is more efficient than 4A molecular sieves in the desiccation of acetonitrile. The inefficiency of the 4A sieves is brought about by competitive adsorption of acetonitrile at the water binding sites. This apparently does not occur with Drierite.

Summary

Anhydrous calcium sulfate (Drierite) is a moderately efficient desiccant for the drying of organic solvents. The material loses drying activity if heated to about 250 °C and has a limited water capacity (~5% w/w). It is therefore not appropriate for efficiently drying grossly wet solvents as earlier observed.[9]

Experimental Section

Solvent water content was determined by the radiotracer method previously described.[7,12,14] Anhydrous calcium sulfate (Drierite), 10–20 mesh, was kindly supplied as a gift from W. A. Hammond Drierite Company. Details of solvents and other desiccants have already been described.[7]

Registry No. $CaSO_4$, 7778-18-9.

(14) Burfield, D. R. *Anal. Chem.* **1976**, *48*, 2285.

Carbon Monosulfide Chemistry in Solution. 2.[1] Synthesis and Reactions of Trichloromethyl Chlorodithioformate

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Recently we were able to demonstrate that the insertion of CS into the sulfur–chlorine bond of sulfenyl chlorides appears to be a general and synthetically useful reaction.[1] While our previous examples (1) and (2) involve highly

$$C_6H_5SCl + CS \rightarrow C_6H_5SC(S)Cl \quad (1)$$

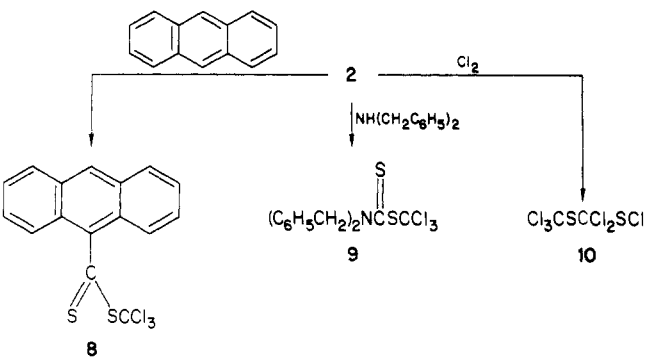
$$ClSSCl + 2CS \rightarrow ClC(S)SSC(S)Cl \quad (2)$$

reactive sulfenyl chlorides, it was not obvious that trichloromethanesulfenyl chloride **1** would react according to (3). In a number of reactions **1** is considerably less

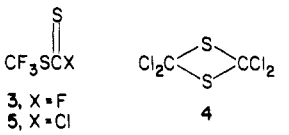
$$\underset{\mathbf{1}}{Cl_3CSCl} + CS \rightarrow \underset{\mathbf{2}}{Cl_3CSC(S)Cl} \quad (3)$$

reactive than "typical" aliphatic or aromatic sulfenyl chlorides; for instance, the normally rapid uncatalyzed addition of sulfenyl chlorides to ethylene does not take place in the case of **1**;[3] moreover, **1** can be steam distilled with little decomposition[4] while "typical" sulfenyl chlorides must be protected from moisture. On the other hand, **1** does react readily in the α-addition to isocyanides[5] (it should be noted that isocyanides are isoelectronic with CS) and, according to very recent reports,[6] **1** and S_2Cl_2 add to certain thiocarbonyl compounds with comparable ease.

Scheme I



It should be noted that there are no obvious alternative synthetic pathways leading to **2**.[7] While the perfluoro analogue **3** is accessible by potassium fluoride catalyzed dimerization of thiocarbonyl fluoride[8] and by treatment of thiocarbonyl chloride fluoride with mercury(II) trifluoromethanethiolate,[9] the photochemical dimerization of thiophosgene leads to 2,2,4,4-tetrachloro-1,3-dithietane (**4**),[10] and there is no reaction between thiophosgene and



KF.[11] Unlike $Hg(SCF_3)_2$, mercury(II) trichloromethanethiolate, $Hg(SCCl_3)_2$, is unknown because of the inherent instability of trichloromethanethiol.[12] Likewise, the reported synthesis of trifluoromethyl chlorodithioformate (**5**)[13] does not lend itself to any modification leading to **2**.

We can now report that reaction 3 does in fact occur readily and in good yield.[14] Trichloromethyl chlorodithioformate (**2**) is a distillable liquid once preliminary silica gel chromatography has been carried out (distillation of crude **2** only gave a small amount of **10**) and can be stored at room temperature for several months. It could be characterized spectroscopically and by derivatization.

As a minor byproduct some pale-yellow crystals could be isolated. According to our preliminary data this yellow solid is most likely the new thiirane **6**, which probably is formed according to (4) in analogy with the formation of 2,2,3,3-tetrachlorothiirane.[15] This reaction mechanism is also supported by recent results of our work on reactions between CS and thiocarbonyl compounds. The 1,4-dithiane structure **7** is also consistent with the analytical and spectral data, but according to the mass spectrum **6** is the most probable structure.

(1) Paper 1 in this series: Klabunde, K. J.; Kramer, M. P.; Senning, A.; Moltzen, E. K. *J. Am. Chem. Soc.* **1984**, *106*, 263.
(2) (a) Aarhus University, Denmark. (b) Kansas State University.
(3) Douglass, I. B.; Martin, F. T.; Addor, R. *J. Org. Chem.* **1951**, *16*, 1297.
(4) Klason, P. *Ber.* **1887**, *20*, 2376.
(5) Enders, E.; Kühle, E.; Malz, H. Belg. Patent 610175, 1960; *Chem. Abstr.* **1962**, *57*, 13694.
(6) We are very grateful to a referee who made us aware of these reports (Barany et al. *J. Org. Chem.* **1983**, *48*, 4750; *J. Org. Chem.* **1984**, *49*, 1043).
(7) Previously the dimerization product **4** of thiophosgene was erroneously believed to possess structure **2** ("Beilsteins Handbuch der Organischen Chemie", Vol. 3, 4th ed.; Springer-Verlag: Berlin, 1921; p 215).
(8) Haas, A.; Klug, W. *Chem. Ber.* **1968**, *101*, 2609.
(9) Haas, A.; Klug, W.; Marsmann, H. *Chem. Ber.* **1972**, *105*, 820.
(10) Schönberg, A.; Stephensen, A. *Ber.* **1933**, *66*, 567.
(11) Moltzen, E. K.; Senning, A., unpublished results.
(12) Senning, A. *Chem. Rev.* **1965**, *65*, 385.
(13) Haas, A.; Yazdanbakhsch, M. *Chem. Ber.* **1976**, *109*, 1976.
(14) No effort was made to optimize the yields of the reported reactions, but it is important to note the absence of significant amounts of byproducts.
(15) Seyferth, D.; Tronich, W. *J. Am. Chem. Soc.* **1969**, *91*, 2138.

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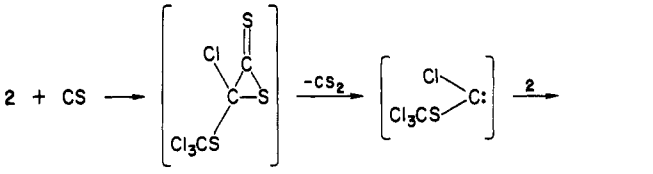
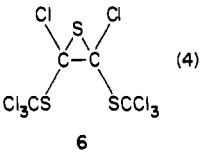
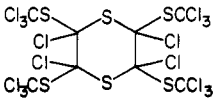




(4)

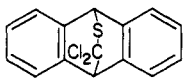
6



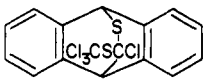
7

As shown in Scheme I three derivatives of **2** were prepared. These reactions clearly demonstrate the synthetic potential of **2**.

The formation of **8** was unexpected since the analogous reaction with thiophosgene is known to give the Diels–Alder adduct **11**.[16] Acylation of anthracene by acyl halides



11



12

is known to occur also without catalyst,[17] but in view of the claimed pseudohalogen character of the (trichloromethyl)thio group[18] the cycloaddition product **12** could be expected. Therefore, the analogy or lack thereof in the chemistry of **2** and that of thiophosgene clearly needs further investigation. Considering the relatively few known examples of anthracenedithiocarboxylic acids and derivatives of these acids this reaction might be of considerable interest.

The dithiocarbamic ester **9** is a representative of a new class of compounds which might be of great interest as potential pesticides because of their great resemblance with known biologically active compounds.[19] The chlorination of **2** is analogous to the reactions **3** and **5** undergo when treated with chlorine.[8,13]

In summary, the formation of **2** emphasizes the applicability of CS as a synthon for the preparation of new thiocarbonyl compounds in high yields. Moreover, **2** provides access to a class of compounds containing the novel $Cl_3CSC(S)$ group previously inaccessible because of the unavailability of trichloromethanethiol.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer. ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL 100 spectrometer. Me_4Si was used as an internal standard and chemical shifts are expressed in δ values. $CDCl_3$ and C_6D_6 were used as solvents. IR spectra were recorded on a Nicolet 5MX fourier transform spectrometer or a Perkin-Elmer Infracord spectrometer. Mass spectra were recorded on a Micromass 7070E spectrometer operating at 70 eV using direct inlet. Elemental analyses were carried out by Novo Microanalytical Laboratory, DK-2880 Bagsvaerd.

Trichloromethyl Chlorodithioformate (2). Carbon monosulfide was generated in a conventional vacuum line by passing CS_2 vapor through a high-voltage AC discharge as previously described.[1,20] After leaving the discharge tube the CS was immediately passed through a stirred solution of 37.2 g (200 mmol) **1** in 50 mL of toluene kept at −78 °C. A color change from yellow to red took place and after the passage of 54 mL (900 mmol) of CS_2,[21] the reaction was stopped. A small amount of precipitate was removed by filtration and toluene, excess **1**, and excess CS_2 were removed in vacuo. The remaining red oil was purified on a chromatographic column (silica gel; eluent petroleum ether)[22] and yielded 25.2 g (75%, corrected for 9.7 g of recovered **1**) of an orange oil identified as **2**. Attempted distillation of crude **2** only led to the isolation of a small amount of **10** while chromatographically purified **2** was distillable (bp 98–100 °C (14 torr); yield of distillation, 21.7 g): η^{17}_D 1.6178; MS, m/z 228 (M^+), 193 ($M^+ - Cl$), 117 (CCl_3^+), 111 ($M^+ - CCl_3$), 79 ($CSCl^+$), 76 (CS_2^+); IR (NaCl, cm^{-1}) 1123 (vs), 802 (s), 750 (vs), 728 (vs); ^{13}C NMR ($CDCl_3$) δ 94.90, 183.05. Anal. Calcd for $C_2Cl_4S_2$: C, 10.45; Cl, 61.68; S, 27.89. Found: C, 10.66; Cl, 62.21; S, 26.95. The precipitate was recrystallized from petroleum ether giving 1.5 g of pale-yellow crystals (mp 83–85 °C), tentatively identified as 2,3-bis[(trichloromethyl)thio]-2,3-dichlorothiirane (**6**); MS, m/z 392 ($M^+ - S$), 307 ($M^+ - CCl_3$), 275 ($M^+ - SCCl_3$), 240 ($M^+ - CCl_4S$), 205 ($M^+ - CCl_5S$), 190 ($M^+ - C_2Cl_6$), 117 (CCl_3^+); IR (KBr, cm^{-1}) 830 (vs), 780 (s), 750 (vs), 730 (vs); ^{13}C NMR ($CDCl_3$) δ 74.34, 96.07. Anal. Calcd for $C_4Cl_8S_3$: C, 11.23; Cl, 66.29; S, 22.48. Found: C, 11.59; Cl, 65.74; S, 22.55.

9-Anthracenecarbodithioic Acid, Trichloromethyl Ester (8). The procedure of Allgeier and Winkler[16] for the corresponding reaction of thiophosgene was followed. Thus, 5.0 g (21.8 mmol) of **2** and 3.6 g (20.0 mmol) of anthracene were heated at 70 °C for 4 h in 75 mL of xylene under stirring (the anthracene went only partially into solution). Subsequently the reaction mixture was kept at room temperature for 16 h. Excess anthracene was removed by filtration and extracted with xylene. The xylene was removed in vacuo, and the remaining solid was separated by chromatography (silica gel column; eluent petroleum ether): yield, 2.2 g (26%) of a red crystalline compound (mp 161.5–162.5 °C), which could be identified as **8**;[23] MS, m/z 370 (M^+), 253 ($M^+ - CCl_3$), 221 ($M^+ - SCCl_3$), 177 ($M^+ - CS_2CCl_3$); IR (KBr, cm^{-1}) 3060 (m), 1460 (w), 1270 (w), 1190 (m), 1170 (w), 1145 (m), 998 (s), 890 (s), 873 (m), 781 (s), 757 (s), 733 (vs), 600 (m), 544 (m); ^1H NMR ($CDCl_3$, Me_4Si) δ 7.25–7.56 (m, 4 H), 7.78–8.06 (m, 4 H), 8.43 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 94.93, 124.17, 125.58, 127.46, 127.85, 128.50, 129.95, 130.99, 135.91, 216.13. Anal. Calcd for $C_{16}H_9Cl_3S_2$: C, 51.59; H, 2.45; Cl, 28.61; S, 17.25. Found: C, 52.36; H, 2.40; Cl, 29.95; S, 17.52.

***N*,*N*-Bis(phenylmethyl)carbamodithioic Acid, (*S*)-Trichloromethyl Ester (9).** The dithioester was prepared by slowly adding 8.7 g (43.6 mmol) of dibenzylamine in 50 mL of CH_2Cl_2 to a stirred solution of 5.0 g (21.8 mmol) of **2** in 150 mL of CH_2Cl_2 at 0 °C. A white precipitate of dibenzylamine hydrochloride formed immediately. After 5 h the reaction mixture was washed with water and dried over $CaSO_4$. The solvent was removed in vacuo and excess petroleum ether was added. After cooling, a yellow precipitate was formed which was purified on a column (silica gel; eluent 1:1 mixture of ether and petroleum ether) and recrystallized from petroleum ether: yield, 2.4 g (28%) of yellow crystals (mp 94.5–95.5 °C); MS, m/z 389 (M^+), 345 ($M^+ - CS$), 272 ($M^+ - CCl_3$), 240 ($M^+ - SCCl_3$), 196 ($N(CH_2C_6H_5)_2^+$); IR (KBr, cm^{-1}) 3020 (w), 1500 (m), 1470 (s), 1460 (s), 1440 (s), 1418 (vs), 1345 (m), 1260 (m), 1215 (vs), 1135 (s), 1080 (m), 1030 (m), 1020 (m), 965 (m), 940 (w), 793 (m), 772 (m), 748 (vs), 731 (vs), 700 (vs); ^1H NMR ($CDCl_3$, Me_4Si) δ 4.94 (s, 4 H), 7.19 (s, 10 H); ^{13}C

(16) Allgeier, H.; Winkler, T. *Tetrahedron Lett.* **1976**, 215.
(17) E.g., Nenitzescu, C. D.; Isăcescu, D. A.; Ionescu, C. N. *Liebigs Ann. Chem.* **1931**, *491*, 210. Bokova, A. I.; Buchina, I. K.; Sidorova, N. G.; Teteneva, S. *Zh. Org. Khim.* **1977**, *13*, 1471; *Chem. Abstr.* **1977**, *87*, 134801.
(18) Haas, A. *Chem.-Ztg.* **1982**, *106*, 239.
(19) Galli, R.; Palla, O.; Gozzo, F. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2813.
(20) Klabunde, K. J.; White, C. M.; Efner, H. F. *Inorg. Chem.* **1974**, *13*, 1778.
(21) The yield of CS is sensitive to small variations in reaction conditions. As a rule of thumb we therefore use at least a four-fold excess of CS_2, which in this case turned out to be too small an amount as demonstrated by the amount of recovered **1**.
(22) The silica gel used in this work was of the type Merck, Kieselgel 60 with a particle size of 0.063–0.200 mm. The petroleum ether used had a boiling range below 50 °C.
(23) The position of the thioacyl group follows from the symmetry of the ^1H NMR spectrum.

NMR ($CDCl_3$) δ 53.65, 96.84, 127.33, 128.05, 129.01, 134.29, 189.49. Anal. Calcd for $C_{16}H_{14}Cl_3NS_2$: C, 49.18; H, 3.62; Cl, 27.20; N, 3.58; S, 16.41. Found: C, 49.35; H, 3.64; Cl, 26.93; N, 3.52; S, 16.44.

Dichloro[(trichloromethyl)thio]methanesulfenyl Chloride (10). A solution of 1.1 g (15 mmol) of Cl_2 in 25 mL of CCl_4 was added to 3.5 g (15 mmol) of **2** in 25 mL of CCl_4 at 0 °C. The reaction mixture was allowed to warm to room temperature and after 5 h the solvent was removed in vacuo. The remaining yellow oil was distilled in vacuo, giving 2.7 g (60%) of a yellow oil (bp 134-137 °C (11 torr)), which could be identified as **10**: MS, *m/z* 298 (M^+), 263 ($M^+ - Cl$), 228 ($M^+ - Cl_2$), 193 ($M^+ - 3Cl$), 184 ($M^+ - Cl_2CS$), 149 (Cl_3CS^+), 117 (CCl_3^+), 79 ($CSCl^+$), 76 (CS_2^+); IR (NaCl, cm^{-1}) 830 (vs), 770 (vs), 745 (vs); ^{13}C NMR (C_6D_6) δ 95.63, 95.72. Anal. Calcd for $C_2Cl_6S_2$: C, 7.99; Cl, 70.70; S, 21.31. Found: C, 8.56; Cl, 70.83; S, 21.50.

Acknowledgment. We thank NATO for a joint travel-study grant (K.J.K. and A.S.). K.J.K. acknowledges with gratitude the National Science Foundation for program support.

Registry No. 1, 594-42-3; **2**, 91631-89-9; **6**, 91631-90-2; **8**, 91631-91-3; **9**, 91631-92-4; **10**, 91631-93-5; $(PhCH_2)_2NH$, 103-49-1; Cl_2, 7782-50-5; CS, 2944-05-0; anthracene, 120-12-7.

Table I. Aldehydes by Reaction of Grignard and Organolithium Reagents with *N*-Formylmorpholine

RMgX or RLi	yield,[a] %	solvent	bp [°C/mmHg] found	bp [°C/mmHg] lit.[3]
$C_6H_5CH_2CH_2$-MgCl	70	ether	88/1	87/1
$C_6H_5CH{=}CH$-MgBr	81	ether	84/2	85/2
$C_6H_5CH_2MgCl$	84	ether	76-79/10	76-78/10
norbornyl-MgBr	74[b]	ether	51-53/7	52/7
c-C_5H_9MgBr	69	ether	74-75/100	73-76/100
1-naphthyl-MgBr	92	ether	142/6	142/6
C_6H_5MgBr	89	ether	51-52/2.2	63-64/10
C_6H_5Li	90	benzene	50/2.2	63-64/10
n-BuLi	78	*n*-hexane	100/760	102-103/760
$C_6H_5C{\equiv}CLi$	80	ether	65/0.1	65/0.1

[a] Yields of aldehydes refer to isolated (distilled) products; they gave IR, ^1H NMR, and ^{13}C NMR spectra which were identical with those of the authentic compounds. [b] Starting with pure *exo*-norbornyl bromide produces a mixture of *exo*- and *endo*-norbornene carboxaldehyde (3:1), which was characterized by NMR spectroscopy.

Synthetic Methods and Reactions. 119.[1] *N*-Formylmorpholine: A New and Effective Formylating Agent for the Preparation of Aldehydes and Dialkyl (1-Formylalkyl)phosphonates from Grignard or Organolithium Reagents

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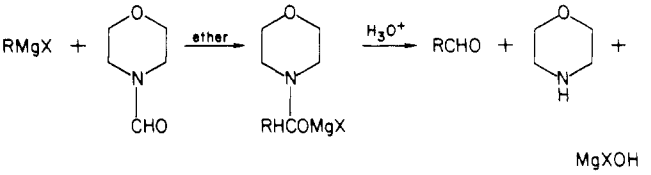
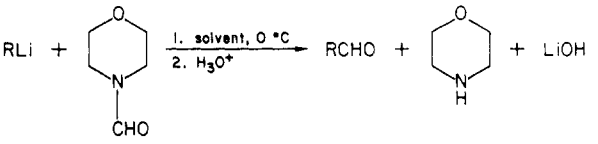
Received March 12, 1984

In recents years a number of reagents have been developed for formylation in organic synthesis. 2-(Formylmethylamino)pyridine has been used by Comins and Meyers[2] for the preparation of aldehydes from Grignard reagents. The presence of the additional ligand (pyridyl nitrogen) and the ready formation of a six-membered chelate ring was considered to prohibit release of aldehyde under the reaction conditions and thus protect the aldehydic product from the further reaction with the organometallic reagent. We subsequently reported[3] the use of *N*-formylpiperidine in related reactions and found that no additional ligand is in fact necessary for the reaction to be successful. More recently, Amaratunga and Frechet reported[4] a more extensive investigation of the formylation of Grignard reagents with alkylformylamines. The ready availability of dialkylformamides such as DMF makes them also increasingly useful in the preparation of aldehydes.[5] The reactions, however, have limitations and generally proceed satisfactorily with Grignard but not with organolithium reagents. Aboujaoude and Collignon reported[6] the preparation of dialkyl (1-formylalkyl)phosphonates, via treatment of dimethylformamide with the dialkyl (α-lithioalkyl)phosphonates. The isolated yields were from 52% to 88%.

Our continued interest in developing alternative and improved formylating systems prompted us to examine the readily available and inexpensive *N*-formylmorpholine as a formylating reagent. The reagent is commercially available or easily prepared by the reaction of morpholine with carbon monoxide. *N*-Formylmorpholine readily reacts with organometallic compounds. Reaction in ether at 0 °C with wide variety of organolithium or Grignard reagents results in formation, upon acidic workup, of the corresponding aldehydes (Table I) in good to excellent yield and high purity. The examples in Table I indicate the effectiveness of the method for aryl, alkyl, vinyl, and acetylenic Grignard or organolithium reagents alike.





The reaction of dialkyl (α-lithioalkyl)phosphonates with *N*-formylmorpholine in THF at −78 °C upon acidic workup also gives in excellent yield dialkyl (1-formylalkyl)phosphonates, affording a method of wide applicability for their one-step preparation from the parent phosphonates (Table II).[7]

The ease of the reactions and mild conditions, giving excellent preparative yields, make this formylating reagent

(1) For part 118, see: Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *Synthesis* **1983**, *636*.
(2) Comins, D. L.; Meyers, A. I. *Synthesis* **1978**, 403 and references cited therein. Meyers, A. I.; Comins, D. L. *Tetrahydron Lett.* **1978**, 5179.
(3) Olah, G. A.; Arvanaghi, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 878; *Organic Synthesis*, in press.
(4) Amaratunga W.; Frechet, J. M. J. *Tetrahedron Lett.* **1983**, *24*, 1143.
(5) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Synthesis*, in press, and references given therein.
(6) Aboujaoude, E. E.; Collignon, N. *Synthesis* **1983**, 634 and references cited therein.
(7) Ford-Moore, A. H.; Perry, B. J. "Organic Syntheses"; Wiely: New York, 1963; Collect. Vol. IV, p 325.

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