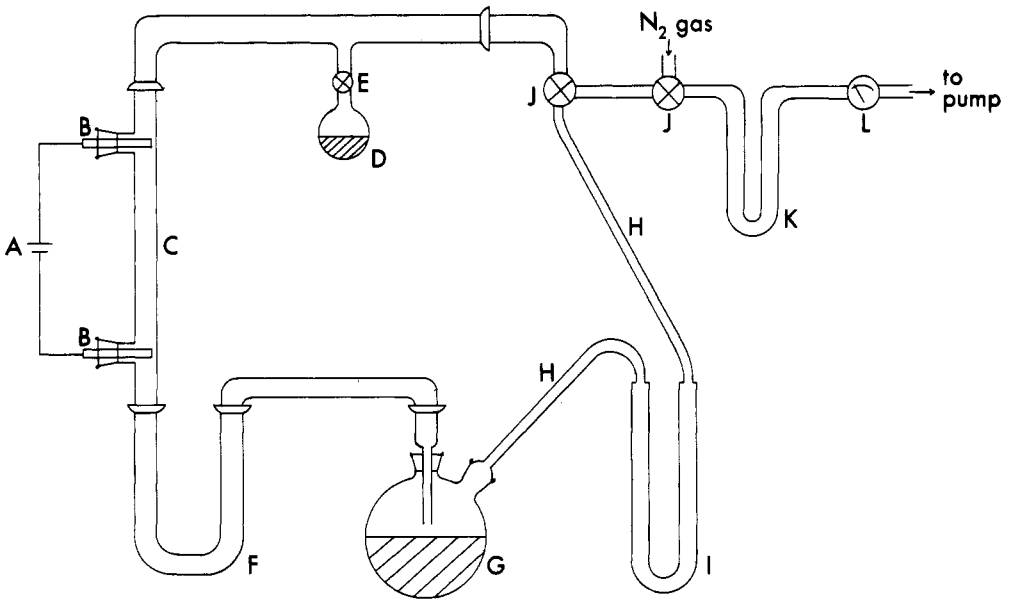


Figure 1. Key: A, power supply; B, brass electrodes; C, discharge tube; D, CS_2 container; E, needle valve; F, metal cold trap; G, reaction flask; H, rubber vacuum tubes; I, metal cold trap; J, three-way valves; K, glass cold trap; L, vacuum gauge.

and electron-rich carbenes holds throughout the known reactions of CS. The reactions of CS with sulfenyl chlorides do not fit entirely in this picture, and preliminary results indicate that a frontier orbital approach[21] is necessary in order to get a completely coherent picture of the reactivity of CS.

From a synthetic point of view the reactions with thiols are of minor importance since the resulting bis(alkylthio)methanes are readily available by conventional routes.[22] The reactions with amines, however, have some very interesting aspects. In contrast to the known methods of thioformamide preparations,[23] the CS reactions occur at low temperature in a neutral and nonpolar media, thus allowing the introduction of thioformyl groups in sensitive compounds which do not survive conventional treatments. At present this method is most useful with secondary, sterically unhindered amines, but undoubtedly ways can be found to increase the yields of thioformamides from primary amines, thus giving the method a wide scope.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer or at 400.1 MHz on a Bruker WM-400 spectrometer. Me_4Si was used as an internal standard. ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100 spectrometer or at 100.6 MHz on a Bruker WM-400 spectrometer. Me_4Si or $CDCl_3$ (set at 77.0 ppm) was used as an internal standard. All chemical shifts are expressed in δ values and $CDCl_3$ was used as solvent. IR spectra were recorded on a Nicolet 5MX Fourier transform spectrometer or on a Perkin Elmer BE-1330 spectrometer. Mass spectra were recorded on a Micromass 7070E spectrometer or on a Finnegan 4000 quadrupol spectrometer using direct inlet on both spectrometers. Elemental analyses were carried out by Lovens Kemiske Fabrik, DK-2750 Ballerup, Denmark, or by Galbraith Laboratories, Inc., Knoxville, TN 37921. The silica gel used was either of the type Merck Kieselgel 60, 230–400 mesh, or Aldrich 28,860-8, 130–270 mesh. The petroleum ether used had a boiling range below 50 °C.

General Procedure for the CS Experiments. Carbon monosulfide was generated in a conventional vacuum line (Figure 1) by passing CS_2 vapor through a high-voltage AC discharge. The internal diameter of the discharge tube was 15 mm and the distance between the electrodes 450 mm. The power supply was a conventional neon transformer operating at 12 kV and a maximum of 20 mA. Depending on whether the substrate reacts with CS_2 or not, two different methods were applied.

Method A. The gas mixture leaving the discharge tube consisting of approximately 70% CS and 30% CS_2 together with minor amounts of carbon subsulfide and elementary sulfur was passed directly into the reaction flask containing a stirred solution of the substrate. A detailed description of this procedure is given elsewhere[9b] and will not be repeated here.

Method B. The gas mixture was passed through a metal cold trap kept at ca. −112 °C before entering the reaction flask (see Figure 1). By this procedure a gas mixture consisting of approximately 85% CS and 15% CS_2 with a CS yield of 10–20% (based on the amount of CS_2 consumed) could be obtained.

The system was first evacuated to a pressure of 0.02–0.05 torr for at least 2–3 h. If the substrate or the expected products are very air-sensitive, it is recommended to flush the system with nitrogen several times. The system was then filled with nitrogen and the solution of the substrate was placed in the reaction flask with a stirring bar, followed by cooling to the appropriate reaction temperature with stirring. The reaction temperature depends on the vapor pressures of substrate and solvent which must be less than the pressure in the line during the reaction (ca. 0.05 torr). The three-way valves, J, were opened in the direction K–J–J–H and the system was evacuated to ca. 0.05 torr. When the stirred solution had stopped degassing, the cold trap F was cooled with an ethanol slush bath to ca. −112 °C and the cold traps I and K were cooled with liquid nitrogen. The high voltage was turned on and the needle valve E was opened to allow a stream of 25–30 mL/h of CS_2 vapor to pass through the discharge tube. It is recommended to use at least 6–8 equiv of CS_2 relative to substrate. The CS_2 container, D, was placed in a cold-water bath to maintain a constant evaporation temperature. During the reaction the glass tubes between the cold trap F and the reaction flask quickly turned brown-black due to formation of polymeric CS. The rate of formation of $(CS)_n$ in the reaction mixture depends on the reactivity of the substrate toward CS; e.g., in the reaction with morpholine no polymer formation could be observed until the end

(21) A theoretical study of the CS reactions in terms of frontier orbitals is underway.

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of the reaction while in the reaction with diisopropylamine $(CS)_n$ started to form immediately and several explosions in the cold trap I due to the violent polymerization of condensed monomeric CS could be heard. *These explosions are the reason for using metal traps since glass would be liable to break.*

It is crucial to maintain the temperature of the cold trap F. At higher temperatures than ca. −110 °C undissociated CS_2 will not be trapped efficiently and *at lower temperatures than ca. −117 °C the bulk of the CS will be trapped with a large risk of very violent explosions.*

When the reaction was finished the discharge was turned off and the needle valve E closed. The system was filled with nitrogen gas, the cold traps F and I were removed, and the reaction mixture was allowed to warm to room temperature followed by the usual workup procedures. The layer of $(CS)_n$ and sulfur that had built-up on the inner walls of the glass equipment can be removed by careful treatment with nitric or fuming nitric acid.

The reactions with aniline, *p*-nitroaniline, *N*-methylaniline, diphenylamine, pyridine, triethylamine, thiophenol, *n*-butanethiol, and phenylmethanethiol were performed by applying method A on 50–100 mL of 0.5–1 M toluene solutions at −78 °C and by using 4–6 equiv of CS_2 relative to substrate. The reactions with benzylamine, *tert*-octylamine, morpholine, di-*n*-butylamine, and diisopropylamine were performed by applying method B on 50–100 mL of 0.5 M toluene solutions at −78 °C and by using 8–10 equiv of CS_2 relative to substrate, while the reaction with piperazine was performed in DMF solution (100 mL, 0.25 M) at −35 °C by method B (8–10 equiv of CS_2 relative to substrate).

***N,N'*-Diphenylformamidine (2). (a) From $PhNH_2$/CS.** A color change from colorless to dark red could be observed together with polymer formation. Filtration and removal of solvent and excess CS_2 in vacuo gave a dark red oil. Separation on a chromatographic column (silica gel; eluent 1:1 mixture of ether (E) and petroleum ether (PE)) gave a colorless solid which could be recrystallized from E/PE, giving 0.4 g (2%, based on 9.5 g of used amine) of colorless needles, **2**,[26] mp 134–136 °C (lit.[24] mp 138–139 °C). Repetition of the experiment with 20.5 g of neat aniline at 0 °C gave 2.2 g (6%) of **2**.

(b) From $PhNH_2$/9. A solution of 3.0 g (22 mmol) of **9**[23] and 4.1 g (44 mmol) of $PhNH_2$ in 50 mL of toluene was heated to 60 °C. Evolution of H_2S started immediately and after 1 h the solvent was removed in vacuo. The remaining heavy oil was dissolved in a 1:1 mixture of E/PE and the solution was left in the cold for 12 h, giving 3.6 g of colorless needles, **2** (mp 142–144 °C). Yield: 84%.

***N*-Benzylthioformamide (3).** The reaction mixture went quickly black (polymer formation). Filtration and removal of the toluene in vacuo gave a heavy black oil. Addition of a cold mixture of 150 mL of E and 50 mL of PE gave a colorless precipitate of the benzylammonium salt of *N*-benzyldithiocarbamic acid and a black precipitate of polymeric CS. Filtration through charcoal and removal of the solvent in vacuo gave a yellow solid which could be purified by means of TLC (silica gel; eluent 3:1 mixture of E/PE). Recrystallization from E/PE gave 0.1 g (1.3%, based on 5.4 g of used amime) of colorless crystals which could be identified as **3**,[26] mp 63–65 °C (lit.[23] mp 63–64 °C). The reaction was repeated with addition of 0.4 g (4 mmol) of CuCl. The added CuCl turned the initial solution dark blue. Formation of $(CS)_n$ in the reaction mixture started immediately. Filtration and removal of solvent in vacuo gave a black oil. Remaining polymeric CS was precipitated by addition of a mixture of 100 mL of CH_2Cl_2 and 25 mL of E and storage at −10 °C for 12 h. Filtration through charcoal and removal of solvents in vacuo gave an orange oil. Addition of 150 mL of E gave a colorless precipitate of CS_2 products which were removed by washing with 3 × 200 mL of water. Drying over molecular sieves (3 Å) and removal of solvent gave an orange oil which was purified on a chromatographic column (silica gel; eluent 3:1 mixture of E/P), giving a colorless solid which could be crystallized from CH_2Cl_2/pentane (P), yielding 180 mg of colorless crystals, **10**,[26] mp 146–147 °C (lit.[24] mp 148 °C).

Repetition of the reaction with 0.4 g (4 mmol) of Cu_2O instead of CuCl gave 190 mg of **10** following the same workup procedure as described above.

***N*-*tert*-Octylthioformamide (4).** Similar to the other primary amines, the reaction mixture rapidly turned black. Filtration and removal of the solvent in vacuo gave a black oil which could be separated on a chromatographic column (silica gel; eluent 1:4 mixture of E/PE), giving an orange oil. Addition of E/PE yielded 25 mg (0.5%, based on 4.0 g of used amine) of slightly yellow crystals which could be identified as **4**,[26] mp 57–59 °C (lit.[23] mp 58–60 °C).

***N*-Thioformylmorpholine (5).** After consumption of 10 mL of CS_2 a colorless precipitate of the morpholinium salt of morpholinodithiocarbamic acid started to form. After consumption of 25 mL of CS_2 black particles of polymeric CS could be observed in the reaction mixture. Filtration and removal of the solvent in vacuo gave a yellow solid which could be recrystallized from E, yielding 3.2 g (49%, based on 4.4 g of used amine) of colorless crystals identified as **5**,[26] mp 67–69 °C (lit.[23] mp 67–68 °C).

***N,N*-Di-*n*-butylthioformamide (6).** After consumption of 10 mL of CS_2, formation of polymeric CS could be observed. Filtration and removal of the toluene gave a dark red oil which could be purified on a chromatographic column (silica gel; eluent 1:3 mixture of E/PE), giving 1.2 g (14%, based on 6.5 g of used amine) of a yellow oil identified as **6**.[23,26]

***N*-Thioformylpiperazine (7) and *N,N'*-Bis(thioformyl)-piperazine (8).** By the initial cooling of the DMF solution the piperazine precipitated partially. During the reaction a color change from colorless to red took place without formation of polymeric CS. After the reaction mixture was heated to room temperature, a small amount of piperazine/CS_2 product was filtered off and removal of the solvent in vacuo gave a dark red oil. Separation on a chromatographic column (silica gel; eluent methanol) gave two fractions: (1) a yellow solid which could be recrystallized from CH_2Cl_2, yielding 1.2 g (40%, based on 2.0 g of used amine) of slightly yellow crystals (mp 186–188 °C) identified as **8** [IR (KBr, cm^{-1}) 2990 (vw), 2950 (vw), 2900 (w), 1500 (vs), 1430 (vs), 1410 (m), 1355 (m), 1345 (m), 1250 (w), 1215 (vs), 1150 (m), 1050 (vw), 1020 (m), 1000 (s), 925 (m), 910 (m), 635 (w), 465 (w), 450 (w); MS, *m/z* 174 (M^+), 141 (M^+ − HS); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.71 (m, 4 H), 4.11 (m, 4 H), 9.26 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 43.49, 44.92, 53.04, 54.52, 188.48. Anal. Calcd for $C_6H_{10}N_2S_2$: C, 41.35; H, 5.78; N, 16.07; S, 36.80. Found: C, 40.96; H, 5.79; N, 15.50; S, 36.54.] and (2) a colorless oil (1.2 g, 30%, based on 2.0 g of starting amine) which could be identified as **7** [IR (NaCl, cm^{-1}) 3300 (m), 2960 (s), 2920 (s), 2840 (m), 2760 (w), 1510 (vs), 1445 (vs), 1400 (m), 1360 (s), 1320 (m), 1290 (w), 1245 (vs), 1140 (s), 1120 (s), 1060 (m), 1030 (vs), 975 (m), 920 (m), 800 (m), 770 (m), 735 (w); MS, *m/z* 130 (M^+), 97 (M^+ − HS), 85 (M^+ − HCS); ^1H NMR ($CDCl_3$, Me_4Si) δ 2.03 (s, 1 H), 2.92 (t, 4 H), 3.63 (t, 2 H), 4.02 (t, 2 H), 9.19 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 45.17, 46.42, 46.60, 56.42, 186.44. Due to inseparable impurities, no useful elemental analyses could be obtained.

Bis(phenylthio)methane (13). The reaction mixture turned slowly dark red with formation of polymeric CS. Filtration and removal of the toluene gave a dark red oil which was separated on a chromatographic column (silica gel; eluent P). A colorless oil was obtained which could be crystallized from E/P, giving 1.45 g (25%, based on 5.5 g of used thiol) of colorless crystals identified as **13**,[26] mp 35–36 °C (lit.[22] mp 39.5–40.5 °C).

Repetition of the reaction in the presence of 0.2 g (2 mmol) of CuCl gave, after the same workup procedure, 1.54 g (27%) of **13**. With 0.5 g (5 mmol) of CuCl, 1.1 g (19%) of **13** was obtained.

Bis(*n*-butylthio)methane (14). The reaction mixture turned slowly dark red under polymer formation. Filtration and removal of solvent gave a black oil which was distilled in vacuo, giving 0.78 g (16%, based on 4.5 g of used thiol) of a slightly yellow oil identified as **14**,[26] bp 120 °C/20 torr (lit.[24] bp 146 °C/43 torr). By workup on a chromatographic column (silica gel; eluent P) instead of distillation, 0.88 g (18%) of **14** was obtained together with 0.59 g (13%) of a colorless oil identified as **16**.[25,26] Repetition of the reaction in the presence of 0.2 g (2 mmol) of CuCl gave same result.

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Bis(benzylthio)methane (15). The reaction mixture turned quickly dark red with polymer formation. Filtration and removal of the toluene gave a dark red oil which was separated on a chromatographic column (silica gel; eluent 1:19 mixture of E/P). Two fractions were obtained: (1) a colorless oil which was crystallized from pentane, giving 0.83 g (13%, based on 6.2 g of used thiol) of colorless crystals, **15**,[26] mp 47–49 °C (lit.[24] mp 55 °C), and (2) a red oil which could be crystallized from E/P to give 0.27 g (4%) of slightly yellow crystals identified as **17**,[26] mp 98–100 °C (lit.[25] mp 102.2–103.2° C).

By performing the reaction in the presence of 0.2 g (2 mmol) of CuCl, 0.65 g (10%) of **15** and 80 mg (1%) of **17** were obtained.

Attempted Reaction with Methanol. This reaction has been reported previously[11a] and a repetition with neat methanol at −78 °C applying the experimental set-up used in this work only resulted in polymer formation. The methanol could be quantitatively recovered.

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Registry No. **2**, 622-15-1; **3**, 20278-32-4; **4**, 106712-04-3; **5**, 5780-30-3; **6**, 13749-55-8; **7**, 106712-05-4; **8**, 106712-06-5; **9**, 637-51-4; **10**, 1424-14-2; **13**, 3561-67-9; **14**, 4431-80-5; **15**, 4431-79-2; **16**, 16754-60-2; **17**, 10606-38-9; CS, 2944-05-0; CS_2, 75-15-0; PhSH, 108-98-5; BuSH, 109-79-5; $PhCH_2SH$, 100-53-8; CS (polymer), 69822-67-9; diisopropylamine, 108-18-9; aniline, 62-53-3; benzylamine, 100-46-9; *tert*-octylamine, 107-45-9; morpholine, 110-91-8; dibutylamine, 111-92-2; piperazine, 110-85-0; *p*-nitroaniline, 100-01-6; *N*-methylaniline, 100-61-8; diphenylamine, 122-39-4; pyridine, 110-86-1; triethylamine, 121-44-8; *N*-benzyldithiocarbamic acid benzylammonium salt, 106712-07-6; morpholinomethanedisulfonic acid morpholinium salt, 5327-10-6; methanol, 67-56-1.

Homogeneous Catalysis with a Heterogeneous Pd Catalyst. An Effective Method for the Cyclotrimerization of Alkynes

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Introduction

In 1866, Berthelot discovered the formation of benzene in small yields by high temperature treatment of acetylene.[1] In 1949, Reppe reported that homogeneous nickel complexes can be employed for the preparative cyclization of acetylene to benzene.[2] This key observation was followed by the development of a variety of transition-metal systems for cyclotrimerization of alkynes.[3]

The oligomerization of alkynes has been reviewed.[3,4] In the following we list only a few selected examples demonstrating the diverseness of methods and catalysts developed. Substituted benzenes have been prepared by the cyclotrimerization of alkynes in the presence of metal carbonyls $HgNi(CO)_4$ and $Hg(Co(CO)_4)_2$,[5,6] $Fe(CO)_5$ and $Fe(CO)_4H_2$,[7] $Co_2(CO)_8$,[8,9] trialkyl- and triarylchromium compounds,[10] and Ziegler catalysts.[11] Ziegler catalysts require careful optimization of the ratio of alkylaluminum and transition-metal halide to avoid polymer formation and thereby improve yield of trimers.[11a] High yields of hexaethylbenzene were obtained with optimized ratios of i-Bu_3Al and $TiCl_4$.[11b] Good yields of hexaethyl-, hexamethyl-, and hexaphenylbenzene were obtained from the corresponding alkyne with i-Bu_2AlH.[12] Monosubstituted alkynes and acetylene itself can be trimerized in moderate to good yields with this Ziegler-type catalyst system.[11,13] Hexaisopropylbenzene, the most hindered benzene prepared to date by alkyne trimerization (see MM2 molecular mechanics calculations below), utilizes Co complexes, apparently the most effective catalysts for alkyne trimerization.[6,9] Careful examinations of such cobalt-mediated trimerizations led to the development of highly efficient and selective syntheses of steroids and other complex molecules.[14]

Bis(acrylonitrile)nickel(0)[15] and bis(benzonitrile)palladium chloride[16] can catalyze trimerization of tolane to give hexaphenylbenzene. Bis(benzonitrile)palladium chloride[17] was found suitable for cyclotrimerization. The reaction with 1-phenylpropyne resulted in a complex mixture which after tedious workup afforded all the three possible isomers.[17a] $NaBH_4$ with $NiCl_2$[18] has also been utilized for the cyclotrimerization of alkynes. The cyclization of 3-hexyne gave reasonable yields of hexaethylbenzene while cyclization of diphenylacetylene afforded poor yields of hexaphenylbenzene using this catalyst.

The use of uncomplexed $PdCl_2$ for the cyclotrimerization of 1-phenylpropyne and 1-phenyl-1-butyne resulted in low yields of unsymmetrical trimer, polymer products, and several complexes.[19] Tantalum and niobium compounds like $Ta_2Cl_6(THT)_3$ and $Nb_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) were found to trimerize terminal alkynes effectively while polymerization predominated with unsymmetrically disubstituted acetylenes.[20] Rhodium complexes were found to effect a low yield trimerization of 3-hexyne and tolane on prolonged heating.[21] Even iron atoms can induce the cyclotrimerization of alkynes.[22]

Many of these methods produce complex reaction mixtures which afford low yields of the desired trimers while all require very stringent reaction conditions. The development of a more convenient method for the trimerization of alkynes is therefore still desirable.

Although the trimerization of alkynes has remained

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