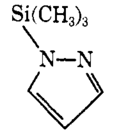
the nonequivalent methyls of **2** could be resolved up to 150° ($k_{\mathrm{inv}} \leq 1.55\ \mathrm{sec}^{-1}$, $\Delta F^{\ddagger} \geq 24.6$ kcal/mol). Extrapolation of the rate of silyl migration[5] to 150° gives a stereospecificity of one part in 59,000, or 99.99998% retention.[5a]

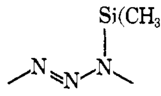
It should be emphasized that for neither **1** nor **2** was a clear-cut coalescence of the $Si(CH_3)_2$ resonances observed. The chemical-shift difference is sufficiently small ($\approx$0.7 Hz at 25 MHz) that the distinction between coalescence and failure to resolve closely spaced peaks is difficult to make.

Although the degenerate silyl shifts in **1**, **2**, **4**,[1b] **5**,[1d] and **6**[1e] can be considered as [1,9], [1,5], [1,5], [1,3], and [1,2] sigmatropic rearrangements, respectively, the facility with which all of these reactions proceed suggests that they are best considered as internal nucleophilic displacements.[6] Orbital symmetry rules predict that the suprafacial migrations with retention of configuration at silicon in **5** and **6** are disallowed, yet these systems do not have unusually high barriers when compared with the symmetry-allowed reactions of **1**, **2**, and **4**.



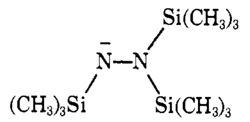
4

E_a = 24 kcal/mol



5

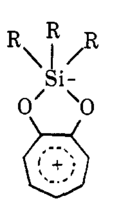
$\Delta F^{\ddagger}$ = 16.1 kcal/mol



6

$\Delta F^{\ddagger}$ = 10.9 kcal/mol

The extremely low barrier to rearrangement in **1** offers support for the suggestion[1a,7] of a pentacoordinate silicon intermediate in these reactions, since here the dipolar species is highly stabilized (**7**). However, neither in **1** nor in **2** can the two oxygens adopt diequatorial positions (*e.g.*, **8**) in the trigonal-bipyramidal intermediate, since this would result in inversion of configuration at silicon. Such an intermediate must have the six-membered ring (**9**) or five-membered ring (for **1**) in apical-equatorial positions, and the barrier for pseudorotation to an ee intermediate like **8** must be at least 9.2 kcal/mol for **2** and 9.9 kcal/mol for **1**.



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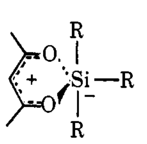

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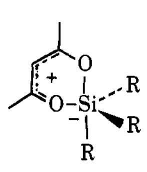

9

Intramolecular nucleophilic displacements at silicon for which the stereochemistry is known[8] have involved three- or four-membered cyclic transition states, and all have proceeded with predominant retention of configuration. Our results strongly suggest that intramolecular displacements involving five- and six-membered cyclic transition states also proceed with high retention, at least where both entering and leaving groups are electronegative elements. This offers support to the many suggestions in the literature[9] that intermolecular displacements at silicon proceeding with retention of configuration do so because interactions between entering and leaving groups result in a cyclic transition state.

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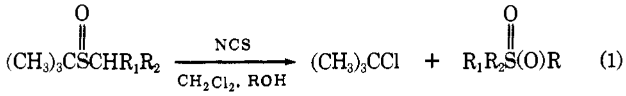
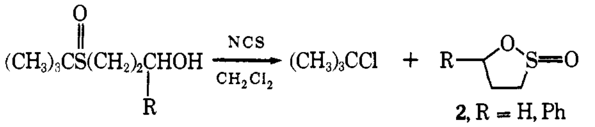
β-Sultines. Intermediates in a Sulfur Analog of the Wittig Olefin Synthesis

Sir:

We have recently reported that *tert*-butyl alkyl or aryl sulfoxides undergo carbon–sulfur bond cleavage upon treatment with positive halogen species such as *N*-bromo- or *N*-chlorosuccinimide.[1] When the cleavage reactions were carried out in the presence of alcohols, the products were sulfinic esters and *tert*-butyl halides (eq 1). Incorporation of the hydroxyl group into the γ or δ position of the alkyl group resulted in the formation of γ- or δ-sultines,[1,2] *e.g.*, **1** → **2** (85%).



$$(CH_3)_3C\overset{O}{\overset{\|}{S}}CHR_1R_2 \xrightarrow[CH_2Cl_2,\ ROH]{NCS} (CH_3)_3CCl + R_1R_2\overset{O}{\overset{\|}{S}}(O)R \quad (1)$$



(2)

1, R = H, Ph

2, R = H, Ph

We have found that β-hydroxy sulfoxides (**3**) also react with NBS, NCS, or SO_2Cl_2 in CH_2Cl_2 or CCl_4 at

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(5a) Note Added in Proof. I. K. Kusnezowa, K. Rühlmann, and E. Gründemann (*J. Organometal. Chem.*, **47**, 53 (1973)) have reported the preparation of optically active silyl acetylacetonates. If the observed optical activity is not entirely due to the *E* isomer (3, SiR_3 = Si(Ph)(Me)(α-Naph)) then their results also demonstrate silyl migration with retention of configuration at silicon in the *Z* isomer.

(6) The barrier to [1,3] migration in crotyltrimethylsilane is E_a = 47.7 kcal/mol: H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

(7) M. Gielen, C. Dehouk, H. Mokhtar-Jamai, and J. Topart, *Rev. Silicon, Germanium, Tin, Lead Compounds*, **1**, 1 (1972).

(8) (a) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Amer. Chem. Soc.*, **89**, 5493 (1967); (b) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967); A. G. Brook and J. D. Pascoe, *J. Amer. Chem. Soc.*, **93**, 6224 (1971); (c) J. F. Klebe, *ibid.*, **90**, 5246 (1968).

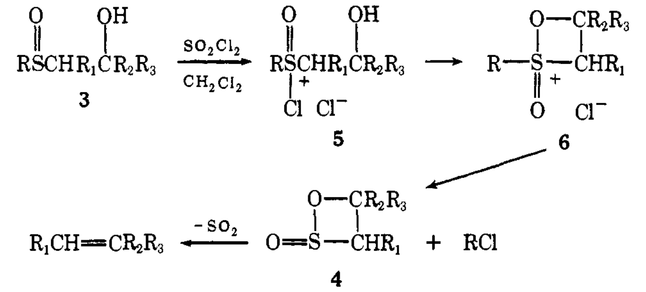
(9) (a) D. G. Anderson and D. E. Webster, *J. Chem. Soc. B*, 878 (1968); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, **86**, 3276 (1964); (c) L. H. Sommer and J. D. Citron, *ibid.*, **89**, 5797 (1967); (d) L. H. Sommer and J. E. Lyons, *ibid.*, **91**, 7061 (1969).

(1) F. Jung and T. Durst, *J. Chem. Soc., Chem. Commun.*, 4 (1973).

(2) The synthesis and properties of very few γ- and δ-sultines have been described; *cf.* (a) D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969); *J. Org. Chem.*, **36**, 1314 (1971); (b) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970); (c) R. M. Dodson, P. D. Hammen, and R. A. Davis, *J. Org. Chem.*, **36**, 2693 (1971); (d) D. C. Dittmer, R. S. Henion, and N. Takashina, *ibid.*, **34**, 1310 (1969). Because of the accessibility of a variety of compounds of the type **1**, the above route, eq 2, leads to sultines of varying ring size and substitution. Work in this area will be reported shortly.

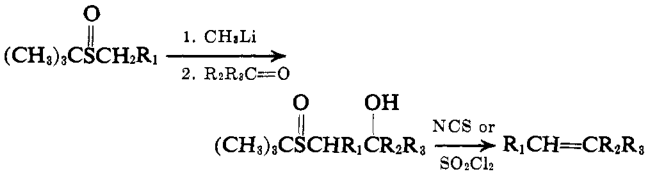
room temperature to give initially the β-sultines[3] **4**. These substances have only limited thermal stability. They readily lose SO_2, in most cases within a few minutes at room temperature, and give olefins (Scheme I). The yield of olefins from the β-hydroxy sulfoxides is generally good to excellent (see Table I).

Scheme I. Formation of Olefins from β-Hydroxy Sulfoxides



R = *tert*-butyl, R_1, R_2, R_3 = alkyl or aryl

Table I



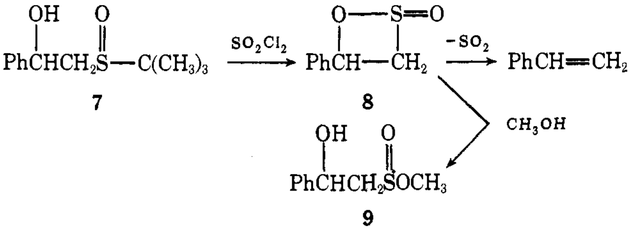
$$(CH_3)_3C\overset{O}{\overset{\|}{S}}CH_2R_1 \xrightarrow[2.\ R_2R_3C{=}O]{1.\ CH_3Li} (CH_3)_3C\overset{O}{\overset{\|}{S}}CHR_1\overset{OH}{\overset{|}{C}}R_2R_3 \xrightarrow[SO_2Cl_2]{NCS\ or} R_1CH{=}CR_2R_3$$

tert-Butyl alkyl sulfoxide, alkyl	Carbonyl compd	Yield (%)^a Hydroxy sulfoxide	Olefin^b
Methyl	Benzaldehyde	95	82^a
Methyl	Cinnamaldehyde	95	75
Methyl	Δ^3-Cyclohexenecarboxaldehyde	75	62^a
Methyl	Benzophenone	98	92
Methyl	Δ^5-Cholesten-3-one	77	62
Ethyl	Benzaldehyde	94	70
n-Butyl	Benzaldehyde	94	60
n-Butyl	Δ^3-Cyclohexenecarboxaldehyde	96	50
Ethyl	Benzophenone	95	96
Ethyl	Acetophenone	78	93
n-Butyl	4-*tert*-Butylcyclohexanone	80	57
n-Butyl	2-Octanone	51	74
Isopropyl	Benzophenone	97	53

^{a} All yields refer to isolated yields except those noted by the superscript *a*; these are vpc yields. ^{b} Based on hydroxy sulfoxide.

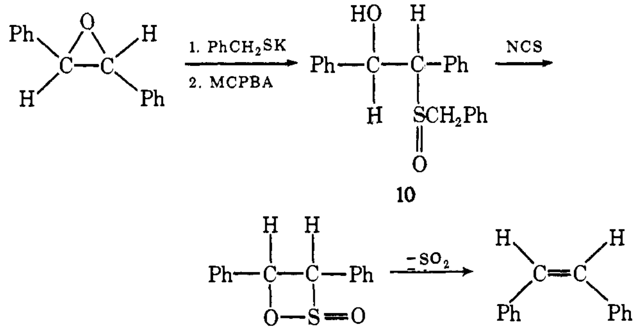
The β-sultines **4** are probably formed *via* intramolecular cyclization of the initially formed β-hydroxychlorooxosulfonium chloride **5** to the alkoxyoxosulfonium salt **6**[4] which undergoes fragmentation to **4** and *tert*-butyl chloride.[1,5]

In several instances, the β-sultines have a sufficient lifetime to allow determination of some spectroscopic properties and interception by nucleophilic reagents. Thus reaction of **7**[6] with SO_2Cl_2 in CH_2Cl_2 at room temperature for 15 min, followed by evaporation of the solvent, gave a crude product having nmr peaks at δ 3.5–3.9 (m, 2 H), 5.2–5.5 (m, 1 H), and 7.2–7.5 (m, 5 H) which can reasonably be ascribed to the methylene, benzylic, and aromatic hydrogens, respectively, of the β-sultine **8**. When the solution was allowed to stand at room temperature for several hours, the above peaks were replaced by those belonging to styrene. Addition of CH_3OH to the reaction mixture prior to evaporation gave the β-hydroxy sulfinate ester **9**.[7]



The loss of SO_2 from β-sultines occurs by a stereospecific cis elimination as shown by the formation of *cis*-stilbene (45% yield, >99% purity) from the reaction of **10** with NCS in CH_2Cl_2 (Scheme II). The decomposition of the β-sultines is reminiscent of the stereospecific cis elimination of CO_2 and isocyanates from β-lactones[8] and β-lactams,[9] respectively. These decompositions, especially the latter, generally occur at a considerably higher temperature than the SO_2 loss from β-sultines.

Scheme II. Stereochemistry of the Decomposition of β-Sultines



The most general method of preparation of the β-hydroxy sulfoxides **3** is the condensation of the lithio derivative of the appropriate *tert*-butyl alkyl sulfoxide **11** with a variety of ketones and aldehydes.[10] The combined sequence, represented by eq 3, has a close analogy to the Wittig olefin synthesis in which sulfur plays the role of the heteroatom and *tert*-butyl thiol and the sulfoxides **11** are the equivalent of triphenylphosphine and the triphenylphosphonium halides, re-

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(3) β-Sultines in contrast to β-sultones, especially polychlorinated and polyfluorinated β-sultones [I. L. Knunyants and G. A. Sokolski, *Angew. Chem., Int. Ed. Engl.*, **11**, 583 (1972)], have to the best of our knowledge not been isolated. A fluorinated β-sultine has been suggested as an intermediate in the reaction

$$CF_2{=}CF_2 + SO_2 \xrightarrow{h\nu} F(O)CCF_2S(O)F$$

D. Sianesi, G. C. Bernardi, and G. Maggi, *Tetrahedron Lett.*, 1313 (1970).

(4) The intermediacy of salts such as **5** in the chlorination of hydroxy sulfoxides and their rapid cyclization to cyclic alkoxyoxosulfonium salts, *e.g.*, **6**, has been documented: T. Durst and K. C. Tin, *Can. J. Chem.*, **49**, 2374 (1971).

(5) Another possible route to **4** from **5** would involve cleavage of **5** to *tert*-butyl chloride and a β-hydroxy sulfinyl chloride followed by cyclization of the latter.

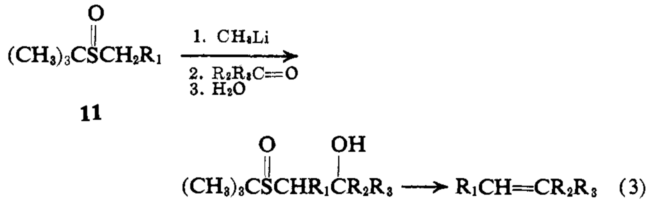
(6) All new compounds were characterized by adequate analyses and spectra.

(7) The ester **9** was identified by oxidation to the corresponding β-hydroxy sulfonate ester which was synthesized according to $LiCH_2SO_2OCH_3$ + PhCHO: E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **88**, 5656 (1966).

(8) (a) T. L. James and C. A. Wellington, *J. Amer. Chem. Soc.*, **91**, 7743 (1969); (b) M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968); (c) O. L. Chapman and W. H. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968); D. S. Noyce and E. H. Benitt, *J. Org. Chem.*, **31**, 4043 (1966).

(9) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970).

(10) T. Durst, R. Viau, and M. R. McClory, *ibid.*, **93**, 3077 (1971).



$$\underset{\mathbf{11}}{(CH_3)_3C\overset{O}{\overset{\|}{S}}CH_2R_1} \xrightarrow[\substack{2.\ R_2R_3C{=}O\\ 3.\ H_2O}]{1.\ CH_3Li} (CH_3)_3C\overset{O}{\overset{\|}{S}}CHR_1\overset{OH}{\overset{|}{C}}R_2R_3 \longrightarrow R_1CH{=}CR_2R_3 \quad (3)$$

spectively, of the Wittig reaction. An earlier, rather limited Wittig-like olefin synthesis based on sulfur as the heteroatom involved the thermal decomposition of β-hydroxy sulfinamides.[11]

In order to evaluate the potential of the hydroxy sulfoxide route, we have carried out the preparation of a number of representative olefins. In general, the yields of the required adducts **3** from **11** were highly satisfactory. The best olefin yields are obtained when trisubstituted olefins are formed; fair to good yields were observed for the mono- and disubstituted olefins. In one example, a tetrasubstituted olefin was obtained in 53% yield.[12]

When isomeric olefins can be produced in the overall sequence, the E/Z ratio is determined by the diastereomer ratio due to the asymmetry at the two adjacent carbon atoms obtained in the condensation reaction of the lithio derivatives of **11** with carbonyl compounds.[13] In the limited examples we have carried out, this ratio is generally not greater than 7:3. In most instances, we have found that the diastereomers were readily separable by column chromatography. Decomposition of each purified isomer led to isomerically pure olefin. β-Sultines leading to the trans olefins decomposed more readily than those leading to the cis isomer.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

[11] E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **90**, 5548, 5553 (1968).

[12] Tetrasubstituted olefin will probably not be formed in much greater than 50% yield from the appropiate β-hydroxy sulfoxides since the sulfoxide bond is flanked by two tertiary carbon atoms and cleavage of either C–S bond can occur, one leading to β-sultines (olefins) and the other to sulfinate esters.

[13] The configuration at the sulfur has no bearing on the E/Z ratio.

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Received January 12, 1973

Di- and Tri-*tert*-butylmethyl, Two Aliphatic Radicals of Unusual Stability[1]

Sir:

The stability of carbon radicals such as triphenylmethyl,[2] Koelsch's radical,[3] tetraphenylallyl,[4] and pentaphenylcyclopentadienyl[5] depends on a combination of steric hindrance to dimerization and a lowering of the energy of the orbital containing the free electron by rehybridization within a π system. We wish to report preliminary results that show nonbonded interactions alone are sufficient to confer remarkable stability on some carbon radicals derived from alkanes and their silicon analogs.

We prepared radicals **1–4** in concentrations of 1–10 μM by photolysis directly in the cavity of an epr spectrometer of degassed solutions of the parent hydrocarbons dissolved in di-*tert*-butyl peroxide. From **1**-H and **3**-H we also observed less stable primary alkyl radicals, and from **2**-H two other radicals were formed on prolonged photolysis. The most stable of the above species is **4**, which has previously been prepared[6] by reaction of triethylsilyl radicals with $(Me_3Si)_3CBr$, under which conditions it had a half-life of 5 sec at −40°. Under our own conditions, where reaction with solvent is slow or absent, the radical persists for several days in dilute solution at 25°. At higher temperatures (50–90°) first-order decay kinetics were observed yielding the expression $k\ (\text{sec}^{-1}) = 10^{12.3} \exp(-24{,}100\ \text{cal}/RT)$.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + RH \longrightarrow R\cdot + t\text{-BuOH}$$

$$R\cdot = \underset{\substack{\mathbf{1}\\ a_H\ 21.89\ G\\ g\ 2.0027}}{Me_3C\dot{C}HCMe_3} \qquad \underset{\substack{\mathbf{2}\\ a_H\ 15.2\\ 2.0034}}{Me_3Si\dot{C}HSiMe_3} \qquad \underset{\substack{\mathbf{3}\\ 2.0026}}{(Me_3C)_3C\cdot} \qquad \underset{\substack{\mathbf{4}\\ 2.0027}}{(Me_3Si)_3C\cdot}$$

2,2,4,4-Tetramethyl-3-pentyl (**1**) is stable at $10^{-5}\ M$ in solution below about −30°. Between −30 and −130° the signal appeared to decrease reversibly, but comparison of the double integral with that of 2,2,6,6-tetramethylpiperidine-*N*-oxyl solutions indicated that anisotropic line broadening rather than dimerization was largely responsible for the effect. Between 10 and 65° the decay can be expressed as $k\ (\text{sec}^{-1}) = 10^{12.0} \exp(-18{,}900\ \text{cal}/RT)$. At 25° the half-life is 50 sec and did not change on dilution with $CFCl_3$.

Radical **1** was also prepared by photolysis of di-*tert*-butylmethyl chloride in the presence of hexamethylditin and in the presence of di-*tert*-butyl peroxide and trimethylsilane. In these two systems the lifetime of **1** was greatly reduced but the signal was more intense and it was easy to resolve coupling by the methyl protons, $a_H{}^{CH_3} = 0.68$ G, and by the methyl ^{13}C, $a_{(^{13}C)}{}^{CH_3} = 11.7$ G. (For comparison in **4**, $a_H{}^{CH_3} = 0.375$ G and $a_{(^{13}C)}{}^{CH_3} = 5.2$ G[6]).

Tri-*tert*-butylmethyl (**3**) was observed as a broad singlet on photolysis of a single solution of a few milligrams of the methane in the peroxide. The decay rates were not of a definite order and depended on the length of photolysis, but we estimate the stability of **3** to be comparable to that of **1**.

A weak doublet assigned structure **2** was the first of several radicals formed from **2**-H and peroxide. The decay of **2** was extremely rapid and apparently second order with $2k_t = 10^{8.6\pm0.5}\ M^{-1}\ \text{sec}^{-1}$.

It is clear from these results that whereas α substitution of aliphatic carbon radicals has only a minor effect on the bimolecular termination rate,[7] extensive β substitution can totally inhibit such bimolecular reactions. This occurs even when, as in **1**, the radical is on a sec-

[1] Issued as N.R.C.C. No. 13231.

[2] M. Gomberg, *J. Amer. Chem. Soc.*, **22**, 757 (1900); *Ber.*, **33**, 3150 (1900).

[3] C. F. Koelsch, *J. Amer. Chem. Soc.*, **79**, 4439 (1957).

[4] K. Ziegler, G. Bremer, F. Thiel, and F. Thielmann, *Justus Liebigs Ann. Chem.*, **434**, 34 (1923).

[5] K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).

[6] A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

[7] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).