(23.8), 94 (26.0), 93 (61.4), 80 (25.0), 79 (27.1), 31 (100.0), 29 (50.2).

Anal. Calcd for $C_{12}H_{16}O$: M_r 176.1202. Found (high-resolution mass spectrometry): M_r 176.1201.

The following spectra data were obtained for 14: ^{1}H NMR ($CDCl_3$) δ 0.8–1.3 (m, 2 H), 1.68 (s, 3 H), 1.8–3.0 (m, 9 H), 3.3 (m, 1 H), 5.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.26 (q), 37.45 (d), 39.28 (t), 39.57 (t), 42.39 (d), 44.44 (t), 44.62 (d), 45.67 (t), 52.72 (d), 129.8 (d), 139.0 (s), 220.6 (s); IR (neat) 3040 (w), 2940 (s), 1735 (s), 1650 (w), 1440 (m), 1410 (m), 1140 (m), 1020 (m), 820 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 176 (molecular ion, 43.6), 147 (23.4), 106 (50.2), 95 (84.3), 94 (38.9), 93 (56.9), 91 (49.4), 82 (21.7), 80 (31.8), 79 (44.4), 77 (28.7), 41 (37.9), 39 (26.2), 31 (100.0), 29 (59.5).

Anal. Calcd for $C_{12}H_{16}O$: M_r 176.1202. Found (high-resolution mass spectrometry): M_r 176.1205.

Hydrogenation of 13 and 14. A solution of either **13** or **14** (10 mg, 0.56 mmol) in ethyl acetate (2 mL) was hydrogenated over 10% palladized charcoal catalyst (2 mg) at a hydrogen pressure of 12 psig for 40 min. The reaction mixture was filtered to remove catalyst, and the filtrate was concentrated in vacuo to afford **15** (10 mg, 100%) which was purified via bulb-to-bulb distillation under reduced pressure: bp 130 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6 Hz), 1.6–3.0 (m, 15 H); IR (neat) 2945 (s), 2870 (w), 1740 (s), 1460 (m), 1410 (m), 1380 (w), 1160 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 178 (molecular ion, 17.4), 95 (27.3), 82 (48.6), 81 (24.9), 41 (20.3), 31 (100.0), 29 (55.9).

Anal. Calcd for $C_{12}H_{18}O$: M_r 178.1358. Found (high-resolution mass spectrometry): M_r 178.1358.

Acknowledgment. Financial support of our study by the Naval Air Systems Command, the Robert A. Welch Foundation (Grant B-963), the Air Force Office of Scientific Research (Grant No. AFOSR-84-0085), and the North Texas State University Faculty Research Committee is gratefully acknowledged. K.S.R. gratefully acknowledges receipt of a fellowship from the CSIR, New Delhi, India. We thank Professor H.-J. Liu (University of Alberta) for kindly obtaining the high-resolution mass spectra of compounds **6**, **7**, **8**, **11b**, and **12b** and Mr. N. Omkaram for kindly obtaining the high-resolution mass spectra of compounds **13**–**15**.

Registry No. **5**, 87830-51-1; **6**, 91632-94-9; **7**, 91632-95-0; **8**, 91632-96-1; **9**, 91632-97-2; **10**, 25282-60-4; **11a**, 91632-98-3; **11b**, 91632-99-4; **12a**, 91633-00-0; **12b**, 91633-01-1; **13**, 91633-02-2; **14**, 91633-03-3; **15**, 91633-04-4.

Desiccant Efficiency in Solvent and Reagent Drying.[1,2] 9. A Reassessment of Calcium Sulfate as a Drying Agent

David R. Burfield

Department of Chemistry, University of Malaya,
Kuala Lumpur 22-11, Malaysia

Received March 1, 1984

Anhydrous calcium sulfate (Drierite) has been applied to the problem of solvent desiccation for over 50 years[3] and has received general endorsement[4] as an efficient and generally applicable low cost drying agent. However, many of the extravagent claims[5] made for the efficiency of this product are based on very early results,[3,6] and in our recent studies,[7–10] where calcium sulfate has been examined alongside other desiccants it has been found to have only very modest efficiency. Thus Drierite approaches the foot of the "drying league" in a recent[9] evaluation of 12 desiccants for the drying of wet ether extracts and is similarly placed in studies of the drying of benzene, dioxane, acetonitrile,[7] various dipolar aprotic solvents[8], and amines.[10] However, in our earliest studies[7,8,10] in an attempt to attain uniform and hence comparable experimental conditions desiccants were activated at 300–320 °C for 15 h before use. Since it is possible that such activation conditions may have had a deleterious effect on the activity of the calcium sulfate[11] and in view of the widespread utilization of this product it appeared pertinent to reevaluate its desiccant potential. This paper thus centers on a reappraisal of Drierite as a desiccant for solvent drying with particular attention being payed to the effect of activation temperature. Comparison with two other important desiccants, viz., calcium chloride and molecular sieves, is also made.

Table I. Effect of Calcium Sulfate Activation Temperature on Its Efficiency in Dioxane Drying[a]

activation temperature, °C	residual solvent water content, ppm 1 h	6 h	24 h	72 h
no activation	1700	1140	540	240
100	1820	1460	1190	1130
150	2000	1230	485	240
200	1690	1080	500	250
225	1950	1200	535	250
250	1770	1290	660	310
300	1930	1430	970	970

[a] Initial water content = 2500 ppm; desiccant loading = 5% w/v; desiccant samples activated overnight (16 h).

Table II. Effect of Calcium Chloride Activation Temperature on Its Efficiency in Dioxane Drying[a]

activation temperature, °C	residual solvent water content, ppm 1 h	6 h	24 h	72 h
no activation	1820	1020	430	350
150	1840	1230	420	290
225	1700	1090	370	290
300	1750	1040	385	325

[a] Initial water content = 2500 ppm; desiccant loading = 5% w/v; desiccant samples activated overnight (16 h).

Results and Discussion

Influence of Desiccant Activation Temperature. Dioxane was choosen for initial tests as it is moderately

---

[1] Part 7: Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1983**, *48*, 2420.

[2] Part 8: Burfield, D. R.; Hefter, G. T.; Koh, S. P. *J. Chem. Technol. Biotechnol.* **1984**, *34A*, 187.

[3] Hammond, W. A.; Withrow, J. R. *Ind. Eng. Chem.* **1933**, *25*, 1112.

[4] See: (a) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley; New York, 1967; p 107, 1103. (b) Vogel, A. I. "Vogel's Textbook of Practical Organic Chemistry"; Longmans: London, 1978; p 139. (c) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon: Oxford, 1980; p 23.

[5] For example: "The last detectable traces of water are removed by Drierite from any liquid which is sufficiently fluid to make intimate contact with the porous solid" and "Regular Drierite is unsurpassed for the drying of organic liquids in the liquid or vapour phase. Moisture residue after treatment with Drierite is so low it cannot be measured, leaving the organic liquid truly anhydrous". Quoted in; Hammond, W. A. "Drierite"; W. A. Hammond Company: Xenia, OH.

[6] Thus calcium sulfate was surpassed only by barium oxide, magnesium perchlorate, and calcium oxide in evaluations based on gas drying efficiency reported by: Bower, J. H. *J. Res. Natl. Bur. Stand.* **1934**, *12*, 241.

[7] Burfield, D. R.; Lee, K. H.; Smithers, R. H. *J. Org. Chem.* **1977**, *42*, 3060.

[8] Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, 43, 3966.

[9] Burfield, D. R.; Smithers, R. H. *J. Chem. Educ.* **1982**, *59*, 703.

[10] Burfield, D. R.; Smithers, R. H.; Tan, A. S. C. *J. Org. Chem.* **1981**, *46*, 629.

[11] Thus it has been shown[11a] that calcium sulfate heated above 400 °C rehydrates only slowly and it has been suggested[11b] that the transition to the inactive form occurs at around 313 °C. (a) Glasenapp, M. *J. Soc. Chem. Ind., London* **1908**, *27*, 858. (b) Chassevent, L. *Liebigs Ann. Chem.* **1927**, *7*, 43.

Table III. Dependence of Drying Efficiency on Desiccant Loading in the Drying of Grossly Wet Diethyl Ether[a]

desiccant	desiccant loading % w/v	residual solvent water content, ppm					capacity[d] % w/w
		5 min	15 min	30 min	60 min	360 min	
CaSO$_4$	10[b]		11400	9200	10200	10700	2.8–3.9
	20[b]	6400	3800	2100			4.5
	20[c]	9700	7500	5800			3.1
CaCl$_2$	5[c]			2100	2100	850	19.6
	10[c]		2400	2100	1900	390	10.1
	20[c]	2100	1400	900			4.9

[a] Initial water content = 14 700 ppm; drying temperature = 22 °C. Activation temperature: [b] = 220 °C. [c] = 350 °C. [d] Given by weight of water absorbed per unit of desiccant expressed as a percentage.

Table IV. Dependence of Drying Efficiency on Desiccant Loading in the Drying of Dioxane[a]

desiccant	desiccant loading % w/v	residual solvent water content, ppm				capacity % w/w
		1 h	6 h	24 h	72 h	
CaSO$_4$[b]	1.24	2600	2300	2020	1950	4.5
	2.5	2020	1610	1220	1130	5.6
	5	1700	1140	540	240	4.7
	10	2140	760	150	110	2.5
	20	1600	510	120	80	1.3
CaCl$_2$[c]	1.25	2250	1880	2320[d]	2500[d]	
	2.5	1940	1340	540	390	9.1
	5	1750	1040	385	325	4.5

[a] Initial water content = 2500 ppm; drying temperature ≃ 27–30 °C. [b] Activated at 225 °C. [c] Activated at 350 °C. [d] CaCl$_2$ granules observed to disintegrate.

difficult to dry and a fairly extensive set of drying data has already been accumulated for this solvent.[7,12,13] Activation of the desiccant was carried out at temperatures in the range 100–300 °C. The marked influence of activation temperature on drying efficiency is shown in Table I. Activation of Drierite in the temperature range 150–225 °C provides a product whose activity is little different from the *as-received* material. However, activation at temperatures of 250 °C and above is accompanied by a distinct deterioration in drying efficiency. Interestingly, a similar reduction in efficiency is observed on activation at 100 °C and this must be ascribed to the absorption of water by the desiccant when equilibrated in an air oven at the high ambient humidities experienced in Malaysia. This supports the earlier contention[3] that Drierite binds water at temperatures up to at least 107 °C. The optimum activation temperature for this material would appear to be in the range 200–225 °C.

An examination of another commonly used desiccant, calcium chloride, reveals that in this case the use of high activation temperatures does not have a deleterious effect on the drying activity (Table II).

Since the drying activities of these two materials under optimum activation conditions appear quite similar, the earlier poor showing of calcium sulfate in our desiccant evaluation studies[7,8,10] must in part be ascribed to the inactivation of the material by inappropriate high-temperature treatment.

Drying Capacity of Desiccant Materials. The overall drying efficiency of a desiccant is determined not only by its intrinsic affinity for water but also by its capacity to contain the bound water. The drying capacity is an important parameter since it will dictate the appropriate desiccant loadings for practical use. Determination of the drying efficiency as a function of desiccant loading (Tables III and IV) gives a measure of the inherent capacity of the material.

Table V. Comparison of Desiccant Drying Efficiency for Dioxane and Acetonitrile[a]

desiccant	residual solvent water content, ppm	
	dioxane	acetonitrile
CaSO$_4$[b]	240	180
CaCl$_2$[b]	290	*d*
3A molecular sieve[c]	19	52
4A molecular sieve[c]	30	450

[a] Initial water content = 2500 ppm; drying time 72 h. Activation temperature: [b] = 225 °C. [c] = 350 °C. Drying temperature 27–30 °C. [d] CaCl$_2$ induces a base-catalyzed tritium exchange with acetonitrile which precludes determination;[7] desiccant loading = 5% w/v.

In the drying of grossly wet ether samples the maximum observed water capacity is only 4.5% w/w for Drierite compared to nearly 20% w/w for calcium chloride (Table III). Interestingly at low desiccant loadings the Drierite is observed to lose its effectiveness with increasing drying time and this may be symptomatic of a breakdown of this material in the presence of large water excesses. It is also clear (Table III) that activation of Drierite at 350 °C leads to a reduction in drying capacity, and this again emphasises the importance of moderate activation temperatures for this material.

A somewhat similar maximum drying capacity of 5.6% w/w is observed for the Drierite drying of dioxane (Table IV). In contrast, for calcium chloride the maximum observable drying capacity is sharply reduced to about 9% and at low desiccant loadings the granular material is observed to break up with complete loss of water retention. Since calcium chloride appears quite stable in the presence of water-saturated diethyl ether, it would appear that some specific interaction with dioxane must occur. The somewhat higher ambient temperatures (27–30 °C) encountered during the dioxane drying experiments may also have adversely affected the capacity of the calcium chloride.

Overall, it appears that calcium chloride has a significantly higher water capacity than Drierite. The optimum value for calcium chloride is quite similar to the 18–20% w/w capacity observed[12] for 3A molecular sieves in the drying of dioxane.

Comparative Drying Efficiency. By employing suitably high desiccant loadings it is possible to offset the effects imposed by variable capacity and hence to probe the inherent drying efficiency of the desiccant materials. The relative efficiencies for the drying of dioxane and acetonitrile by Drierite, calcium chloride, and molecular sieves are summarized in Table V. It is apparent that calcium chloride and calcium sulfate are quite similar in drying ability but that the residual water content is of an order of magnitude higher than that attainable with molecular sieves. It is of some interest however that Drierite

---

(12) Burfield, D. R.; Gan, G. H.; Smithers, R. H. *J. App. Chem. Biotechnol.* **1978**, *28*, 23.

(13) Burfield, D. R.; Smithers, R. H. *J. Chem. Technol. Biotechnol.* **1980**, *30*, 491.

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

Ejner K. Moltzen,[2a] Alexander Senning,*[2a]
Michael P. Kramer,[2b] and Kenneth J. Klabunde*[2b]

Departments of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark, and Kansas State University, Manhattan, Kansas 66506

Received February 3, 1984

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

$$C_6H_5SCl + CS \rightarrow C_6H_5SC(S)Cl \tag{1}$$

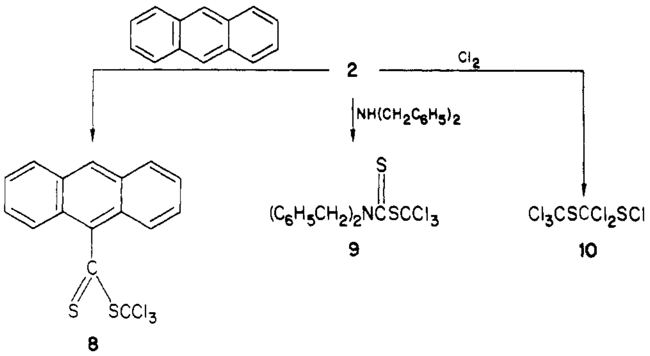
$$ClSSCl + 2CS \rightarrow ClC(S)SSC(S)Cl \tag{2}$$

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

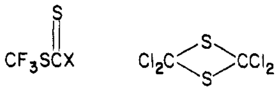
$$\underset{\mathbf{1}}{Cl_3CSCl} + CS \rightarrow \underset{\mathbf{2}}{Cl_3CSC(S)Cl} \tag{3}$$

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



3, X = F
5, X = Cl
4

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.

0022-3263/84/1949-3854$01.50/0