(entries 7 and 8). Thus, simple control of solvent and temperature provides selenenyl oxetanes D and adducts C with synthetically useful selectivities.

To extend the scope of the methodology, we examined secondary carbinol **2**[2c] and found less tendency toward intramolecular cyclization. When the reaction was carried out with PhSeCl under standard conditions a 84:16 mixture of **12**:**13** was obtained; even at low temperature a 58:42 mixture of adduct and oxetane was produced. PhSCl ($CHCl_3$/room temperature) gave a 50:50 mixture **14** and **15**. At low temperature the amount of oxetane **15** was increased slightly (33:67, **14**:**15**). Oxetane formation was improved when the addition of PhSCl was conducted on the preformed lithium alkoxide of **2** (*n*-BuLi/CH_2Cl_2/−78 °C) and produced a 17:83 mixture of carbinol **14** and tricyclic oxetane **15** (entries 9–13). These results may be rationalized in terms of small skeletal distortions that place the alcohol functionality farther from the reactive episulfonium ion. Vinyl-substituted tertiary alcohol **3**[6a] behaved similarly to methylcarbinol **1**, and a good yield of the 4,7-dioxatricyclo[3.2.1.$0^{3,6}$]octane derivative **16** was obtained at −78 °C (entry 14); however, in this case the amount of electrophile (PhSCl) had to be strictly controlled to avoid addition to the exocyclic double bond.

Finally, we conducted preliminary experiments to test whether oxetanes D could serve as precursors of oxanorbornenic vinyl sulfides. Treatment of **5** (Scheme II) with 3 equiv of *n*-BuLi in THF at −78 °C resulted in a clean conversion to vinyl sulfide **17** (90% yield of pure compound after a simple chromatography). Similarly, oxetane **16** afforded 85% of pure vinyl sulfide **18**. We are currently addressing the synthetic utility of these products and of the related oxanorbornenic vinyl sulfoxides. These results will be published in due course.

In conclusion, an efficient method for the synthesis of tricyclic oxetanes derived from 7-oxanorbornenic systems has been described. This intramolecular cyclization is favored by low temperature and chlorinated solvents, even for soft selenium electrophiles. This process is less effective for secondary alcohols like **2**, although the use of base to preform the alkoxide afforded oxetanes in fair yields. In some cases, the reaction can be directed to the bicyclic adduct C by a change in the solvent and reaction temperature (CH_3CN/reflux). Additionally, treatment of these sulfide oxetanes with base efficiently yields 7-oxanorbornenic vinyl sulfides.

Experimental Section

General. For procedures and conditions, see refs 3b and c. PhSeCl, 2-$NO_2C_6H_4SCl$, and 2,4-$(NO_2)_2C_6H_3SCl$ were purchased from Aldrich. The resulting products were separated chromatographically and fully characterized. Analytical TLC was carried out on 0.20-mm E. Merck precoated silica gel plates (60 F-254). All the NMR spectra were recorded in $CDCl_3$. All the new compounds are racemic and are numbered arbitrarily to facilitate comparison of the data.

***5-endo*-Chloro-6-*exo*-[(2,4-dinitrophenyl)sulfenyl]-2-*exo*-methyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (8) and 2-*exo*-[(2,4-Dinitrophenyl)sulfenyl]-5-*exo*-methyl-4,7-dioxatricyclo[3.2.1.$0^{3,6}$]octane (9).** From **1** and 2,4-DNBSCl, a 13:87 separable mixture of **8** and **9** was obtained in 88% combined yield. Data of **8**, R_f = 0.26 (CH_2Cl_2). ^{1}H NMR: δ 1.53 (3 H, s, CH_3), 1.91 (1 H, ddd, *J* = 13.4, 5.8, 1.5 Hz, H-3x), 2.40 (1 H, d, *J* = 13.4 Hz, H-3n), 4.01 (1 H, s, H-1), 4.18 (1 H, td, *J* = 4.9, 1.5 Hz, H-5), 4.39 (1 H, d, *J* = 4.6 Hz, H-6), 4.68 (1 H, td, *J* = 5.4, 1.5 Hz, H-4), 7.86 (1 H, d, *J* = 9.0 Hz, ArH), 8.41 (1 H, dd, *J* = 9.0, 2.4 Hz, ArH), 9.11 (1 H, d, *J* = 2.4 Hz, ArH). ^{13}C NMR: δ 29.4, 39.1, 50.1, 61.0, 78.0, 81.9, 89.4, 121.7, 127.5, 127.9, 144.2, 145.8. IR ($CHCl_3$): 3620, 3020, 2930, 1590, 1520, 1340, 1010 cm^{-1}. Anal. Calcd for $C_{13}H_{13}ClN_2O_6S$: C, 43.28; H, 3.63; N, 7.76. Found: C, 43.04; H, 3.78; N, 7.70. Data of **9**, mp 159–161 °C. R_f = 0.35 (CH_2Cl_2). ^{1}H NMR: δ 1.49 (1 H, s, CH_3), 1.79 (1 H, dd, *J* = 12.7, 4.6 Hz, H-3x), 2.23 (1 H, d, *J* = 12.7 Hz, H-3n), 3.82 (1 H, s, H-5), 4.65 (1 H, dd, *J* = 3.4, 1.7 Hz, H-6), 5.08 (1 H, dd, *J* = 4.6, 1.2 Hz, H-4), 5.17 (1 H, d, *J* = 3.7 Hz, H-1), 7.65 (1 H, *J* = 9.0 Hz, ArH), 8.36 (1 H, dd, *J* = 9.0, 2.7 Hz, ArH), 9.05 (1 H, d, *J* = 2.4 Hz, ArH). ^{13}C NMR: δ 20.9, 44.0, 51.6, 80.6, 81.5, 83.4, 92.9, 121.9, 127.0, 142.1, 144.2, 144.7. IR ($CHCl_3$): 3090, 3010, 2980, 1590, 1520, 1340, 1050, 980 cm^{-1}. Anal. Calcd for $C_{13}H_{12}N_2O_6S$: C, 48.15; H, 3.73; N, 8.64. Found: C, 48.18; H, 3.61; N, 8.15.

2-*exo*-(Phenylsulfenyl)-5-*exo*-vinyl-4,7-dioxatricyclo[3.2.1.$0^{3,6}$]octane (16). From **3** and PhSCl, **16** was obtained in 80% yield, mp 83–84 °C. R_f = 0.28 (hexane/ethyl acetate (5:1)). ^{1}H NMR: δ 1.84 (1 H, dd, *J* = 12.8, 4.6 Hz, H-3x), 2.09 (1 H, d, *J* = 12.8 Hz, H-3n), 3.70 (1 H, s, H-5), 4.63 (1 H, dd, *J* = 3.5, 1.6 Hz, H-6), 5.00 (1 H, dt, *J* = 4.6, 1.3 Hz, H-4), 5.19 (1 H, dd, *J* = 3.2, 1.0 Hz, H-1), 5.21 (1 H, dd, *J* = 10.8, 1.5 Hz, H-2′cis), 5.31 (1 H, dd, *J* = 17.3, 1.5 Hz, H-2′trans), 5.89 (1 H, dd, *J* = 17.3, 10.8 Hz, H-1′), 7.20–7.50 (5 H, m, ArH). ^{13}C NMR: δ 42.8, 53.5, 81.3, 82.3, 83.8, 93.4, 116.0, 126.8, 129.0, 130.5, 130.6, 135.3. IR (KBr): 3000, 1590, 1490, 1060, 750 cm^{-1}. Anal. Calcd. for $C_{14}H_{14}O_2S$: C, 68.27; H, 5.73. Found: C, 67.95; H, 5.69.

5-(Phenylsulfenyl)-2-*exo*-vinyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (18). From **16** and *n*-BuLi, **18** was obtained in 85% yield, mp 70–71 °C. R_f = 0.36 (hexane/ethyl acetate (5:1)). ^{1}H NMR: δ 1.44 (1 H, d, *J* = 12.1 Hz, H-3n), 1.68 (1 H, brs, OH), 2.13 (1 H, dd, *J* = 12.1, 4.9 Hz, H-3x), 4.57 (1 H, dd, *J* = 1.9, 1.0 Hz, H-1), 4.77 (1 H, brd, *J* = 4.9 Hz, H-4), 5.14 (1 H, dd, *J* = 10.8, 1.2 Hz, H-2′trans), 5.33 (1 H, dd, *J* = 17.4, 1.2 Hz, H-2′cis), 6.14 (1 H, dd, *J* = 17.4, 10.2 Hz, H-1′), 6.24 (1 H, d, *J* = 1.9 Hz, H-6), 7.25–7.49 (5 H, m, ArH). ^{13}C NMR: δ 42.7, 80.4, 82.1, 86.3, 111.6, 127.8, 129.0, 129.3, 131.2, 132.6, 143.3, 145.9. IR ($CHCl_3$): 3420, 3050, 2950, 1720, 1640, 1580, 1560, 1480, 1440, 1010, 930, 900 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.27; H, 5.73. Found: C, 68.11; H, 5.73.

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Supplementary Material Available: Experimental and spectroscopic data for compounds **6**, **7**, **12**–**15**, and **17** (2 pages). Ordering information is given on any current masthead page.

On Pentaorganylstiborane. 2. Reactions of Pentaorganylstiboranes with Acyl Chlorides and Ketones[†]

Li-Jun Zhang, Yao-Zeng Huang,* Hong-Xia Jiang, Jun Duan-Mu, and Yi Liao

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Lingling Lu, Shanghai 200032, China

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Introduction

It has been shown that quaternary stibonium salts have a much greater tendency to form pentaorganylstiboranes than the corresponding phosphonium and arsonium salts.[1] Generally, for phosphorus and arsenic, the ylides are produced on treating their quaternary salts with either LDA (lithium diisopropylamide), *t*-BuOK, or RLi (R = alkyl, aryl). However, for antimony, treatment of the quaternary stibonium salts with the less nucleophilic strong base LDA or *t*-BuOK affords stibonium ylides, while with the strong nucleophilic base RLi pentaorganylstiboranes are produced. Although many pentaorganylstiboranes are known, scarce attention has been paid to their application

[†] This paper is the 97th report on the studies of the synthetic application of elementoorganic compounds of 15th and 16th groups.

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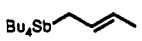
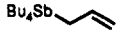
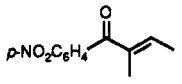
Table I. Synthesis of Benzylic and Allylic Ketones[a]

entry	stiborane	RCOCl	product	yield[b] (%)
a		C_6H_5COCl	**3a**	87
b		p-$CH_3C_6H_4COCl$	**3b**	90
c		p-ClC_6H_4COCl	**3c**	85
d	Bu_4SbCH_2Ph	p-BrC_6H_4COCl	**3d**	87
e		C_6H_5CH=$CHCOCl$	**3e**	76
f		$CH_3(CH_2)_4COCl$	**3f**	66
g		$CH_3(CH_2)_9COCl$	**3g**	70
h		C_6H_5COCl	**5h**	85
i		p-ClC_6H_4COCl	**5i**	86
j		p-$CH_3C_6H_4COCl$	**5j**	78
k		p-$NO_2C_6H_4COCl$	**5k**	71[c]
l		$C_6H_5CH_2COCl$	**5l**	83
m		$CH_3(CH_2)_6COCl$	**5m**	77
n		C_6H_5COCl	**8n**	15
o		p-ClC_6H_4COCl	**8o**	40

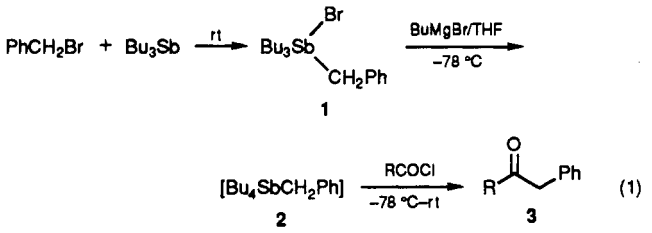
[a] All reactions were carried out according to method A. [b] Isolated yield based on acyl chloride. [c] The product was isomer: 

in organic synthesis. In our previous paper,[1] the reaction of pentaorganylstiboranes with aldehydes was reported. In continuation of our studies on pentaorganylstiboranes, we report here the reaction of pentaorganylstiboranes with acyl chlorides. Additionally, we report on the reaction of ketones with pentaorganylstiboranes as a followup to our initial report.[1]

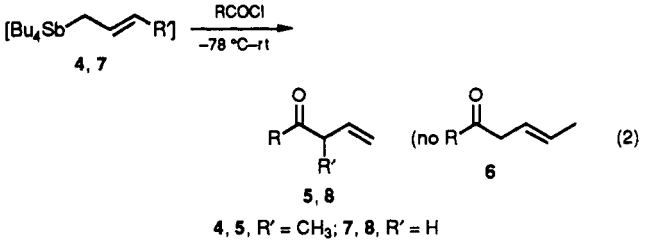
Results and Discussion

Reaction with Acyl Chloride. Generally, pentaorganylstiboranes were unreactive toward ketones but very reactive toward aldehydes. Thus, the reaction of pentaorganylstiboranes with acyl chlorides should produce the corresponding ketones, and our experimental results confirm this presumption.

As described previously, benzyltributylstibonium bromide 1 was readily obtained by mixing tributylstibine with benzyl bromide at room temperature. This quarternary stibonium salt was converted into benzyltetrabutylstiborane (2) by reaction with butylmagnesium bromide in THF at low temperature. In the absence of any additional catalyst, benzyltetrabutylstiborane (2) reacted with acyl chlorides to give the corresponding benzyl ketones in good yields. The results are summarized in Table I (entries a–g).



Benzyl ketone 3 was the sole product from this reaction. No butyl ketone, resulting from the coupling reaction of a butyl group with the acyl chloride, was observed. Thus, the benzyl group selectively transferred from benzyltetrabutylstiborane, and the butyl groups on antimony only serve as anchoring groups and do not transfer. This result was different from the reaction of the benzyltin with acyl chloride, in which a palladium catalyst was necessary for the coupling reaction and generally resulted in a mixture of products.[2]

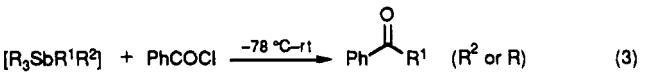


Similarly, the crotyltetrabutylstiborane (4), formed by reaction of butylmagnesium bromide with crotyltributylstibonium bromide (resulting from the reaction of crotyl bromide and tributylstibine), reacted with acyl chlorides to give the corresponding α-methyl allyl ketones 5 in good yields, instead of the crotyl ketone 6 (eq 2 and entries h–m). This result was also different from that of crotyltin; i.e., in the presence of tetrakis(triphenylphosphine)palladium(0), crotyltributyltin reacted with acyl chloride to give a mixture of crotyl and α-methyl allyl ketones as products,[2] but in the presence of chlorotris(triphenylphosphine)rhodium(1) gives the crotyl ketone as the sole product.[3]

Surprisingly, the results of the reaction of allyltetrabutylstiborane (7) with acyl chlorides were not satisfactory. The reaction of 7 with 4-chlorobenzoyl chloride gave a 40% yield of **8o**, but a 15% yield of **8n** was isolated when benzoyl chloride was used as the substrate. The reason accounting for this result is not clear at present.

Allyl ketones generally are difficult to isolate from acidic or basic reaction mediums because they isomerize very easily into the corresponding conjugated enones under such conditions.[4] However, the allylic ketones 5 and 8 could be isolated readily from our reaction mixture by chromatography on a silica gel column, with the exception of 4-nitrobenzoyl chloride (entry k). The product, isolated from the reaction mixture of 4-nitrobenzoyl chloride and crotyltetrabutylstiborane (4), was the conjugated enone 2-methyl-1-(4-nitrophenyl)-2-buten-1-one instead of 2-methyl-1-(4-nitrophenyl)-3-buten-1-one.

Other kinds of pentaorganylstiboranes also react with acyl chlorides to give the corresponding ketones in good yields (eq 3 and Table II). Reaction of pentabutyl-



stiborane **9a** with benzoyl chloride gave a 92% yield of valerophenone **10a**, which was also the sole product obtained when unsymmetrical diphenyltributylstiborane (**9b**), dimethyltributylstiborane (**9c**), and dimethyltriphenylstiborane (**9d**) were used. But, the reaction of diethyltributylstiborane (**9e**) with benzoyl chloride gave a 71:29 mixture of propiophenone (**10e**) and valerophenone (**10a**). In addition, a 60:40 mixture of deoxybenzoin (**3a**) and benzophenone (**10b**) was obtained in the case of benzylphenyltributylstiborane **9f**, while a 58:42 mixture of 2-methyl-1-phenyl-3-buten-1-one (**5h**) and benzophenone (**10b**) was obtained in the case of crotylphenyltributylstiborane (**9g**). So the order of transfer is CH_3CH=CH-CH_2 > Ph > $PhCH_2$ > Me > Et > n-Bu.

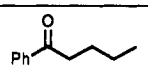
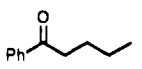
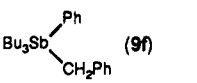
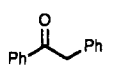
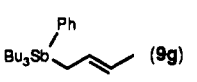
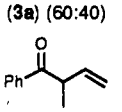
(1) (a) Huang, Y. Z.; Liao, Y.; Chen, C. *J. Chem. Soc., Chem. Commun.* **1990**, 85. (b) Huang, Y. Z.; Liao, Y. *J. Org. Chem.* **1991**, *56*, 1381.

(2) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634.

(3) Kosugi, M.; Shimizu, Y.; Migita, T. *J. Organomet. Chem.* **1977**, *129*, C36.

(4) Calas, R.; Dunogues, J.; Pillot, J. P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149.

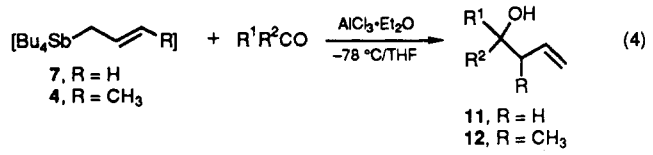
Table II. Synthesis of Ketones via Pentaorganylstiboranes[a]

entry	$R_3SbR^1R^2$	product	yield[b] (%)
a	Bu_5Sb (**9a**)	 (**10a**)	92
b	Bu_3SbPh_2 (**9b**)	 (**10b**)	88
c	Bu_3SbMe_2 (**9c**)	 (**10c**)	79
d	Ph_3SbMe_2 (**9d**)	 (**10d**)	88
e	Bu_3SbEt_2 (**9e**)	 (**10e**)	62
		 (**10a**) (71:29)	25
f	 (**9f**)	 (**10b**)	54
		 (**3a**) (60:40)	36
g	 (**9g**)	 (**5h**)	44
		 (**10b**) (58:42)	32

[a] The reactions of entries a–e were carried out according to method B and entries f,g according to method A. [b] Isolated yield.

The reaction of pentaorganylstiborane with an acyl chloride is a new method for the synthesis of ketones. There is no further reaction of the product ketone, which often occurs as the side reaction of most organometallic reagents (cadmium, zinc, magnesium). In addition, under the same conditions, ethyl benzoate and benzyl cyanide are unreactive toward pentaorganylstiboranes. Therefore, this reaction is especially useful in that there are other functional groups, such as ester, nitro, nitrile, and halo present in the acid chloride.

Reaction with Ketones. The rate of reaction of pentaorganylstiborane with ketone is generally very slow, but the reaction could be promoted by the Lewis acid $AlCl_3$. Thus, in the presence of $AlCl_3$, allyltetrabutylstiborane **7** or crotyltetrabutylstiborane **4** reacted with ketones to give allylic alcohols **11** or **12** in good yields (eq 4 and Table III).



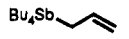
(4)

7, R = H
4, R = CH_3

11, R = H
12, R = CH_3

In conclusion, the pentaorganylstiboranes can react with acyl chlorides to give ketones in good yields. This reaction is a new method for the synthesis of ketones. In addition, in the presence of $AlCl_3$ pentaorganylstiboranes can react with ketones to give tertiary alcohols in good yields.

Table III. Synthesis of Allylic Alcohols 11 and 12[a]

entry	stiborane	ketone	product	yield[b] (%)
a		acetophenone	**11a**	85
b		cyclohexanone	**11b**	88
c		cyclopentanone	**11c**	88
d		3-pentanone	**11d**	63
e		cyclohexanone	**12e**	85
f		3-pentanone	**12f**	75

[a] All reactions were performed as described in the text. [b] Isolated yield based on ketone.

Experimental Section

Proton magnetic resonance (^1H NMR) spectra were recorded on a Varian 360L instrument in CCl_4 solution. Infrared spectra were recorded with neat liquid films unless indicated otherwise. All reactions were carried out under nitrogen. All solvents were dried by standard methods and redistilled before use. Boiling and melting points are uncorrected. Tri-*n*-butylstibine was prepared according to the literature method.[5]

General Procedure for Preparation of Ketone. Method A. Tributylstibine (2.5 mmol) and reactive bromide (2.5 mmol) (benzyl, crotyl, or allyl bromide) were stirred at room temperature for 12 h to give quaternary stibonium salt as a solid. Dry THF (3–4 mL) was added, and the resulting solution was cooled to −78 °C. To the cooled solution was added *n*-BuMgBr or PhMgBr (2.4 mmol, 1 M, THF) dropwise with vigorous stirring. After 5 min, acyl chloride (2.0 mmol) was added dropwise. The reaction temperature was allowed to rise to room temperature, and the solution was stirred for 1 h. After aqueous workup and chromatography on a silica column (petroleum ether/ethyl acetate (10:1)), the ketone product was obtained in good yield.

Method B. To a solution of tributylstibine or triphenylstibine (2.5 mmol) in THF (4 mL) was added Br_2 (2.5 mmol) dropwise at −78 °C, resulting in dibromotributylstiborane or dibromotriphenylstiborane. After 5 min, MeMgI, EtMgBr, or PhMgBr (4.8 mmol, 1 M, Et_2O) was added dropwise with vigorous stirring to yield the corresponding pentaorganylstiborane. The resulting mixture was allowed to stir for 10 min, and then acyl chloride (2.0 mmol) was added. The reaction temperature was allowed to rise to room temperature, and the solution was stirred for 1–2 h. After aqueous workup and chromatography on a silica column or thin-layer plate (petroleum ether/ethyl acetate (10:1)), the ketone product was obtained in good yield.

Ketones **3a–g**, **5h–m**, and **8n,o** were prepared by Method A.

2-Methyl-1-(4-methylphenyl)-3-buten-1-one (5j): ^1H NMR 1.20 (d, J_1 = 7.0 Hz, 3 H), 2.32 (s, 3 H), 3.60–4.10 (m, 1 H), 4.80–5.20 (m, 2 H), 5.60–6.10 (m, 1 H), 7.25 (d, J_2 = 9.5 Hz, 2 H), 7.80 (d, J_2 = 9.5 Hz, 2 H); IR 1680 cm^{-1}; MS 175 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.64; H, 7.96.

3-Methyl-1-phenyl-4-penten-2-one (51): ^1H NMR 1.10 (d, J = 7.0 Hz, 3 H), 3.10 (m, 1 H), 3.40 (s, 2 H), 4.50–5.0 (m, 2 H), 5.10–5.90 (m, 1 H), 7.05 (s, 5 H); IR 1720 cm^{-1}; MS 175 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.52; H, 8.18.

Coupling of 9a–e with Benzoyl Chloride. The reactions were carried out according to method B.

Coupling of 9f,g with Benzoyl Chloride. The reactions were carried out according to method A.

Reaction with Ketones. General Procedure. The pentaorganylstiborane intermediate **4** or **7** was prepared as described in Method A. To this solution, ketone (2.0 mmol) and $AlCl_3$·Et_2O (2.5 mmol) were added at −78 °C and stirred for 1 h. The reaction was quenched with H_2O at 0 °C. After chromatography on a silica column (petroleum ether/ethyl acetate (6:1)), tertiary alcohols were obtained in good yields.

Products. All the known products were identified either by comparison with authentic samples or by comparison with data reported: 1,2-diphenylethanone,[6] 1-(4-methylphenyl)-2-phenylethanone,[7] 1-(4-chlorophenyl)-2-phenylethanone,[7] 1-(4-bromo-

(5) Seifter, J. *J. Am. Chem. Soc.* **1939**, *61*, 530.
(6) Leake, W. W.; Levine, R. *J. Am. Chem. Soc.* **1959**, *81*, 1169.
(7) Huang, R. L. *J. Chem. Soc.* **1957**, 4089.

phenyl)-2-phenylethanone,[8] 1,4-diphenyl-3-buten-2-one,[9] 1-phenyl-2-dodecanone,[10] 1-phenyl-2-heptanone,[11] 2-methyl-1-phenyl-3-buten-1-one,[12] 1-(4-chlorophenyl)-2-methyl-3-buten-1-one,[12] 2-methyl-1-(4-nitrophenyl)-2-buten-1-one,[2] 3-methyl-1-undecen-4-one,[12] 1-phenyl-3-buten-1-one,[12] 1-(4-chlorophenyl)-3-buten-1-one,[12] valerophenone,[13] 2-phenyl-4-penten-2-ol,[14] 1-allylcyclohexanol,[15] 1-allylcyclopentanol,[15] 3-ethyl-5-hexen-3-ol,[16] 1-(1-methyl-2-propenyl)cyclohexanol,[17] 3-ethyl-4-methyl-5-hexen-3-ol.[18]

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Registry No. **1**, 128160-29-2; **2**, 131973-46-1; **3a**, 451-40-1; **3b**, 2001-28-7; **3c**, 1889-71-0; **3d**, 2001-29-8; **3e**, 5409-59-6; **3f**, 51439-03-3; **3g**, 6683-94-9; **4**, 137626-43-8; **5h**, 50599-02-5; **5i**, 95827-01-3; **5j**, 137626-44-9; **5k**, 87305-73-5; **5l**, 135987-22-3; **5m**, 95827-02-4; **7**, 137626-45-0; **8n**, 6249-80-5; **8o**, 95827-00-2; **9a**, 51439-94-2; **9b**, 137647-69-9; **9c**, 51439-91-9; **9d**, 137626-46-1; **9e**, 137626-47-2; **9f**, 137626-48-3; **9g**, 137626-49-4; **10a**, 1009-14-9; **10b**, 119-61-9; **10c**, 98-86-2; **10e**, 93-55-0; **11a**, 4743-74-2; **11b**, 1123-34-8; **11c**, 36399-21-0; **11d**, 1907-46-6; **12e**, 36971-11-6; **12f**, 25201-42-7; C_6H_5COCl, 98-88-4; *p*-$CH_3C_6H_4COCl$, 874-60-2; *p*-ClC_6H_4COCl, 122-01-0; *p*-BrC_6H_4COCl, 586-75-4; $C_6H_5CH{=}CHCOCl$, 102-92-1; $CH_3(CH_2)_4COCl$, 142-61-0; $CH_3(CH_2)_9COCl$, 17746-05-3; *p*-$NO_2C_6H_4COCl$, 122-04-3; $C_6H_5CH_2COCl$, 103-80-0; $CH_3(CH_2)_6COCl$, 111-64-8; $PhCH_2Br$, 100-39-0; Bu_3Sb, 2155-73-9; BuMgBr, 693-03-8; crotyltributylstibonium bromide, 133896-80-7; crotyl bromide, 4784-77-4; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 3-pentanone, 96-22-0.

Supplementary Material Available: Experimental data for compounds **3a-g**, **5h,i,k,m**, **8n,o**, **10a**, **11a–d**, and **12e,f** (3 pages). Ordering information is available on any current masthead page.

(8) Speer, J. H.; Hill, A. J. *J. Org. Chem.* **1937**, *2*, 139.
(9) Fleming, L.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485.
(10) Decock, P.; Vidal, B.; Goudmand, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, *277*, 407.
(11) Sund, E. H.; Henze, H. R. *J. Chem. Eng. Data* **1970**, *15*, 200.
(12) Reetz, M. T.; Wenderoth, B.; Urz, R. *Chem. Ber.* **1985**, *118*, 348.
(13) Shriner, R. L.; Turner, T. A. *J. Am. Chem. Soc.* **1930**, *52*, 1267.
(14) Jaworsky, W. *Chem. Ber.* **1909**, *42*, 435.
(15) Marcou, A.; Normant, H. *Bull. Soc. Chim. Fr.* **1965**, 3491.
(16) Schirokoff, A.; Saytzeff, A. *Ann. Chem.* **1879**, *196*, 113.
(17) Blais, J.; L'Honore, A.; Soulie, J.; Cadiot, P. *J. Organomet. Chem.* **1974**, *78*(3), 323.
(18) Benkeser, R. A.; Siklosi, M. P.; Mozdzen, E. C. *J. Am. Chem. Soc.* **1978**, *100*, 2134.

Alkyl Radical Displacement Reactions at Sulfur: On the Question of Intermediacy in Alkylsulfuranyl Radicals[1]

Kim F. Ferris* and James A. Franz*

Pacific Northwest Laboratory, Richland, Washington 99353

Carlos Sosa and Rodney J. Bartlett

Quantum Theory Project, University of Florida, Gainesville, Florida 32611

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Introduction

Radical displacement reactions at sulfur centers are of particular interest since the reaction may proceed through a relative energy minimum corresponding to a tricoordinate, hypervalent sulfuranyl radical intermediate.[2] Sulfuranyl radicals have been reported with σ-, σ^*-, and π-type ground-state electronic structures.[3,4] By analogy with closed shell 9-S-4 (9 formal electrons about 4-coordinate sulfur) sulfuranes, one or more electronegative ligands are probably required to achieve stable 9-S-3 sulfuranyl radicals.[5] Previous electronic structure calculations on SF_3 have indicated that the species is a stable intermediate, while SH_3 is probably a transition state.[2] Neither prediction was experimentally verifiable due to limitations in methodology and experiment. While our earlier kinetic studies[6] have revealed that the rate-determining step of alkyl radical displacement at sulfur centers is sensitive to the stability of the displaced radical, the intermediacy of a 9-S-3 alkyl species could not be rigorously excluded. Thus, ab initio molecular orbital calculations were performed on a series of sulfuranyl species ($(H_3C)_3S^\bullet$, $(H_3C)_2HS^\bullet$, and $H_3S^\bullet$) with weakly electron-donating ligands to resolve the question of intermediacy of alkylsulfuranyl radicals and to determine the applicability of many-body perturbation methods[7] for achieving accurate thermochemical estimates of second-row free-radical reaction energetics.

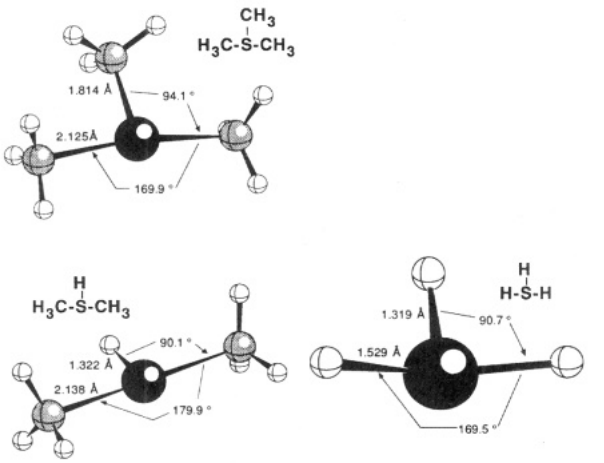

Figure 1. Molecular structure of (a) trimethylsulfuranyl, (b) dimethylsulfuranyl, and (c) sulfuranyl radicals.

Computational Methods

Electronic structure calculations were performed with the ACES[8] and GAUSSIAN-86[9] systems of programs. The geometries for reactants and transition states were optimized at the SCF level with the 4-31G*[10] split valence basis set. Electron correlation

(1) This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC06-76RLO 1830.
(2) Volatron, F.; Demolliens, A.; Lefour, J.-M.; Eisenstein, O. *Chem. Phys. Lett.* **1986**, 419. Volatron, F. THEOCHEM **1989**, 186, 167.
(3) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, 102, 7753 and references cited therein.
(4) Perkins, C. W.; Clarkson, R. B.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, 108, 3206. Perkins, C. W.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, 3211.
(5) Martin, J. C.; Perozzi, E. F. *Science* **1976**, 191, 154. Martin, J. C. *Science* **1983**, 221, 509.
(6) Franz, J. A.; Roberts, D. H.; Ferris, K. F. *J. Org. Chem.* **1987**, 52, 2256.
(7) Bartlett, R. J. Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules. *Ann. Rev. Phys. Chem.* **1981**, 32, 359. Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, 76, 1910. Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, 83, 4041.
(8) ACES (Advanced Concepts in Electronic Structure), an ab initio program system authored by Bartlett, R. J.; Purvis, G. D., III; Fitzgerald, G. B.; Harrison, R. J.; Lee, Y. S.; Laidig, W. D.; Cole, S. J.; Magers, D. H.; Salter, E. A.; Trucks, G. W.; Sosa, C.; Rittby, M.; Pal, S. Quantum Theory Project, University of Florida, Gainesville, FL, 1987.
(9) GAUSSIAN 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, 1984.

0022-3263/92/1957-0777$03.00/0