Apart from the mechanistic interest of the present work, the experiments reported above represent a simple, stereoselective route to the important amino deoxysugar derivatives **7** and **8** and a general entry to chiral secondary amines. Further synthetic applications of the stereochemically rich, highly functionalized chiral synthons **5** and **6** are in progress.

Acknowledgment. We thank Farmitalia-Carlo Erba, SpA, Milan, Italy, for a grant (to G.P.F.). This work has been financially supported by Piano Finalizzato CNR Chimica Fine Secondaria.

Registry No. **1**, 84519-53-9; **2**, 84472-94-6; **3**, 82010-51-3; **4**, 84519-54-0; **5** (isomer 1), 81069-01-4; **5** (isomer 2), 81130-78-1; **6** (isomer 1), 84519-55-1; **6** (isomer 2), 84519-56-2; **7**, 81176-31-0; **8**, 84519-57-3; **9**, 81176-32-1; **10**, 81176-33-2; diallylzinc, 1802-55-7; allyl bromide, 106-95-6.

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Application of the Catalytic Two-Phase System to Carbanionic Reactions of Allyl Sulfones[1]

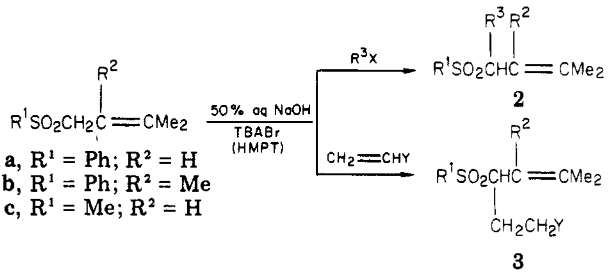
Summary: Allyl sulfones are easily converted into carbanions in the presence of concentrated aqueous NaOH solution and a quaternary ammonium catalyst. These carbanions readily react with alkyl halides, electrophilic alkenes, or perchloroalkanes.

Sir: Considerable interest has been recently focused on the chemical transformations of allyl sulfones.[2-4] The key step of these transformations is the generation of allylsulfonyl carbanions and their reactions with electrophilic compounds, leading to the formation of new C–C bonds. Subsequently, the RSO_2 group is removed from the product via reduction, elimination, or substitution, affording the target molecule.

A pertinent search of the literature reveals that very strong bases like BuLi or RMgX are usually used for the generation of allylsulfonyl carbanions.[4]

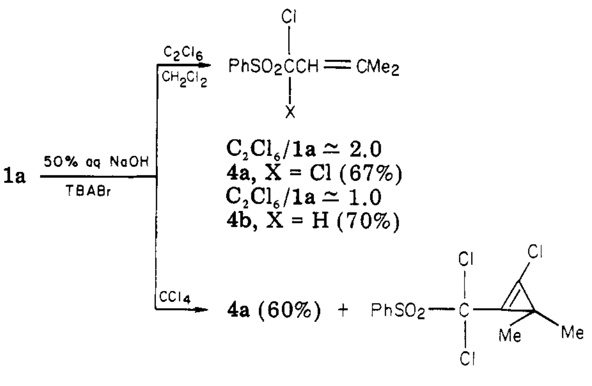
We report that the catalytic two-phase (CTP) system,[5] which consists of a concentrated aqueous NaOH solution and a quaternary ammonium salt as a catalyst, can be successfully applied for generation of allylsulfonyl carbanions[6] and their reactions with a variety of electrophilic compounds. Thus, sulfones **1a–c** react smoothly in the presence of 50% aqueous NaOH solution and tetrabutylammonium bromide (TBABr) as catalyst with alkyl halides or electrophilic alkenes to give respectively products[7] **2** and **3** in high yields (Scheme I, Table I). In the case of less active alkyl halides, the reactions were advantageously carried out with a small amount of aprotic dipolar solvent. Sulfones **1a,b** react in the CTP system with perchloroethane to give either α-mono- or α,α-dichlorinated derivatives. The degree of chlorination is easily controlled by the C_2Cl_6/sulfone ratio (Scheme II). The reaction of **1a** with an excess of CCl_4 resulted in the formation of the cyclopropene derivative **5**[11] in addition to

Scheme I



1a, R^1 = Ph; R^2 = H
b, R^1 = Ph; R^2 = Me
c, R^1 = Me; R^2 = H

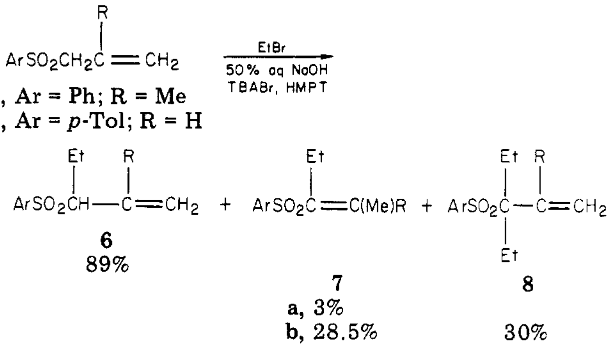
Scheme II[12]



C_2Cl_6/**1a** ≃ 2.0
4a, X = Cl (67%)
C_2Cl_6/**1a** ≃ 1.0
4b, X = H (70%)

5 (12%)

Scheme III



1d, Ar = Ph; R = Me
e, Ar = *p*-Tol; R = H

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(1) Paper 102 in the series "Reactions of Organic Anions". Part 101: Mąkosza, M.; Goliński, J.; Pankowski, J. *Synthesis*, in press.

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(4) For recent examples, see: Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 123. Lythgoe, B.; Waterhouse, I. *Ibid.* **1979**, 2429. Ueno, Y.; Seiichi, A.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1980**, 683.

(5) Dehmlow, E. V.; Dehmlow, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinheim/Bergstr., Germany, 1980; Mąkosza, M. In "Survey of Progress in Chemistry"; Scott, A. F., Ed; Academic Press: New York, 1980; Vol 9, p 1.

(6) There are two examples of the application of the CTP system to carbanionic reactions of allyl sulfones: (a) condensation of **1a** with benzaldehyde, leading to 4-methyl-1-phenyl-2-(phenylsulfonyl)penta-1,3-diene, yield 25% (Cardillo, G.; Sovoia, D.; Umani-Ronchi, A. *Synthesis* **1975**; 453) and (b) rearrangement of **1e** to propenyl *p*-tolyl sulfone, yield 63% (Steinbeck, K. *Liebigs Ann. Chem.* **1979**, 920).

(7) The NMR and IR spectra were consistent with the assigned structure; satisfactory combustion analysis were obtained for all compounds.

(8) Chabardes, P.; Julia, M.; Menet, A. German Offen. 2305215, 1973; Chem. Abstr. **1973**, *79*, 126671u.

(9) Oroshnik, W.; Mallory, R. A. *J. Am. Chem. Soc.* **1950**, *72*, 4608.

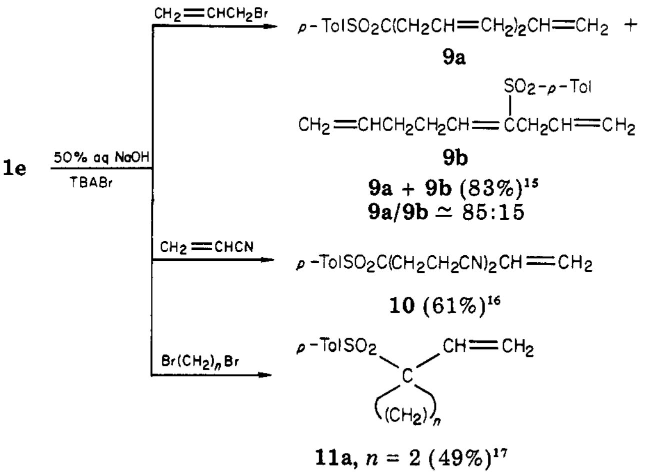
(10) Chabardes, P.; Julia, M.; Menet, A. German Offen. 2305267, 1973; Chem. Abstr. **1973**, *79*, 126670t.

Table I

product	R^1	R^2	R^3	Y	yield, %	mp (°C), solvent for cryst
2a	C_6H_5	H	C_2H_5[a]		89[b]	72-73, hexane
2b	C_6H_5	H	C_4H_9[a]		80	57-59.5, hexane
2c	C_6H_5	H	$CH_2{=}C(CH_3)CH_2$[c]		91	95-96.5,[d] hexane
2d	C_6H_5	H	$HOCH_2CH{=}C(CH_3)CH_2$[c,e]		32	85-86.5,[f] hexane-EtOH
2e	C_6H_5	CH_3	C_4H_9[a]		63	oil isolated by CC
2f	C_6H_5	CH_3	$CH_2{=}CHCH_2$[a]		85	oil isolated by CC
2g	CH_3	H	$C_6H_5CH_2$[c]		58	49.5-50.5, hexane-EtOH
2h	CH_3	H	$CH_2{=}CHCH_2$		79	bp 110-114/0.2 mm (bath temp)
3a	C_6H_5	H		NC	72	110-112.5, MeOH
3b	C_6H_5	H		$C_6H_5SO_2$	73	135-138, MeOH
3c	C_6H_5	H		HOOC[g]	76	161-162.5 dec, hexane-EtOH

[a] Reactions were carried out with HMPT (ca. 0.6 mol/1.0 mol of sulfone). [b] Without HMPT the yield is 49%. [c] Chlorides; in other cases bromides were used. [d] lit.[8] mp 98 °C. [e] THP derivative (prepared from isoprene hypochlorination product[9]) was used as an alkylating agent; the mixture was treated with a catalytic amount of TsOH in MeOH before isolation of the product. [f] Lit.[10] oil. [g] *tert*-Butyl acrylate was used; the crude product was hydrolyzed with concentrated hydrochloric acid in aqueous solution of dioxane.

Scheme IV



11a, $n = 2$ (49%)[17]
b, $n = 4$ (67%)[17]

the expected product **4a**. During the PTC alkylation of **1a–c**, the formation of only α-monosubstituted, β,γ-unsaturated sulfones was observed. However, this is not the case with sulfones **1d,e** (Scheme III). Although the former still predominantly forms product **6** accompanied by a small amount of α,β-unsaturated isomer **7a**, the latter affords a rather complex mixture consisting of **7b**, **8**, and other unidentified products.[13,14] Evidently the anion $ArSO_2CR{=}{=}C^-H{=}{=}CH_2$ is protonated faster at the γ position to give **7** than alkylated by moderately active ethyl bromide. However, if the reaction of this anion with electrophiles competes effectively with protonation at the γ position, the α,α-disubstituted products are formed with satisfactory yields, provided that the electrophiles are used in excess (Scheme IV).

Our data demonstrate the applicability of the CTP system for carbanionic reaction of allyl sulfones. The method is very simple, as can be seen from the examples.

4-(Phenylsulfonyl)-2-methylhex-2-ene (2a). Sulfone **1a** (3.15 g, 15 mmol), ethyl bromide (3.27 g, 30 mmol), TBABr (0.24 g), HMPT (1.8 mL), and 50% aqueous NaOH (15 mL) were stirred at 30–35 °C for 1.5 h. The mixture was worked up,[18] and the product was purified by crystallization (3.17 g, 89%; Table I).

4-(Methylsulfonyl)-2-methylhepta-2,6-diene (2h). Sulfone **1c** (1.48 g, 10 mmol), allyl bromide (1.33 g, 11 mmol), TBABr (0.15 g), and 50% aqueous NaOH (10 mL) were stirred at 35–40 °C for 3.5 h. The mixture was worked up[18] and the product was distilled "bulb to bulb" (1.5 g, 79%; Table I).

1-Cyano-3-(phenylsulfonyl)-5-methylhex-4-ene (3a). The solution of **1a** (1.05 g, 5 mmol) and acrylonitrile (0.40 g, 7.5 mmol) in acetonitrile (2 mL) was added dropwise to the stirred mixture of 50% aqueous NaOH (5 mL) and TBABr (0.08 g) at 12–15 °C. The mixture was then stirred at 15 °C for 1.5 h and worked up[18] and the product was crystallized (0.95 g, 72%; Table I).

1-Vinyl-1-(*p*-tolylsulfonyl)cyclopentane (11b). Sulfone **1e** (1.96 g, 10 mmol), 1,4-dibromobutane (3.24 g, 15 mmol), TBABr (0.15 g), HMPT (1.0 mL), and 50% aqueous NaOH (10 mL) were stirred at ca. 35 °C for 2 h. The mixture was worked up,[18] and the product was isolated by column chromatography on silica gel and crystallized (hexane), mp 63.5–65 °C (1.68 g, 67%).

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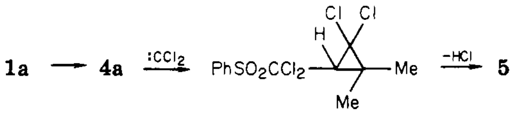
(11) The chemistry of **5** will be published elsewhere. Its origin can be rationalized as follows:



For application of CCl_4 for chlorination of CH acids in the CTP system, see: Jończyk, A.; Kwast, A.; Mąkosza, M. *J. Org. Chem.* **1979**, *44*, 1192. Lauritzen, S. E.; Rømming, C.; Škattebøl, L. *Acta Chem. Scand., Ser. B* **1981**, *35*, 263.

(12) **4a** (mp 55–56 °C) and **4b** (mp, 114–116.5 °C) were isolated by crystallization (hexane–EtOH). The conversion **1a** $\xrightarrow{C_2Cl_6}$ **4a** is practically quantitative; in the case of the reaction **1a** $\xrightarrow{C_2Cl_6}$ **4b**, the crude mixture contains traces of **1a** and **4a**. The yields of **4a** and **5** in the reaction **1a** $\xrightarrow{CCl_4}$ **4a** + **5** were estimated from ^1H NMR spectrum; a sample of **5** was isolated by column chromatography and crystallized (hexane–EtOH), mp 92–94 °C.

(13) Relative amounts of α,β-unsaturated isomers are in line with base-catalyzed equilibrations of allyl sulfones (Sataty, I.; Meyers, C. Y. *Tetrahedron Lett.* **1974**, 4161):

	$PhSO_2CHR^1CR^2{=}CH_2$	$PhSO_2CR^1{=}CR^2Me$
$R^1 = R^2 = H$	28%	72% ($Z + E$)
$R^1 = H$; $R^2 = Me$	70%	30%
$R^1 = Me$; $R^2 = H$	0%	100% (E)

(14) The yields of **6** and **7a** were estimated from the ^1H NMR spectrum; pure **6** was isolated by column chromatography (yield 83%) and crystallized (hexane–EtOH), mp 81–83 °C. The sulfones **7b** and **8** were isolated by column chromatography and crystallized: **7b**, mp 68–69.5 C (hexane–EtOH); **8**, mp 65–67 °C (hexane).

(15) The mixture of **9a** + **9b** was isolated by column chromatography as an oil; its composition was deduced from the ^1H NMR spectrum.

(16) **10** was isolated by crystallization (MeOH), mp 117–118.5 °C. Its mixture with the monocyanoethyl derivative of **1e** is described as an oil (Bruson, H. A. U.S. Patent 2435552, 1948; *Chem. Abstr.* **1948**, *42*, 3779a).

(17) **11a** was isolated by column chromatography and crystallized (hexane–EtOH), mp 98.5–99.5 °C; **11b**, see the procedure given for this compound.

(18) The workup consists of dilution of the mixture with water, extraction with $CHCl_3$, washing of the organic extracts with diluted hydrochloric acid, water, and then brine, drying ($MgSO_4$), and evaporation of the solvent on a rotary evaporator.

Acknowledgment. We are grateful for the support of this work by the Polish Academy of Sciences under Grant MR-I-12.

Registry No. **1a**, 15874-80-3; **1b**, 84602-85-7; **1c**, 5897-46-1; **1d**, 49639-05-6; **1e**, 3112-87-6; **2a**, 84602-86-8; **2b**, 74866-54-9; **2c**, 50464-16-9; **2d**, 50465-67-3; **2e**, 84602-87-9; **2f**, 84602-88-0; **2g**, 84602-89-1; **2h**, 84602-90-4; **3a**, 84602-91-5; **3b**, 84602-92-6; **3c**, 84602-93-7; **4a**, 84602-94-8; **4b**, 84602-95-9; **5**, 84602-96-0; **6a**, 84602-97-1; **7b**, 84602-98-2; **8b**, 84602-99-3; **9a**, 84603-00-9; **9b**, 84603-01-0; **10**, 84603-03-2; **11a**, 84603-02-1; **11b**, 84603-04-3; TBABr, 1643-19-2; C_2Cl_6, 67-72-1; CCl_4, 56-23-5; EtBr, 74-96-4; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CHCN$, 107-13-1; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_4Br$, 110-52-1.

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Generation of Metal-Free Silyl Anions from Disilanes and Fluoride Catalyst. Synthetic Reactions with Aldehydes and 1,3-Dienes

Summary: The Si–Si bond of disilanes is found to be cleaved by tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide to produce metal-free silyl anion and triorganosilyl fluoride. The disilane/TBAF reagent was studied spectrometrically. Synthetic application of the reagent with a catalytic amount of TBAF is illustrated by the reaction with aldehydes and 1,3-dienes.

Sir: Triorganosilyl anions have recently emerged as synthetic tools for introduction of silyl group into organic compounds.[1] Generation of the anionic species hitherto reported includes reduction of Si–X or Si–Si bond with alkaline metal or magnesium[1c] or nucleophilic substitution of one of the disilane silicon atoms with metal alkoxide or methyllithium at the sacrifice of half the molecule.[1] The chemical behavior of the silyl anions thus produced should be understood in association with the metal gegenion. Herewith we report that the disilane Si–Si bond is cleaved by tetrabutylammonium fluoride (TBAF) to give metal-free triorganosilyl anion and also that both silicon elements of disilanes are incorporated into aldehyde carbonyl and 1,3-diene units effectively.

We first studied the spectrometric behavior of disilane/TBAF reagent. Hexamethyldisilane (1.1 mmol) and anhydrous TBAF[2] (1.0 mmol) were dissolved in hexamethylphosphoric triamide (HMPA) (1.5 mL) to give a yellow solution, which showed ^{19}F NMR absorptions (CF_3COOH, standard) at δ 15.0 and 72.8 in ca. 2:1 intensity ratio in place of the absorption of TBAF δ 34.5. These new absorptions may be attributed to 5-coordinate silicon intermediate **1**[3] and trimethylsilyl fluoride,[4] respectively, on the basis of the reported values. ^1H NMR analysis (C_6H_6 as a standard)[5] gave a broad singlet at δ 0.0. Evaporation of all the volatile material gave a singlet peak at δ −0.17 (9 H intensity per 4 Bu)[6] consistent with structure **2**, which gave tetramethylsilane (δ 0.00) on treatment with excess methyl iodide. Thus, it seems reasonable to conclude that the following equilibrium exists in HMPA solution. It should be emphasized that trimethylsilyl anion in **2** is completely metal-free and will exhibit unique reactivity compared with the conventional R_3SiM reagents.[1c,7]

$$\mathrm{Me_3SiSiMe_3 + Bu_4N^+F^- \rightleftarrows \underset{\textbf{1}}{Bu_4N^+[Me_3SiSiMe_3F]^-} \rightleftarrows \underset{\textbf{2}}{Bu_4N^+SiMe_3^-} + Me_3SiF}$$

Upon addition to unsaturated functional group A=B, trimethylsilyl anion gives $\equiv$SiAB$^-$, which is subsequently silylated by Me_3SiF to regenerate the fluoride catalyst. Thus, catalytic amount of TBAF should be enough for the $\equiv$SiABSi$\equiv$ production. This concept is visualized by the reaction with alkanals.[8]

To the pale yellow reagent solution prepared by treatment of hexamethyldisilane (0.31 mL, 1.5 mmol) with TBAF (0.1 mmol or 0.5 M THF solution, 0.2 mL) in HMPA (2 mL) (room temperature, 5 min) was added undecanal (0.21 mL, 1.0 mmol), and the mixture was stirred for 4.5 h. The color ascribed to the trimethylsilyl anion vanished at this moment. GLC analysis of the reaction mixture revealed the presence of 1-(trimethylsilyl)-1-((trimethylsilyl)oxy)undecane and undecyl trimethylsilyl ether only. Workup effected by treatment with concentrated HCl/MeOH (1:10) (1 mL), extraction with ether, washing with aqueous NH_4Cl solution and then with brine, concentration, followed by purification by silica gel column chromatography (hexane/ethyl acetate, 10:1), gave 1-(trimethylsilyl)-1-undecanol[9] (0.163 g, 67% yield) along with 1-undecanol (44 mg, 26%).

$$\mathrm{RCHO + Me_3SiSiR'_3 \xrightarrow[HMPA]{TBAF\ (5\ mol\ \%)} RCH(OSiMe_3)SiR'_3 \xrightarrow{H_3O^+} RCH(OH)SiR'_3}$$

The procedure is applied to various aldehydes and disilanes, and the results are given in the order of aldehyde,

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(1) (a) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. Fleming, I.; Newton, T. W.; Roessier, F. *Ibid.* **1981**, 2527. (b) Tamao, K.; Akita, M.; Kanatani, R.; Ishida, N.; Kumada, M. *J. Organomet. Chem.* **1982**, 226, C9. (c) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 134–140 and references cited therein.

(2) Kuwajima, I.; Nakamura, E. *J. Am. Chem. Soc.* **1975**, *97*, 3257.

(3) ^{19}F NMR (MeCN, CF_3COOH standard, room temperature) of $Ph_3SiF_2^-NPr_4^+$ is reported to give an absorption at δ 18.8 [Kuroda, K.; Ishikawa, N. *Nippon Kagaku Zasshi* **1970**, *91*, 77], while the spectra (CH_2Cl_2 solution, $CFCl_3$ standard) of $Ph_2SiF_3^-NEt_4^+$ at low temperatures exhibit two peaks at δ 98.0 (axial) and 134.0 (equatorial) in a ratio of 2:1 [Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155]. According to Muetterties and his co-worker, the peaks coalesce into a single one at δ 110 on warming to room temperature, in agreement with the observation of Ishikawa and Kuroda (δ 38.9, CF_3COOH). Since organic ligands prefer the equatorial position of five-coordinate trigonal-bipyramidal silicon species (loc. cit.), the absorption at δ 15.0 from CF_3COOH (δ 93 calculated on the basis of $CFCl_3$) in our experiment can be ascribed to the axial fluorine. This assignment is supported by the data in: Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608.

(4) Hunter, B. K., Reeves, L. W. *Can. J. Chem.* **1968**, *46*, 1399.

(5) The chemical shift of benzene in HMPA was found to be δ 7.40 (tetramethylsilane, standard).

(6) (Trimethylsilyl)sodium in HMPA prepared according to the procedure by Sakurai et al. [Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511] showed singlet peaks at δ −0.18 and −0.12. (Trimethylsilyl)lithium exhibits an absorption at δ 1.73 (in dimethoxyethane) or δ 1.33 (in cyclopentane) higher field than that of cyclopentane (generally δ 1.51): Schaaf, T. F.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, *91*, 4327.

(7) Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 283.

(8) Addition of trimethylsilyl anion to carbonyl compounds: (a) Jutzi, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, C43. (b) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.

(9) ^1H NMR (CCl_4) δ 0.00 (s, 9 H), 0.88 (t, $J = 6$ Hz, 3 H), 1.0–1.7 (m, 19 H), 3.20 (t, $J = 6$ Hz, 1 H); IR (neat) 3400, 1245, 835 cm^{-1}; MS; *m/e* (rel %) 229 ($M^+ - 15$, 2), 91 (34), 75 (80), 73 (100), 57 (20), 43 (26).

0022-3263/83/1948-0912$01.50/0