December, 1988] *Bull. Chem. Soc. Jpn., 61, 4323—4327 (1988)* 4323

Reactions of Wittig Reagents with Episulfides or Elemental Sulfur

Kentaro Okuma,* Yuji Tachibana, Jun-ichi Sakata, Takashi Komiya, Isao Kaneko, Yasuo Komiya,
Yusuke Yamasaki, Shin-ichi Yamamoto, and Hiroshi Ohta
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-01

(Received April 25, 1988)

The reactions of Wittig reagents with episulfides gave symmetrical olefins and triphenylphosphine sulfide in moderate yields. The same olefins were obtained by reactions of Wittig reagents with elemental sulfur. These reactions might proceed through thiocarbonyl intermediates, the existence of which was confirmed by Diels-Alder reactions with dienes.

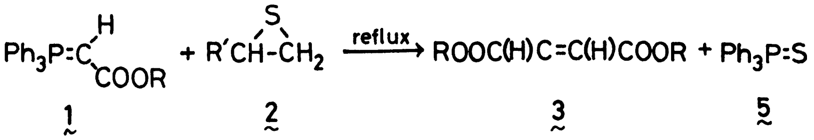
The Wittig reaction has been widely adopted for the synthesis of olefins.[1] During the past decade, several authors have reported on the reactions of Wittig reagents (**1**) with epoxides to afford cyclopropane derivatives.[2] Corey and Kang also reported that the reaction of the methylenetriphenylphosphorane anion with epoxides, followed by the addition of carbonyl compounds, gave 2-hydroxy olefin derivatives.[3] One of the methods for the synthesis of thioketones is the reaction of phosphonium ylides with elemental sulfur.[4] In a previous communication, we reported that the reactions of stable Wittig reagents with episulfides (**2**) afforded olefins (**3**) via thiocarbonyl intermediates in moderate yields.[5] Recently, we also found that the reaction of Wittig reagents with elemental selenium gave the corresponding olefins via selenocarbonyl intermediates.[6] This consideration, in turn, prompted us to investigate the possibility of the formation of **3** and thioaldehydes (**4**) by reactions of elemental sulfur with Wittig reagents. In this paper, we would like to report that the reaction of **1** with **2** or elemental sulfur produced **3** via thioaldehyde intermediates.

Results and Discussion

We first tried the reaction of **1** with **2**. A treatment of carbomethoxymethylenetriphenylphosphorane (**1a**) with styrene sulfide (**2a**) in toluene afforded styrene, dimethyl fumarate (**3a**), dimethyl maleate (**3a′**), and triphenylphosphine sulfide (**5**) in 20, 42.5, 9.5, and 74% yields, respectively. It took 2 days of refluxing to complete this reaction. We then carried out this reaction in refluxing benzene as a solvent. However, the yields of the products were lowered less than half, even after refluxing for 8 days. As shown in Table 1, other dialkyl fumarates and maleates were prepared in a similar manner.

Benzylidenetriphenylphosphorane (**1f**) was thermally decomposed at temperatures over 240 °C to give symmetrical olefins via carbene intermediates.[7] In this case, the reaction might proceed through similar carbene intermediates, as shown in Scheme 2. However, the thermolysis of **1a** in refluxing toluene without episulfide did not afford the olefins, but only the recovered starting materials, even after refluxing for 8 days. This result showed that the above-mentioned mechanism was not correct.

It is well-known that the reaction of benzhydrylidenetriphenylphosphorane with elemental sulfur affords thiobenzophenone, which changes to tetraphenylethylene upon heating at temperatures over 200 °C.[4a] Fluorenylidenetriphenylphosphorane was also found to react with sulfur to give thiofluore-



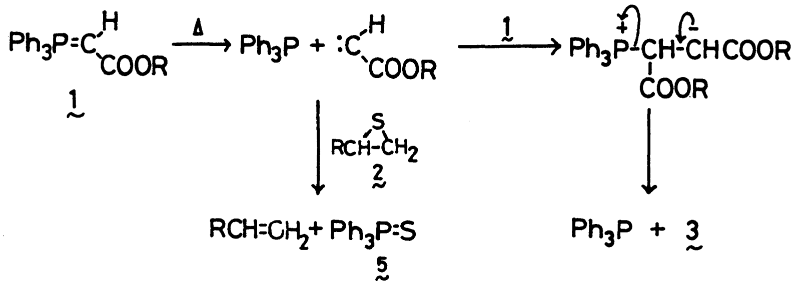
$$Ph_3P{:}CH(COOR) + R'CH(S)CH_2 \xrightarrow{reflux} ROOC(H)C{=}C(H)COOR + Ph_3P{:}S$$

Scheme 1.

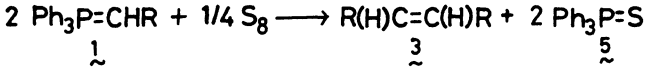
Table 1. Reaction of **1** with Episulfides

Compounds				Conditions		Products (Yields/%)		
1	R	**2**	R′	Solvent	Time/day	Ph3P=S	**3**	Trans/Cis[a)]
a	Me	**a**	Ph	Toluene	2	74	52	4.5
a	Me	**a**	Ph	Benzene	8	27	14	9.0[b)]
a	Me	**b**	Me	Toluene	4	12	6	5.0[b)]
a	Me	**c**	Et	Benzene	8	33	11	9.0[b)]
b	Et	**a**	Ph	Toluene	2	74	58	3.5
c	*i*-Ph	**a**	Ph	Toluene	2	78	62	5.0

a) The ratio was determined by their ^{1}H NMR spectra or capillary GC. b) Starting **1a** was recovered in 50, 55, and 50% yields respectively.



Scheme 2.



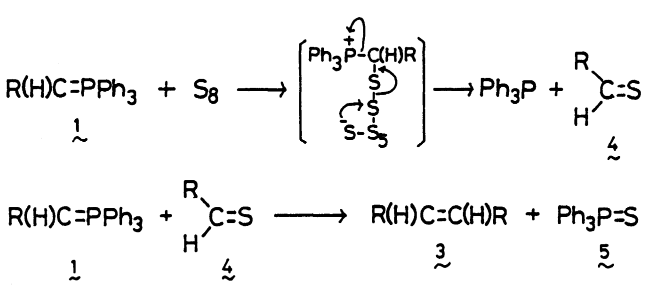
$$\underset{\mathbf{1}}{2\,Ph_3P{=}CHR} + 1/4\,S_8 \longrightarrow \underset{\mathbf{3}}{R(H)C{=}C(H)R} + \underset{\mathbf{5}}{2\,Ph_3P{=}S}$$

Scheme 3.

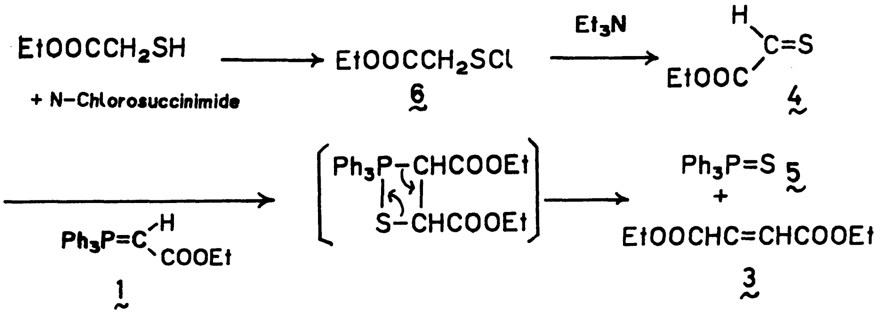
Table 2. Reaction of **1** with Elemental Sulfur

Compound		Conditions		Products (Yield/%)		
1	R	Solvent	Time/h	Sulfide **5**	Olefin **3**	Trans/Cis
a	COOMe	Toluene	3	79	76	5.0[a]
b	COOEt	Toluene	3	98	96	4.0[a]
d	CN	Toluene	3	86	60	Trans only[b]
e	COMe	Toluene	3	60	44	Trans only[b]
f	Ph	Benzene	8[c]	55	38	Trans only[b]
f	Ph	Benzene	3	86	60	150[b]

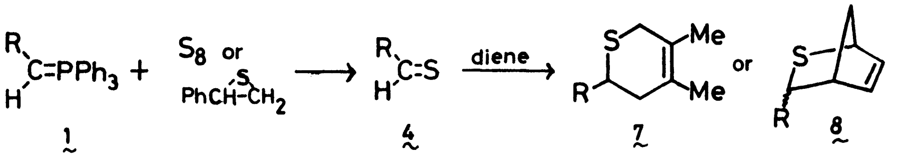
a) The ratio was determined by ^{1}H NMR. b) The ratio was determined by capillary GC. c) The reaction was carried out at room temperature.



Scheme 4.



Scheme 5.

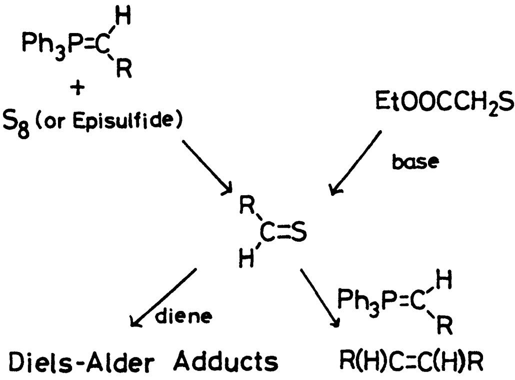


Scheme 6.

Table 3. Reaction of Thioaldehydes with Dienes

Compounds			Diene	Adducts (Yield/%)		
1	R					Endo : Exo[a)]
a	COOMe	Sulfur	2,3-Dimethylbutadiene	**7a**	56[10b)]	
a	COOMe	Styrene sulfide	2,3-Dimethylbutadiene	**7a**	38	
a	COOMe	Sulfur	Cyclopentadiene	**8a**	64	4 : 3
b	COOEt	Sulfur	2,3-Dimethylbutadiene	**7b**	49[12)]	
b	COOEt	Sulfur	Cyclopentadiene	**8b**	84[12)]	3 : 2
d	CN	Sulfur	2,3-Dimethylbutadiene	**7d**	35[12)]	
d	CN	Sulfur	Cyclopentadiene	**8d**	46[12)]	3 : 2
f	Ph	Sulfur	2,3-Dimethylbutadiene	**7f**	60[13)]	
f	Ph	Sulfur	Cyclopentadiene	**8f**	66[10a,14)]	3 : 1

a) The ratio was determined by their ^1H NMR spectra.



Scheme 7.

none.[4b)] Tokunaga and coworkers reported that the reaction of **1f** with sulfur afforded cyclic pentasulfide and a very small amount of stilbene.[8)] We therefore tried a reaction of **1** with sulfur in refluxing toluene. A treatment of **1a** with elemental sulfur gave **3a**, **3a′**, and **5** in 63, 13, and 79% yields, respectively. The reaction was faster than that of **2**. As shown in Table 2, olefins **3** and **5** were obtained in good yields. Mägerlein and Meyer reported the same reaction in the case of **1f** in refluxing toluene.[9)] They also found that only *trans*-stilbene was obtained in this reaction. These results suggested that a reaction of **1** with **2** or sulfur might proceed through thioaldehyde intermediates. The ylide carbanion attacks episulfide sulfur or sulfur to give the corresponding **4**. The resulting thioaldehyde **4** further reacts with the phosphonium ylide to afford olefins via a Wittig-like reaction. Recently, Kirby and coworkers reported the generation of **4b** by the reaction of ethoxycarbonylmethanesulfenyl chloride (**6**) with triethylamine.[10a)] To confirm this mechanism, we tried a similar reaction by using **6**, triethylamine, and **1b**. As shown in Scheme 5, the corresponding **3** and **5** were obtained in good yields (75%, trans/cis=4.5). Compounds **4** were recently prepared by several groups: photolysis of phenacyl sulfide derivatives;[11)] reaction of sulfenylchlorides with bases;[10a)] reaction of Bunte salts with bases;[12)] thermolysis of thiolsulfinates;[13,14)] catalytic base abstraction of trimethylsilyl derivatives.[15)] While most of thioaldehydes were trapped by dienes, Okazaki and coworkers isolated aromatic and aliphatic thioaldehydes.[16)] To confirm the formation of **4** in our case, we carried out a Diels-Alder reaction. A treatment of **1** and elemental sulfur (or styrene sulfide) resulted in the formation of thioaldehydes, which further reacted with dienes to give the corresponding adducts (**7** and **8**) in moderate yields. This result provides another possibility to produce **4**.

In summary, the reaction of **1** with **2** gave symmetrical **3** and **5** in moderate yields. Similarly, the reaction of **1** with elemental sulfur afforded symmetrical **3** and **5** in good yields. Both reactions might proceed through thioaldehyde intermediates, the existence of which was confirmed by a Diels-Alder reaction. We also confirmed that the reaction of thioaldehydes with Wittig reagents gave the corresponding olefins.

Experimental

General Methods. Melting points are uncorrected. NMR spectra were obtained by using JEOL PMX-60 and FX-90Q spectrometers. IR spectra were recorded on a Hitachi IR-345 spectrometer.

Materials. Compounds **1** were prepared by a method mentioned in the literature.[1,3)] Compounds **2** were prepared by reactions of epoxides with KSCN or thiourea.[17)] Cyclopentadiene was obtained from dicyclopentadiene by distillation. 2,3-Dimethyl-1,3-butadiene was obtained from Aldrich Chem. and used without further purification. Authentic alkyl maleates or fumarates were purchased from Wako Pure Chemicals.

Reaction of 1a with 2a in Benzene. To a solution of **2a** (0.68 g, 5.0 mmol) in benzene (30 ml) was added **1a** (1.67 g, 5.0 mmol) in one portion. After refluxing for eight days, the reaction mixture was evaporated and extracted three times with hexane (30 ml×3). The residue was a mixture (1.19 g) of **1a** (50%) and **5** (24%, yields were determined by its NMR spectrum). The combined extracts were subjected to column chromatography (silica gel). Five components were obtained: styrene (0.05 g, 0.5 mmol) was eluted first (eluant, hexane). A complex mixture of unidentified products (0.03 g) was obtained second (eluant, 80% hexane-dichloromethane). A mixture of dimethyl fumarate and dimethyl maleate (0.05 g, 0.35 mmol, 14%, yields were determined by its NMR spectrum) was further eluted (eluant, 50% hexane-dichloromethane). A small amount of **5** (0.05 g, 0.17 mmol, 3%) was eluted last (eluant, dichloromethane).

Other reactions were carried out in a similar manner.

Reaction of 1a with Elemental Sulfur. To a solution of **1a** (3.34 g, 10 mmol) in toluene (100 ml) was added a suspension of sulfur (0.38 g, 12 mmol) in toluene (15 ml). After refluxing for 3 h, the solvent was evaporated from the reaction mixture and the remaining oil was extracted three times with hexane (50 ml×3). The residue was mainly triphenylphosphine sulfide, which was purified by recrystallization with benzene-hexane (2.32 g, 7.9 mmol, 79%). The combined extracts were evaporated and chromatographed over silica gel by elution with hexane-dichloromethane (2 : 1) to give a mixture of dimethyl fumarate and dimethyl maleate in 76% yields (0.51 g, 3.8 mmol, 5 : 1 ratio by NMR).

Other reactions were carried out in a similar manner.

Reaction of Wittig Reagent with Thioaldehyde (4b) Derived from 6. To a suspension of *N*-chlorosuccinimide (0.93 g, 7.0 mmol) in toluene (20 ml) was added dropwise a solution of ethyl thioglycolate (0.72 g, 6.0 mmol) in toluene (10 ml) at room temperature. After stirring for 2 h, the reaction mixture was filtered to give a yellow solution of the corresponding sulfenyl chloride. This solution was added dropwise to a refluxing solution of **1b** (1.74 g, 5.0 mmol) and triethylamine (0.71 g, 7.0 mmol) in toluene (20 ml). After refluxing for 3 h, the reaction mixture was washed with water (20 ml×3), dried over $MgSO_4$, and evaporated to give pale brown oil which was extracted with pentane (20 ml× 3). The combined extract was evaporated to give a crude mixture of olefins (0.54 g, 3.75 mmol, 75% trans/cis=4.5 by NMR). The resulting oil was chromatographed over silica gel by elution with hexane-dichloromethne (5 : 1) to give a mixture of diethyl maleate and diethyl fumarate (0.37 g, 2.6 mmol, 52%).

Reaction of Wittig Reagent with Styrene Sulfide in the Presence of 2,3-Dimethylbutadiene. To a solution of **1a** (1.68 g, 5.0 mmol) and 2,3-dimethyl-1,3-butadiene (2 ml, 20 mmol) in toluene (30 ml) was added a solution of styrene sulfide (2.04 g, 15 mmol) in toluene (15 ml). After refluxing for 30 h, the resulting mixture was evaporated to give pale brown oily crystals, which were chromatographed over silica gel by elution of hexane-dichloromethane (1 : 1) to give adduct **7a** (0.36 g, 1.9 mmol, 38%). ^{1}H NMR ($CDCl_3$) δ=1.73 (6H, s, Me), 2.33—2.47 (2H, br.), 2.98—3.27 (2H, br.), 3.67 (1H, t, J=6.3 Hz), 3.77 (3H, s, Me).

Reactions of 1a with Sulfur in the Presence of Diene. To a solution of **1a** (1.68 g, 5.0 mmol) and 2,3-dimethyl-1,3-butadiene (2 ml, 20 mmol) in toluene (40 ml) was added elemental sulfur (0.64 g, 20 mmol). After refluxing for 20 h, the resulting mixture was evaporated to give reddish-brown oily crystals. This mixture was extracted with methanol (30 ml×2). The combined extracts were evaporated to give a reddish-brown oil, which was chromatographed over silica gel by elution with hexane-dichloromethane (3 : 1) to give adduct **7a** (0.52 g, 2.8 mmol, 56%). Other reactions were carried out in a similar manner. **8a**; 0.54 g (3.2 mmol, 64%). ^{1}H NMR ($CDCl_3$) (Endo) δ=1.66 (br s, CH_2), 3.65 (s, Me), 3.75 (br s, CH), 4.18 (br, CH), 4.44 (d, CH, J=3.9 Hz), 5.73 (dd,=CH, J=3.3 and 5.1 Hz), 6.49 (dd, =CH, J=3.0 and 5.1 Hz); (Exo) δ=1.84 (br s, CH_2), 3.29 (s, CH), 3.54 (br, CH), 3.86 (s, Me), 4.07 (br, CH), 5.91 (dd, =CH, J=3.2 and 6.2 Hz), 6.36 (dd, =CH, J=3.2 and 4.8 Hz). **7b**; 0.49 g, (2.45 mmol, 49%). ^{1}H NMR ($CDCl_3$) δ=1.27 (t, Me, J=7.5 Hz), 1.74 (s, Me), 2.46 (br, CH_2), 3.06 (br, CH_2), 3.62 (t, CH, J=6.0 Hz), 4.19 (q, CH_2, J=7.5 Hz). **8b**; 0.92 g (4.2 mmol, 84%). ^{1}H NMR ($CDCl_3$) (Endo) δ=1.22 (t, Me, J=7.0 Hz), 1.65 (m, CH_2), 3.75 (br, CH), 4.07 (br s, CH), 4.12 (q, CH_2, J=7.0 Hz), 4.42 (d, CH, J=3.6 Hz), 5.70 (dd, =CH, J=5.4 and 2.6 Hz), 6.45 (dd, =CH, J=3.0 and 5.4 Hz). (Exo) δ=1.25 (t, Me, J=7.2 Hz), 1.77 (m, CH_2), 3.27 (s, CH), 3.50 (br s, CH), 4.08 (br, CH), 4.17 (q, CH_2, J=7.2 Hz), 5.92 (dd, =CH, J=3.2 and 5.4 Hz), 6.33 (dd, =CH, J=2.8 and 5.4 Hz). **7d**; 0.27 g (1.76 mmol, 35%). ^{1}H NMR ($CDCl_3$) δ=1.75 (m, Me), 2.47 (br, CH_2), 3.18 (m, CH_2), 3.73 (t, CH, J=2.5 Hz). **8d**; 0.32 g (2.3 mmol, 46%). ^{1}H NMR ($CDCl_3$) (Endo) δ=1.75 (d, CH_2), 3.74 (br s, CH), 4.20 (br s, CH), 4.23 (d, CH, J=3.4 Hz), 6.03 (dd, =CH), 6.57 (dd, =CH). Minor exo product could not be isolated. **7f**; 0.61 g (3.0 mmol, 60%). ^{1}H NMR ($CDCl_3$) δ=1.71 (s, Me), 2.33—2.67 (br m, CH_2), 2.97 (br s, CH_2), 3.31 (br s, CH_2), 3.94 (dd, CH, J=6.0 and 8.0 Hz), 7.27 (br s, Ar). **8f**; 0.58 g, (3.3 mmol, 66%). ^{1}H NMR ($CDCl_3$) (Endo) δ=1.75 (br s, CH_2), 3.38 (br, CH), 4.12 (br, CH), 4.92 (d, CH, J=3.9 Hz), 5.53 (dd, =CH, J=2.9 and 5.4 Hz), 6.47 (dd, =CH, J=2.8 and 4.8 Hz), 7.22 (s, Ar). Minor exo product could not be isolated.

References

1) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954). For reviews, see J. Emsley and D. Hall, "The Chemistry of Phosphorus," Harper & Row Ltd., London (1976), pp. 274—298; A. W. Johnson, "Ylid Chemistry," Academic Press, New York (1966), pp. 132—147; A. Maercker, "Org. Reactions," ed by R. Adams, John Wiley & Sons, Inc., New York (1965), Vol. 14, Chap. 3.

2) D. B. Denney, J. J. Vill, and M. J. Boskin, *J. Am. Chem. Soc.*, **84**, 3944 (1962); A. Turcant and M. Le Corre, *Tetrahedron Lett.*, **1976**, 1277; W. E. McEwen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 676 (1962); W. E. McEwen A. Blade-Font, and C. A. Vanderwelf, *ibid.*, **84**, 677 (1962).

3) E. J. Corey and J. Kang, *J. Am. Chem. Soc.*, **104**, 4724 (1982).

4) a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919). b) A. Schönberg, K-H Brosowski, and E. Singer, *Chem. Ber.*, **95**, 2144 (1962).

5) K. Okuma, Y. Yamasaki, T. Komiya, Y. Kodera, and H. Ohta, *Chem. Lett.*, **1987**, 357.

6) K. Okuma, J. Sakata, Y. Tachibana, T. Honda, and H. Ohta, *Tetrahedron Lett.*, **28**, 6659 (1987). Recently, Elker and coworkers reported a similar reaction; G. Elker R. Hock, and R. Nolte, *J. Am. Chem. Soc.*, **110**, 624 (1988).

7) S. Tripett, *Proc. Chem. Soc.*, **1963**, 19.

8) H. Tokunaga, K. Akiba, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **45**, 506 (1972).

9) H. Mägerlein and G. Meyer, *Chem. Ber.*, **103**, 2995 (1970).

10) a) C. M. Bladen, I. E. G. Fergguson, G. W. Kirby, A. W. Lochead, and D. C. McDougall, *J. Chem. Soc., Chem. Commun.*, **1983**, 423. b) They also generated **4** by base catalyzed cleavage of *N*-(alkoxycarbonylmethylthio)phthalimides. G. W. Kirby and A. W. Lochead, *J. Chem. Soc., Chem. Commun.*, **1983**, 1325.

11) E. Vedejs and D. A. Perry, *J. Am. Chem. Soc.*, **105**, 1683 (1983); E. Vedejs, D. A. Perry, and R. G. Wilde, *J. Am. Chem. Soc.*, **108**, 2985 (1986); E. Vedejs, T. H. Eberlein, D. J. Mazur, C. K. McClure, D. A. Perry, R. Ruggeri, E. Schwartz, J. S. Stults, D. L. Varie, and S. Wittenberger, *J. Org. Chem.*, **51**, 1556 (1986).

12) G. W. Kirby, A. W. Lochead, and G. N. Sheldrake, *J. Chem. Soc., Chem. Commun.*, **1984**, 922.

13) J. E. Baldwin and R. C. Gerald Lopez, *J. Chem. Soc., Chem. Commun.*, **1982**, 1029; *Tetrahedron*, **39**, 1487 (1983); E. Block and S. Ahmad, *J. Am. Chem. Soc.*, **106**, 8295 (1984).

14) G. A. Krafft and P. T. Meinke, *Tetrahedron Lett.*, **26**, 1947 (1985).

15) M. Segi, T. Nakajima, S. Suga, S. Murai, I. Ryu, A. Ogawa, and N. Sonoda, *J. Am. Chem. Soc.*, **110**, 1976 (1988).

16) R. Okazaki, A. Ishii, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1982**, 1187; R. Okazaki, A. Ishii, and N. Inamoto, *J. Am. Chem. Soc.*, **109**, 279 (1987).

17) J. M. Stewart, *J. Org. Chem.*, **28**, 596 (1963); F. K. Lautenschlaeger and N. V. Schwartz, *ibid.*, **34**, 3991 (1969).