Component B.—1-Methoxy-1-phenyl-1,2,2-trifluoropropane was purified by elution chromatography (silica gel/CH_2Cl_2 eluent) to an unstable, nondistillable colorless liquid. The fluorine nmr spectrum contained a quartet ($J_{HF} \sim 19$ cps) centered at ϕ +104.6 and a singlet at ϕ +131.4 in a 2:1 ratio. The proton nmr spectrum consisted of a triplet (J_{HF} = 19 cps) of doublets (J_{HF} = 1.5 cps) centered at δ 1.69, a singlet methoxyl at δ 3.30, and the phenyl protons at δ 7.61 in a 3:3:5 ratio.

Anal. Calcd for $C_{10}H_{11}F_3O$: C, 58.82; H, 5.43; F, 27.92. Found: C, 59.26; H, 5.39; F, 30.90.

Component C.—The 1-phenyl-1,1-dimethoxy-2,2-difluoropropane could not be adequately purified for an elemental analysis but its structure can be indicated by nmr and its hydrolysis to α,α-difluoropropiophenone. The fluorine nmr spectrum of the difluoro ketal consisted of a quartet (J_{HF} = 16 cps) centered at ϕ +102.

Hydrolysis of Trifluoro Ethers (II) and Difluoro Acetals (III).—Both types were readily hydrolyzed by 10% H_2SO_4 at 50° for 3 hr, to the same α,α-difluoro ketone whose properties are listed in Table II.

TABLE II

NMR DATA FOR α,α-DIFLUORO KETONES

Compound	C=O, μ	ϕ (CF_2)	J_{HF}, cps	Ref
$C_6H_5C(=O)CF_2H$	5.83	+131.9 (doublet)	54	*a*
$C_6H_5C(=O)CF_2CH_3$	5.88	+93 (quartet)	19	*b*
$C_6H_5C(=O)CF_2C_6H_5$	5.90	+99.3 (singlet)	...	*c*

[a] M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953). [b] R. M. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965). [c] J. Bornstein and M. R. Borden, *Chem. Ind.* (London), 441 (1958).

Registry No.—Ia, 425-32-1; Ib, 14210-87-8; Ic, 383-18-6; IIa, 14210-88-9; IIb, 14210-89-0; IIc, 14210-90-3; IIIa, 14210-91-4; IIIb, 14320-36-6; IIIc, 14210-92-5.

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Some Reactions of Silanes and Sulfides with Strong Bases in Dimethyl Sulfoxide

CHARLES C. PRICE AND JOHN R. SOWA[1]

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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In this paper we show by studies of nmr spectra that diethyl sulfide exchanges α hydrogens readily with dimethyl-d_6 sulfoxide in the presence of sodium dimsyl at 100°, while tetramethylsilane is unaffected. With potassium *t*-butoxide in dimethyl sulfoxide tetramethylsilane reacts rapidly at 25° to form methane and *t*-butyl trimethylsilyl ether.

Some years ago, Doering and Hoffman[2] showed that hydrogens α to sulfonium and phosphonium groups were much more readily exchangeable in base than those α to ammonium groups. This was interpreted in terms of possible 3d–π bonding in the intermediate carbanions of the reactive salts. In an effort to extend such possible interactions to a carbanion adjacent to uncharged silicon, using strong bases in dimethyl sulfoxide (DMSO), the reactivity of α-hydrogens in silanes has been compared to those in sulfides and amines.

Many physical and chemical properties of organosilicon compounds have been attributed to 3d–2p–π bonding between silicon and carbon, oxygen, or nitrogen.[3] An example is the weak base strength of trisilylamine, ascribed to delocalization of the unshared pair on nitrogen into the 3d orbitals of the silicon atoms.[4] If indeed this delocalization depicted for

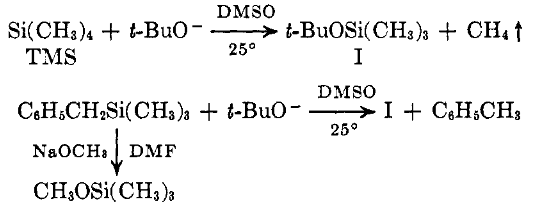
$$(H_3Si)_3\ddot{N} \longleftrightarrow (H_3Si)_2\overset{+}{N}{=}\overset{-}{Si}H_3$$

silylamine is as significant as the very weak basicity for this amine indicates, a similar interaction might influence the acidity of silanes through a stabilization of a carbanion. We have, therefore, made a search for this

$$(CH_3)_4Si \xrightarrow[?]{\text{base}} \left[(CH_3)_3Si\overset{-}{C}H_2 \longleftrightarrow (CH_3)_3\overset{-}{Si}{=}CH_2\right]$$

reaction using strong bases in DMSO. These have included not only potassium *t*-butoxide in DMSO, which has been shown to be many orders of magnitude stronger than alkoxides in conventional solvents,[5,6] but also sodium dimsyl,[7] shown to be 10^7 times stronger than potassium *t*-butoxide.[8]

It was quickly discovered that *t*-butoxide ion would not be suitable for this purpose, as it led to rapid C–Si bond cleavage. For example, potassium *t*-butoxide in DMSO reacted almost immediately with tetramethylsilane to give methane and *t*-butyl trimethylsilyl ether. The latter was also formed from benzyltrimethylsilane, along with toluene. A similar cleavage of the benzyl bond was observed with sodium methoxide in dimethylformmamide (DMF).



$$\underset{\text{TMS}}{Si(CH_3)_4} + t\text{-}BuO^- \xrightarrow[25°]{\text{DMSO}} \underset{\text{I}}{t\text{-}BuOSi(CH_3)_3} + CH_4\uparrow$$

$$C_6H_5CH_2Si(CH_3)_3 + t\text{-}BuO^- \xrightarrow[25°]{\text{DMSO}} \text{I} + C_6H_5CH_3$$

$$C_6H_5CH_2Si(CH_3)_3 \xrightarrow[\text{DMF}]{NaOCH_3} CH_3OSi(CH_3)_3$$

Despite the much greater base strength of dimsyl anion, it was found to give no detectable reaction with tetramethylsilane (TMS), not even proton exchange with deuterated DMSO. Triethylamine was also inert, but dimethyl and diethyl sulfides exchanged α-protons for deuterium on warming in DMSO-d_6 containing dimsyl anion.

$$(CH_3)_2S + (CD_3)_2SO \xrightarrow[95°,\ 60\ \text{min}]{\text{dimsyl}^-} 66\%\ \text{exchange}$$

The exchange was observed by increase of the nmr absorbance at τ 7.38 (DMSO) and corresponding decrease at τ 7.88 (DMS). When diethyl sulfide was studied, the methylene quadruplet (τ 7.42) overlapped the DMSO band. However, two approaches led to estimates of exchange. As methylene was deuter-

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[1] From the Ph.D. Thesis of J. R. Sowa, University of Pennsylvania 1964. Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).

[3] (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960; (b) E. A. U. Ebsworth, "Volatile Silicon Compounds," Pergamon Press Inc., New York, N. Y., 1963.

[4] F. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 460.

[5] D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

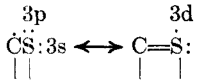
[6] C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

[7] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

[8] A. Ledwith and N. MacFarlane, *Proc. Chem. Soc.*, 108 (1964).

ated, the methyl triplet at τ 8.78 was partially converted to a doublet. Since the doublet peaks appeared between those of the triplet, the doublet to triplet intensity served as one estimate (32% exchange of α-hydrogens in 105 min at 95°). Careful examination of the methylene region showed the outer peaks decreased in intensity compared to the inner. By calculating the intensity expected for the inner region as three times the outer, and deducting this from the integrated absorbance of the inner, the difference may be assumed to be the contribution of hydrogen exchanged into DMSO. The value obtained, 30% exchange, is in excellent agreement with that estimated from the triplet region.

These results are in accord with other recent data indicating a greater ease of metalation[9] and of hydrogen exchange,[10] of hydrogen α to sulfur than α to phosphorus or silicon. These results are in accord with the hypothesis, advanced some years ago on the basis of the much greater stabilization of carbon radicals in vinyl copolymerization by sulfide than by silicon (or phosphide phosphorus),[11] that the enhanced capacity of sulfide to stabilize carbanion or free-radical carbon may be due to 3p–2p–π bonding with promotion of one or two 3p electrons on sulfide sulfur to nonbonding 3d orbitals. This opportunity is open to trivalent phosphorus to only a limited degree (by rehydridization of phosphorus from p^3 geometry to sp^2 geometry) and not at all to silicon or to sulfone sulfur or pentavalent phosphorus.



$$\overset{3p}{\dot{C}\ddot{S}}:3s \longleftrightarrow C{=}\overset{3d}{\dot{S}}:$$

Experimental Section

Solutions of **dimsyl ion** (*ca.* 15%) were prepared by dissolving sodium hydride in deuterated DMSO.[7] About 0.4 ml was placed in a 5-mm-o.d. precision-bore nuclear magnetic resonance (nmr) tube. After addition of 10% by volume of reactant, the tubes were sealed and the nmr spectra were recorded. The tubes were then heated on a steam bath (95–100°) for various intervals and the spectra reexamined. **Tetramethylsilane** and **triethylamine** showed no nmr spectral changes even after 3 hr at 95°. The TMS was insoluble in DMSO; so the tube was shaken at frequent intervals.

Dimethyl Sulfide.—Before heating, the ratio of peak heights at τ 7.38 (DMSO) and 7.88 (DMS) was 1:45. After 15 min at 95°, it became 17:41, after 60 min, 23:11, corresponding to 29 and 66% exchange.

Diethyl Sulfide.—Before heating, the solution showed a quartet at τ 7.42 and a triplet at τ 8.78 ($J = 6.6$ cps). After heating to 95° for 105 min, the triplet area developed a doublet between the triplet peak τ 8.78 ($J = 6.6$ cps), each peak with a fine splitting (by α-^{2}H) of $J' = 1.2$ cps. The ratio of doublet area to triplet was 34.2:72.6 (32% exchange). From the relative integrated area under the outer and inner peaks of the quartet at τ 7.42, exchange at 15, 45, and 105 min corresponded to 14, 21, and 30% of the α-hydrogens, respectively.

When **TMS** was added to **potassium *t*-butoxide** (5%) in DMSO-d_6, gas was immediately released. The solution remaining in the nmr tube was sealed. The nmr showed singlets at $\tau = 7.38$, 8.85, 9.85, and 10 ppm in the approximate ratio of 1:3:3:1. These may be assigned to DMSO, the *t*-butyl and trimethyl silyl groups of ***t*-butyl trimethyl ether** and to excess unreacted TMS, respectively. When this solution was heated to 95° for 75 min, a new singlet at τ 5.96 dominated the nmr spectra while those at τ 8.85, 9.85, and 10.0 were markedly decreased. This interesting observation awaits an explanation.

Benzyltrimethylsilane also reacted rapidly with potassium *t*-butoxide in DMSO, turning red; distillation of such a reaction mixture gave two products. ***t*-Butyl trimethylsilyl ether**, bp 100° [lit.[12] 101° (754 mm)], showed nmr singlets at τ 8.8 and 9.8 and infrared bands at 1000–1100 (ether), 1400 and 1360 (*t*-butyl), and 1410 cm^{-1} (trimethyl silyl). **Toluene** (bp 110°) was confirmed by ultraviolet and nmr spectra. After removal of the DMSO under reduced pressure, an unidentified thick oily reddish brown residue remained.

With sodium methoxide in DMF, benzyltrimethylsilane gave a red reaction mixture. It was stripped under aspirator pressure and the volatile material was redistilled at atmospheric pressure to give **methyl trimethylsilyl ether**, bp 55–57° (lit.[12] 55.5°).

Diethyl sulfide reacted with potassium *t*-butoxide in DMSO-d_6 on heating to 95° for 2 hr. Some of the methylene protons shifted downfield by 3 cps and some of the methyl protons unfield by 3 cps, without change of the splitting pattern. This is *not* due to hydrogen exchange, but its cause has not been established.

Registry No.—Dimethyl sulfoxide, 67-68-5; *t*-butyl trimethylsilyl ether, 13058-24-7; toluene, 108-88-3; methyl trimethylsilyl ether, 1825-61-2.

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(9) D. J. Peterson, *J. Organometal. Chem.*, (Amsterdam), in press; *J. Org. Chem.*, in press.

(10) E. A. Yakovleva, E. N. Tsvetkov, D. I. Lobanov, M. I. Kabachnik, and A. I. Shatenshtein, *Tetrahedron Letters*, 4161 (1966).

(11) See C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, Inc., New York, N. Y., p 27, 1962; C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2670 (1959).

(12) C. Eaborn, *J. Chem. Soc.*, 126 (1955); S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

Enolization of Ketones. IV.[1] The Rate and Orientation of Base-Catalyzed Deuteration of Some Methyl Ketones

CHRISTOFFER RAPPE AND WILLIAM H. SACHS

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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According to the currently accepted mechanism, both base-catalyzed halogenation and deuteration of ketones proceed *via* the same rate-determining step, the formation of the enolate anion (or enol). This means that the orientation and the reaction rates for the two reactions would be identical or nearly identical.[2–6]

In a series of papers, one of us has studied the orientation of base-catalyzed halogenation and deuteration of 2-butanone.[7–13] Evidence was found that two different base-catalyzed halogenations exist for this ketone and, unexpectedly, in neither of these is the orientation of halogenation the same as the orientation of deutera-

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(1) Part III: C. Rappe and W. H. Sachs, *J. Org. Chem.*, **32**, 3700 (1967).

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 557–560.

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, pp 372–374.

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, pp 233–234.

(5) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 160–165.

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 93–94.

(7) C. Rappe, *Acta Chem. Scand.*, **20**, 376 (1966).

(8) C. Rappe, *ibid.*, **20**, 1721 (1966).

(9) C. Rappe, *ibid.*, **20**, 2236 (1966).

(10) C. Rappe, *ibid.*, **20**, 2305 (1966).

(11) C. Rappe, *ibid.*, **21**, 857 (1967).

(12) C. Rappe, *ibid.*, **21**, 1823 (1967).

(13) C. Rappe, *ibid.*, in press.