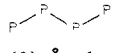
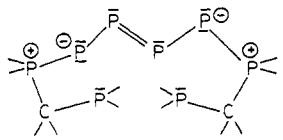
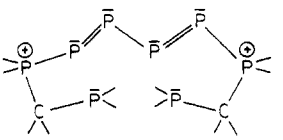
of the structure revealed that a novel ligand $Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2$, resulting from the opening of the P_4 molecule by the attack of two dppm ligands, was formed. Figure 1 shows a perspective view of the complex cation, and Table I reports selected bond distances and angles.

The metal atom has a very distorted octahedral geometry in which the new ligand coordinates through all the phosphorus atoms of the P_4 fragment and two of the four phosphorus atoms belonging to the dppm moieties. Two phosphorus atoms of the dppm remain uncoordinated. Due to the steric requirements of the P_4 fragment which acts as a η^4 ligand, there are significant distortions from octahedral geometry as shown by the values of the axial angles (130.3 (1)°, 149.9 (1)°, 152.7 (1)°). The Co–P bond lengths, involving the phosphorus atoms of the zigzag fragment, have comparable values ranging from 2.281 (2) to 2.305 (2) Å, and, as previously found for *cyclo*-triphosphorus derivatives,[8] are larger than those (2.196 (2) and 2.203 (2) Å) involving the terminal tertiary phosphorus atoms. Of the P–P bond distances within the  chain, the central bond is somewhat larger, 2.197 (3) Å, than the external ones, 2.171 (3) and 2.173 (3) Å. The latter values are significantly larger than those reported for the covalent P=P double bond in noncoordinated bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (2.034 (2) Å)[9] but are somewhat shorter than the values of 2.21 and 2.217 (6) Å, respectively, found in the P_4[10] and $(PhP)_5$[11] molecules, containing covalent P–P single bonds. Although the overall electronic structure must be considered as essentially delocalized, considering that a lengthening of the multiple bonds always occurs upon coordination,[12] we can still assign a partial double bond character to the external P–P bonds of the P_4 chain.

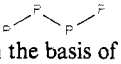
From an electron count point of view, the central atom can reach an 18 outer electron configuration by considering the ligand as either uncharged, $10e^-$ donor (cobalt(I)) (I), or bipositive, $8e^-$ donor (cobalt(−I)) (II).[13] The different P–P bond distances,



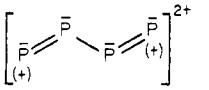
I



II

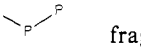
together with the practically identical values of the Co–P distances, seem to be in agreement with the formal resonance structure II. Thus the complex cation may be described as a cobalt(−I) species having a pesudotetrahedral coordination sphere which would involve two double P=P bonds and two ligating phosphines. It is noteworthy that the value of the sole P–Co–P unconstrainted angle, P_1–Co–P_8, is 109.8 (1)°. This approach is further supported by an X-ray structure determination of the $Zr(\eta^5\text{-}C_5H_5)_2$(*s-trans*-PhCH=CH—CH=CHPh) complex,[14] where the diphenylbutadiene exhibits a ligating mode fully comparable to that of the  fragment in the title compound.

On the basis of the structural results presented here we assume that the reaction involves an oxidation of the P_4 molecule to the species III which is then nucleophilically attacked by the dppm



III

phosphorus atoms at the positively charged phosphorus sites of this tetraphosphorus chain.

Preliminary results of the studies on reactivity of this compound can be summarized as follows: (i) the phosphorus atoms of the  fragment are coordinatively unsaturated, the present complex reacting with $W(CO)_6$ to form the derivative $[Co(PhPCH_2PPh_2PPPPPh_2PCH_2PPh_2)W(CO)_5]BPh_4$,[15] and (ii) the complex can be used instead of white phosphorus to obtain *cyclo*-P_3 derivatives.

Registry No. dppm, 2071-20-7; $[Co(Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2)]BF_4$, 90149-67-0; $Co(BF_4)_2$, 26490-63-1; $W(CO)_6$, 14040-11-0; phosphorus, 7723-14-0.

Supplementary Material Available: Listing of observed and calculated structure factors and tables of positional and thermal parameters (30 pages). Ordering information is given on any current masthead page.

(7) Space group $P2_1/n$, a = 19.071 (7) Å, b = 26.712 (9) Å, c = 9.709 (4) Å, β = 93.92 (5)°, Z = 4, V = 4934.4 Å^3, d_c = 1.397 g cm^{-3}. Intensity data were collected on a Philips PW 1100 automatic diffractometer by using the ω–2θ scan technique and monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and, after correction for absorption, refined by full-matrix least-squares using isotropic thermal parameters for the carbon atoms and anisotropic for the heavier ones. The phenyl rings were treated as rigid groups and the hydrogen atoms were introduced in calculated positions but not refined. The final values of the R and R_w factors for 4703 reflections having $I \geq 3\sigma(I)$ are 0.063 and 0.064, respectively.

(8) Di Vaira, M.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330.

(9) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirutsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(10) "Interatomic Distances" *Spec. Publ. Chem. Soc.* **1965**, *No. 18*.

(11) Daly, J. J. *J. Chem. Soc.* **1964**, 6147.

(12) Chatt, J.; Hitchcoock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

(13) Other representations, involving larger charge separations, are evidently unrealistic.

(14) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191.

(15) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A., to be published.

A Chiral Primary Alcohol Equivalent: Silyl-Assisted Asymmetric Induction in the Ester Enolate Claisen Rearrangement[1]

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Received February 13, 1984

In an earlier publication[2] from these laboratories, a scheme for the total synthesis of the prostanoids was presented, and the construction of a racemic derivative of PGA_1 was delineated. This work was an initial example of the power of the ester enolate Claisen rearrangement for the convergent synthesis of complex molecules. The observation[2] that ester enolate geometry could be controlled by choice of reaction conditions led to the use of this Claisen variant for selective production of diastereomeric disubstituted γ,δ-unsaturated acids. When the allylic system is enantiomerically pure, the use of this feature for stereochemical control in the synthesis of acyclic systems with large numbers of contiguous asymmetric centers has led to the construction of ionophores,[3] macrolides,[4] terepenoids,[5] and other natural products.[6]

(1) Contribution No. 6980. Grateful acknowledgement for the support of this investigation through National Science Foundation Grant CHE-78-21066. No reprints available.

(2) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

(3) (a) Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 1155. (b) Ireland, R. E.; Courtney, L.; Fitzsimmons, B. J. *J. Org. Chem.* **1983**, *48*, 5186. (c) Martinez, G. R.; Grieco, P. A.; Williams, E.; Kanai, K.; Srinivasan, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 1436.

(4) (a) Ireland, R. E.: Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479. For synthesis, see: Ireland, R. E.; Daub, J. P.; Mandel, G. S.; Mandel, N. S. *Ibid.* **1983**, *48*, 1312.

(5) Danishefsky, S.; Tsuzuk, K. *J. Am. Chem. Soc.* **1980**, *102*, 6891.

(6) (a) Bartlett, P. A.; Barstow, J. F. *J. Org. Chem.* **1982**, *47*, 3933. (b) Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Ibid.* **1982**, *47*, 3941. (c) Ireland, R. E.; Wuts, P. G. M.; Ernst, B. *J. Am. Chem. Soc.* **1981**, *103*, 3205.

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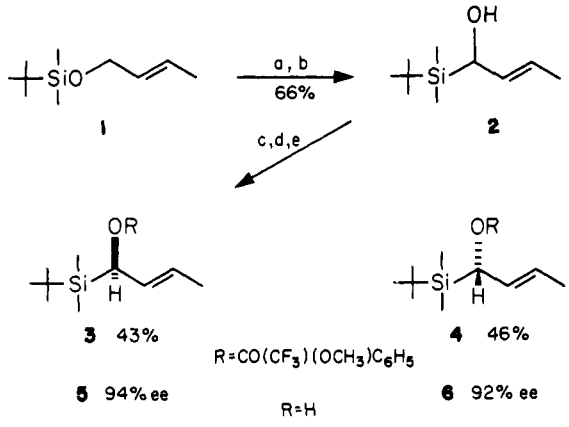
Scheme I. Synthesis of (*R*)- and (*S*)-1-(*tert*-Butyldimethylsilyl)-*trans*-2-butene-1-ols (**5** and **6**)[a]



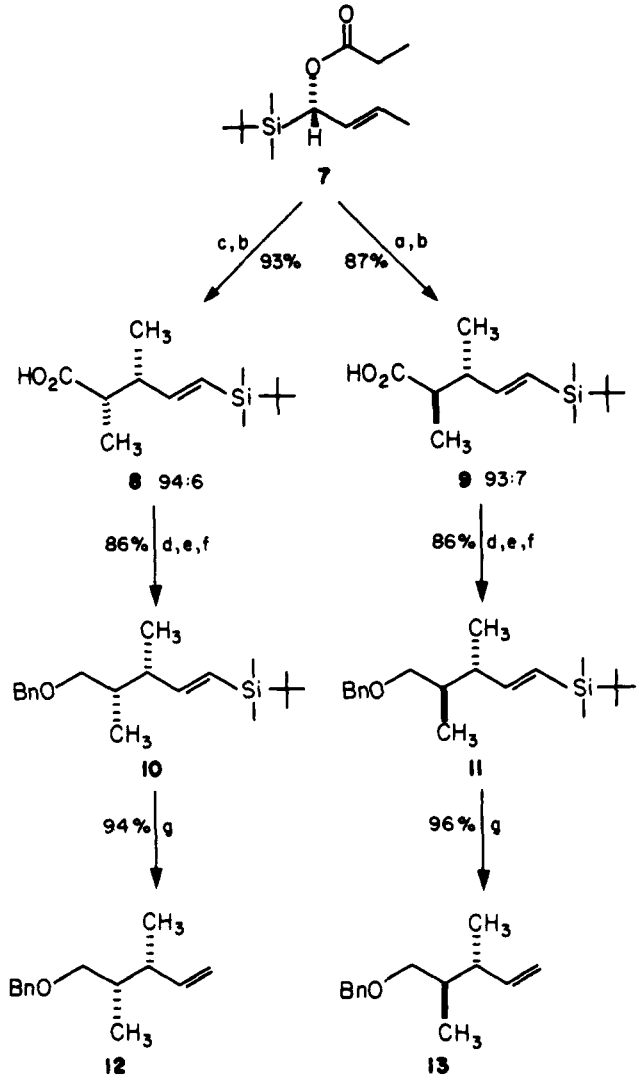
[a] a] 1.5 eq. sec-BuLi, TMEDA, THF, −45°C, 30 min b] CH_3CO_2H, THF, −78°C c] (−)-$C_5H_6(CF_3)(OCH_3)COCl$, CH_2Cl_2, CCl_4, DMAP, pyr., 0°C → RT, 2.5 hr d] LAH, Et_2O, THF, 0°C, 1 hr e] NaOH, $NaBH_4$, MeOH, R.T. 18 hr

Inherent in this process, however, is the requirement that the allylic system be derived from an *Enantiomerically pure secondary or tertiary alcohol*—i.e., primary allylic alcohols, such as that used in the prostanoid work,[2] can only lead to *racemic* diastereoisomeric products. Therefore, to take the fullest advantage of the stereochemical control that is possible in the Claisen rearrangement, there is a necessity for a *chiral primary alcohol equivalent*. Such methodology requires the generation of a "temporary" chiral secondary allylic alcohol, the rearrangement product of which can be converted to the system that would have resulted from the corresponding achiral primary allylic alcohol. An example of such a chiral primary alcohol equivalent is the α-silylcrotyl alcohol **2**, the synthesis and resolution of which is outlined in Scheme I.

Brook[7] rearrangement of *tert*-butyldimethylsilyl crotyl ether (**1**) under the conditions of Still[8] afforded racemic α-silyl alcohol **2** in 66% yield. Resolution of this racemic mixture was accomplished through formation of the diastereoisomeric MTPA[9,10] esters. The esters **3** and **4**, separable by medium-pressure liquid chromatography, were obtained in 43% and 46% yield, respectively. The ^{19}F NMR of these two esters confirmed that complete diastereoisomeric separation had occurred.

The conditions necessary for removal of the MTPA group were found to be different for each diastereomer, and ultimate analysis through reformation of the MTPA ester indicates a slight amount of racemization had occurred in one of these two procedures. For ester **3**, simple LAH reduction afforded the (*R*)-α-silyl alcohol **5**[11,12] in quantitative yield with a 94% enantiomeric excess (^{19}F NMR). In the case of ester **4**, the LAH reduction proceeded only to the hemiacetal stage. Subsequent treatment of this hemiacetal with $NaBH_4$ in basic methanol at room temperature for 18 h was required to remove completely the MTPA group. The (*S*)-α-silyl alcohol **6**[11,12] was obtained in 92% overall yield with a 92% enantiomeric excess. The stability of this *C*-silyl alcohol toward these basic conditions is rather remarkable in view of the reported[13] C → O migration of silicon. The alcohols (*R*)-**5** and (*S*)-**6** were found to be slightly unstable toward air oxidation but were quite stable as their propionate esters.

Scheme II. Ester Enolate Claisen Rearrangement with (*S*)-1-(*tert*-Butyldimethylsilyl)-*trans*-2-buten-1-yl Propionate (**7**)[a]



[a] a] LDA, THF, −78°C b] TBSCl, HMPA, −78°C → RT, 14 hr c] LHMDS, THF, −78°C d] CH_2N_2, Et_2O e] LAH, THF Et_2O, 0°C f] BnBr, KH, THF, 0°C → RT, 1 hr g] 50% HBF_4, CH_3CN, 55°C, 1.5 hr

The ester enolate Claisen rearrangement[2] of the propionate (*S*)-**7** and its enantiomer[14] offered the opportunity to test the utility of the α-silyl alcohols (*R*)-**5** and (*S*)-**6** as chiral primary alcohol equivalents, for the products will have two new asymmetric centers of predictable relative stereochemistry. Chirality transfer from the optically active α-silyl alcohols should then result in enantiomerically enriched vinylsilane acids **8** and **9** (Scheme **II**), and removal of the silicon would complete the process.

In the event, conversion of the ester (*S*)-**7** to its respective silyl ketene acetal with LDA/THF and *tert*-butyldimethylsilyl chloride (*t*-BuSiCl), warming for rearrangement and then hydrolysis afforded the acid **9** in the ratio indicated (^1H NMR). On the other hand, when the ester (*S*)-**7** was enolized with lithium hexa-

(7) Brook, A. G.; Bassindale, A. R. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Essay 9, "Molecular Rearrangements of Organosilicon Compounds", and references cited therein.

(8) (a) Still, W. C.; Macdonald, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 5561; (b) *J. Org. Chem.* **1976**, *41*, 3620.

(9) Mosher, H. S.; Dale, J. A.; Dull, D. L. *J. Org. Chem.* **1969**, *34*, 2543.

(10) Mosher, H. S.; Biernbaum, M. S. *J. Org. Chem.* **1971**, *36*, 3168.

(11) The absolute configuration of the silyl alcohols **5** and **6** were determined as follows: The Claisen acid **8** was ozonized according to ref 2 and the resultant diacid was reduced to the diol. The diol had a rotation of −4.5° (*c* 0.8, Et_2O) and was therefore assigned the *S,S* configuration.[12] On the basis of known enolate geometries and transition state,[2] the alcohol **6** was assigned the *S* configuration.

(12) (a) McCasland, G. E.; Proskow, S. J. *J. Am. Chem. Soc.* **1956**, *78*, 5646–5652. (b) Korver, O.; Sjoberg, S. *Tetrahedron* 1975, *31*, 2603–2606. (c) Carnmalm, B. *Chem. Ind.* (*London*) **1956**, 1093.

(13) Colvin, E. W. "Silicon in Organic Synthesis", Butterworth's Monographs in Chemistry, Butterworth: London, 1981.

(14) This sequence of reactions was performed on the enantiomeric *R* propionate as well, although this is not shown in Scheme II.

methyldisilyl azide in THF and then treated in the same manner, the acid **8** resulted. This high stereoselectivity in the enolization step is responsible for the efficiency of the process and has been observed before in these laboratories.[4a]

Conversion of these acids[15] individually to their corresponding benzyl ethers **10** and **11** followed standard procedures and then protiodesilylation of these ethers **10** and **11** was efficiently accomplished in high yield by treatment with aqueous HBF_4 in hot CH_3CN. Other more standard conditions for desilylation (CsF, KF, I_2, and $ArSO_2H$)[16] either failed to react or destroyed the starting material. This is a useful new method for the non-oxygen-assisted desilylation of vinylsilanes.

These results demonstrate the utility of α-silylallylic alcohols as chiral primary alcohol equivalents, and the value of such a concept for the previous prostanoid synthesis[2] is under investigation. In addition to their use in the ester enolate Claisen rearrangement, chiral α-silylallylic alcohols hold great potential as chiral substrates for other synthetic processes (S_N2', Wittig rearrangements, olefin additions, etc.) and selected of these are currently under investigation. In essence, as a result of this work, the α-silyl group can be envisaged as a "chirality inducing grouping".

Supplementary Material Available: Analytical data (IR, NMR, R_f, rotation) on all compounds, elemental analysis on compounds **1-4** and **7-13**, and experimental procedures for compounds **8** and **9** (8 pages). Ordering information is given on any current masthead page.

(15) The fluorboric acid desilation was attempted on the acid **9**, and a 54% yield of the desired product was obtained. Subsequent experiments indicated the remainder of material consisted of the five-membered lactone with the *tert*-butyldimethylsilyl group still attached to the molecule. Under forcing conditions (HBF_4, CH_3CN, °C, 12 h), this lactone gave the desired product. In order to avoid such cyclizations and possible epimerization, the acid was reduced and the resultant alcohol protected as shown.

(16) (a) Utimoto, K.; Kitai, M.; Hitosi, N. *Tetrahedron Lett.* **1975**, *2825*-2828. (b) Buchi, G.; Wuest, H. *Ibid.* **1977**, 4305-4306 and references cited therein.

Novel Synthesis of Acetylenes and Polyenes via Desulfonylation Reaction

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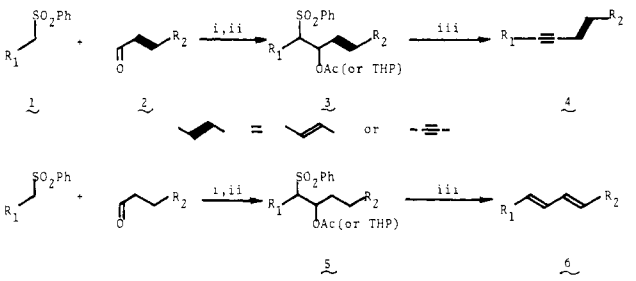
Received March 5, 1984

We wish to communicate a simple and novel synthetic method for a variety of enyne, diyne, and polyene derivatives.[1,2]

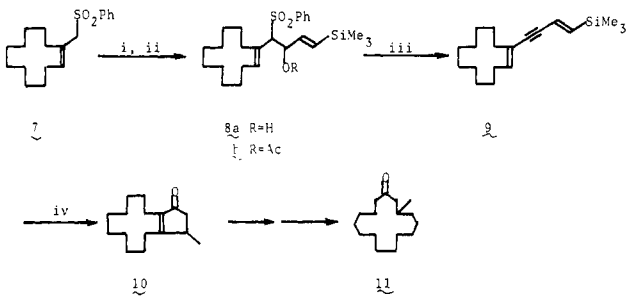
In the course of studies on the synthetic utilization of the desulfonylation reaction,[3] we have previously revealed that phenyl α-methoxyalkyl sulfones are converted into methyl alkenyl ethers on treatment with *t*-BuOK.[3e,4] Now we have found that presence of an acetoxy (OAc) or tetrahydropyranyloxy (OTHP) group at the β-position of the phenylsulfonyl group results in the unique acetylenic or polyenic bond formation, giving rise to a variety of enyne, diyne, and polyene compounds.

Scheme I[a]



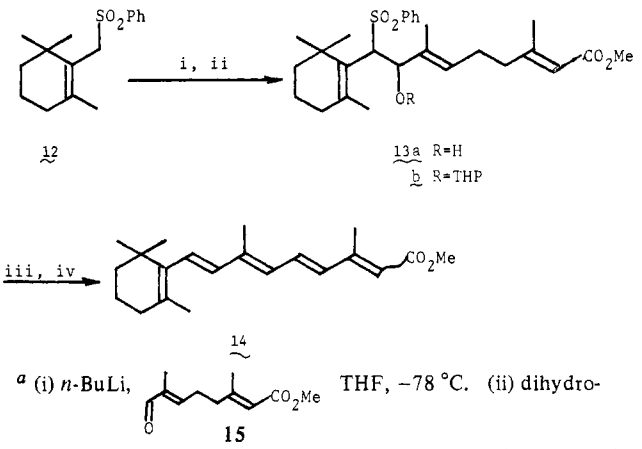
[a] (i) *n*-BuLi, THF, −78 °C. (ii) Ac_2O-Py or dihydropyran, *p*-TsOH. (iii) *t*-BuOK, THF or THF/*t*-BuOH, room temperature/reflux.

Scheme II[a]



[a] (i) *n*-BuLi, $Me_3SiCH{=}CHCHO$, −78 °C, THF. (ii) Ac_2O-Py. (iii) *t*-BuOK, THF, room temperature/reflux. (iv) AcOH-H_2SO_4.

Scheme III[a]



[a] (i) *n*-BuLi, THF, −78 °C. (ii) dihydropyran, *p*-TsOH, CH_2Cl_2. (iii) *t*-BuOK, *t*-BuOH. (iv) CH_2N_2, Et_2O.

As depicted in Scheme I, the procedure is quite simple. One equivalent of a β-acetoxy sulfone or the corresponding tetrahydropyranyl ether **3**, which can be easily prepared from the α-sulfonyl carbanion **1** and an α,β-enal or ynal **2**, and *t*-BuOK (2.5-10 equiv) were stirred in THF or THF/*t*-BuOH (1:1) under the conditions shown in Table I. Extraction of the reaction mixture with hexane-water and usual workup followed by column chromatography (silica gel) yielded the acetylenes **4**. Entries 1-6 in Table I illustrate the versatility of the present method for preparing difficult-to-obtain acetylenic compounds employing readily available starting materials. The broad scope and utility of these acetylenic compounds as synthetic intermediates are apparent from the successful formation of ene-yne, ene-yne-ene, yne-yne, and ene-yne-yne moieties with various functionalities. It should be noted, however, that no acetylenes are obtained from α,β-enals or -ynals with an allylic or properglyic hydrogen in R_2. Formation of acetylenes is also suppressed when alkyl aldehydes are used, except in the case where aldehydes possess no α hydrogens. Polyenes **6** are produced in all of these cases as shown in entries 7-10 in Table I.

(1) For the most recent study of enyne compounds, see: Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383.

(2) For conjugated polyene synthesis, see: (a) Hayashi, T.; Hori, I.; Oishi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2909. (b) Fischetti, W.; Mak, K. T.; Stakem, F. G.; Kim, J.-I.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 948.

(3) (a) Mandai, T.; Yamaguchi, H.; Nishikawa, K.; Kawada, M.; Otera, J. *Tetrahdron Lett.* **1981**, *22*, 763. (b) Mandai, T.; Nishikawa, K.; Yamaguchi, H.; Kawada, M.; Otera, J. *Chem. Lett.* **1981**, 473. (c) Mandai, T.; Iuchi, Y.; Suzuki, K.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1982**, *23*, 4721. (d) Otera, J.; Mandai, T.; Shiba, M.; Saito, T.; Shimohata, K.; Takemori, K.; Kawasaki, Y. *Organometallics* **1983**, *2*, 332. (e) Mandai, T.; Hara, K.; Nakajima, T.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1983**, *24*, 4993.

(4) A few studies of oxidative desulfonylation with *t*-BuOK to give olefinic compounds have been reported: (a) Colter, A. K.; Miller, R. E., Jr. *J. Org. Chem.* **1971**, *36*, 1898. (b) Fuchs, P. L.; Hamann, P. R. *Ibid.* **1983**, *48*, 914.

0002-7863/84/1506-3670$01.50/0