

Carbonyls during the Stoichiometric Hydroformylation.—Solvent, olefin, and reference compound were introduced into the 100-ml flask connected to a gas burette. The flask and the burette were filled with 1 atm of CO and then a solution of $\text{HCo}(\text{CO})_4$ was introduced. After 16 hr of stirring, the flask was cooled with Dry Ice-acetone and N_2 was flushed through until complete elimination of CO took place. The solution was stirred at room temperature and the samples, which were taken after treatment with PPh_3 , were analyzed by glc.

Registry No.— $n\text{-BuCOCo}(\text{CO})_4$, 33520-58-0; $i\text{-BuCOCo}(\text{CO})_4$, 33520-59-1; 1-pentene, 109-67-1.

Acknowledgment.—The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this investigation.

Silicon-Containing Carbanions. I. Synthesis of Vinyl Thioethers and Vinylphosphonates via Silicon-Modified Organolithium Reagents

FRANCIS A. CAREY* AND A. S. COURT

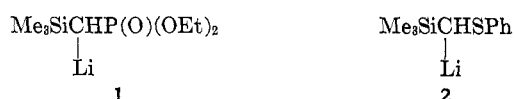
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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Reactions of diethyl 1-lithio-1-trimethylsilylmethylphosphonate (1) and 1-trimethylsilyl-1-phenylthiomethyl-lithium (2) with representative aldehydes and ketones are reported which provide useful routes to diethyl vinylphosphonates (6a-g) and vinyl phenylthioethers (18a-g) by loss of Me_3SiOLi from the presumed intermediate resulting from attack of the organolithium reagent at the carbonyl group. It was found that the exocyclic vinylphosphonate 6e from cyclohexanone and 1 isomerized to the endocyclic isomer 7 under the reaction conditions. The reactions are not highly stereoselective in that 1 and 2 usually give cis-trans mixtures of olefins from aldehydes and unsymmetrical ketones. Methylation and benzylation of 1 are described. Reaction of $\text{Me}_3\text{SiCH}_2\text{-OCH}_3$ resulted in nucleophilic attack at silicon when $n\text{-butyllithium}$ was used and proton abstraction from the methyl group when $tert\text{-butyllithium}$ was used.

A number of silicon-containing ylides¹ and organometallics² have been described in which electron delocalization into silicon 3d orbitals may be important. While the extent of this delocalization remains to be established, the synthetic versatility of carbanions and the expectation of stabilization with modification of chemical reactivity resulting from silicon bonded directly to the carbanionic center suggests the desirability of thorough examination into the reactions of such intermediates.

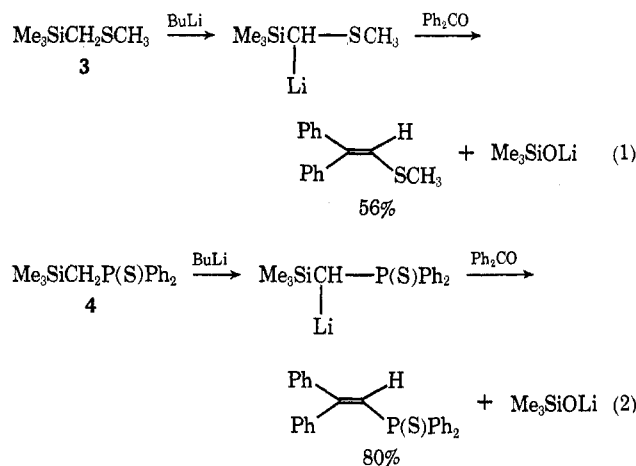
This report describes the generation and some reactions of diethyl 1-lithio-1-trimethylsilylmethylphosphonate (1) and 1-trimethylsilyl-1-phenylthiomethyl-lithium (2).



Peterson³ made the important discoveries that metalation of methylthiomethyltrimethylsilane (3) and (trimethylsilylmethyl)diphenylphosphine sulfide (4) occurred readily using $n\text{-butyllithium}$ and that the resulting lithio reagents reacted with benzophenone to afford olefins resulting from loss of Me_3SiOLi (eq 1 and 2).

The lithio reagent from 3 yielded equal amounts of *cis*- and *trans*-2-phenylvinyl methylthioether (64%) when treated with benzaldehyde.

As will be seen from the results to be described these reactions are very general and provide convenient



routes to a number of interesting hetero-substituted olefins.

Results and Discussion

Synthesis of Diethyl Vinylphosphonates.—Diethyl trimethylsilylmethylphosphonate (5) is conveniently prepared by the Arbusov reaction between chloromethyltrimethylsilane and triethyl phosphite.⁴ Treatment of 5 in tetrahydrofuran with $n\text{-butyllithium}$ in $n\text{-hexane}$ generates the lithio derivative 1, which reacts with aldehydes and ketones to give good yields of substituted diethyl vinylphosphonates (6) according to eq 3. The results are summarized in Table I.

Most of the compounds listed in Table I have previously been prepared by Wysocki and Griffin by the Wadsworth-Emmons procedure employing $\text{CH}_2[\text{P}(\text{O})(\text{OEt})_2]_2$ in $\text{KO-}tert\text{-Bu-THF}$.⁵ The structures of 6a-e were confirmed by comparison of their physical

(1) (a) N. E. Miller, *J. Amer. Chem. Soc.*, **87**, 390 (1965); (b) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965); (c) N. E. Miller and D. R. Mathiason, *ibid.*, **7**, 709 (1968); (d) H. Schmidbaur and W. Malisch, *Chem. Ber.*, **103**, 3448 (1970), and previous papers in this series; (e) D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965); (f) H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

(2) (a) D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967); (b) M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *ibid.*, **24**, 529 (1970); (c) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970).

(3) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).

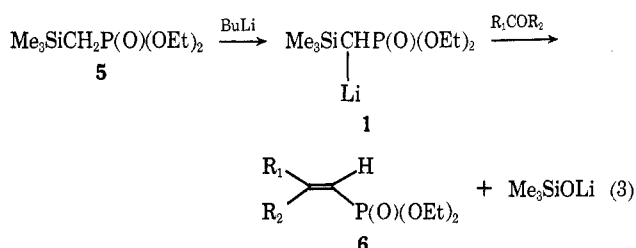
(4) A. R. Gilbert, U. S. Patent 2,768,193 (Oct 23, 1956); *Chem. Abstr.*, **51**, 5816 (1957).

(5) D. C. Wysocki, Ph.D. Thesis, University of Pittsburgh, 1967; C. E. Griffin, adviser. See *Diss. Abstr. B*, **28**, 1437 (1967), for a summary.

TABLE I
 REACTIONS OF 1 WITH ALDEHYDES AND KETONES

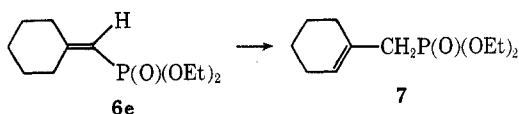
Carbonyl component	Product	R ₁	R ₂	Yield, ^a %
Benzaldehyde	6a	Ph	H	63 ^{b,c}
Benzophenone	6b	Ph	Ph	83 ^c
Fluorenone	6c			42 ^c
Acetone	6d	CH ₃	CH ₃	55 ^c
Cyclohexanone	6e + 7	-(CH ₂) ₅ -		65 ^c
Isobutyraldehyde	6f + 6g	H	(CH ₃) ₂ CH	92 ^d

^a Isolated yields of pure product; not corrected for recovered starting material. ^b Reported by W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961). ^c Reported by D. C. Wysocki, Ph.D. Thesis, University of Pittsburgh, 1967. ^d Cis:trans ratio 2.4:1.

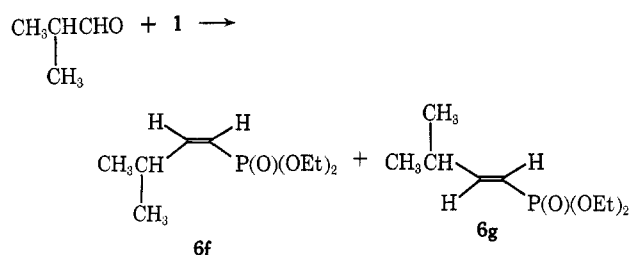


properties, particularly nmr spectra, with those reported by Wysocki.⁵

Several features of these reactions bear mentioning. First, while cyclohexanone reacted normally with 1 it was found that the initial product 6e was unstable under the reaction conditions and was isomerized to the more stable endocyclic double bond isomer 7.⁶ By direct glpc analysis of a reaction mixture it was determined that after 5 min at -67° the ratio of the endocyclic double bond isomer 7 to the exocyclic isomer 6e was 4.5:1 and increased to 17:1 after 88 hr at 25°.



No simple pattern of stereoselective vinylphosphonate formation from 1 and aldehydes is evident, since reaction with benzaldehyde affords diethyl *trans*-2-phenylvinylphosphonate (6a) while reaction with isobutyraldehyde gives a mixture of diethyl *cis*- and *trans*-2-isopropylvinylphosphonate (6f and 6g) in which the cis:trans ratio is 2.4:1.⁷



Assignment of stereochemistry to the isomers 6f and 6g was made from consideration of their nmr spectra at 100 MHz. The signals resulting from the vinyl

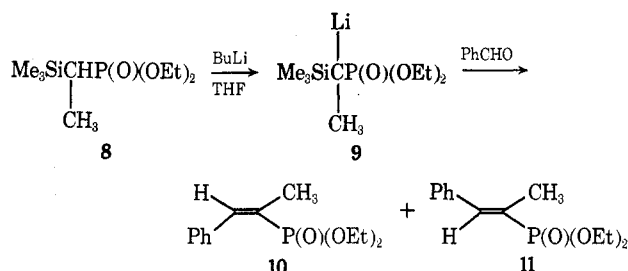
(6) For a discussion of related isomerizations, see F. S. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(7) For a thorough examination of the mechanistic features relating to stereoselectivity of Wittig reactions, see M. Schlosser, *Top. Stereochem.*, **5**, 1 (1969).

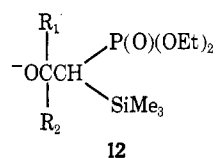
protons in the compound assigned the *cis* geometry appeared as 12 lines which were determined by first-order analysis to result from splitting of the resonance of the vinyl proton at higher field into a doublet of doublets by coupling to the geminal phosphorus nucleus ($J = 20$ Hz) and to the vicinal vinyl proton ($J = 12$ Hz). The resonance of the lower field vinyl proton appeared as a doublet of doublets of doublets because of splitting by the vinyl proton, the proton of the isopropyl group ($J = 10$ Hz) and phosphorus ($J = 52$ Hz). The magnitude of the vicinal phosphorus coupling is consistent with a *trans* orientation of H and P while the vinyl coupling is consistent with *cis* orientation of H and H.^{5,8}

Assignment of the *trans* stereochemistry to the minor isomer follows from the observation that the vicinal vinyl H-H coupling constant was larger (18 Hz) and the vicinal H-P coupling constant smaller (23 Hz) than for the *cis* isomer.

Alkylation of 1 with methyl iodide was carried out in 86% yield to give diethyl 1-trimethylsilylethylphosphonate (8). The derived anion (9) was formed readily from the reaction of 8 with *n*-butyllithium in tetrahydrofuran as evidenced by quantitative incorporation of deuterium when D₂O was added, but was much less reactive than 1 toward benzaldehyde. The vinylphosphonate which resulted from 9 on reaction with benzaldehyde was isolated in 38% yield on distillation and was determined to be an 8:1 mixture of *cis* and *trans* isomers 10⁵ (major) and 11⁵ (minor) by glpc.



The formation of vinylphosphonates by loss of Me₃SiOLi from intermediate 12 rather than formation of vinylsilanes by loss of (EtO)₂P(O)(OLi) is consistent with current thinking regarding reactions of phosphonate carbanions.⁹ The β-hydroxyphosphonates re-

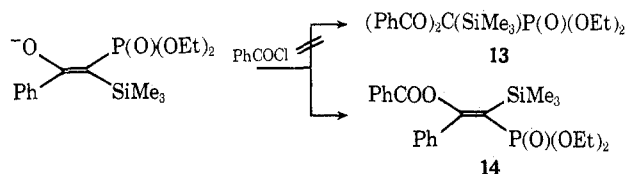


sulting from addition of phosphonate carbanions to carbonyls lose diethyl phosphate only when the carbon atom bearing phosphorus carries an additional electron-withdrawing substituent, while base-catalyzed elimination of β-hydroxysilanes occurs readily.^{2c,3}

(8) (a) C. Benezra and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1825 (1966); (b) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963); (c) W. M. Daniewski, M. Gordon, and C. E. Griffin, *J. Org. Chem.*, **31**, 2083 (1966); T. M. Timofeeva, B. I. Ionin, Y. L. Kleiman, N. V. Morokovin, and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 1208 (1968).

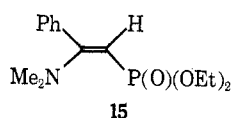
(9) E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966); (b) A. N. Pudovik and G. E. Yastrebova, *Russ. Chem. Rev.*, **39**, 562 (1970).

Reaction of **1** with several different benzoylating agents (benzoyl chloride, methyl benzoate, and *N,N*-dimethylbenzamide) resulted in the novel finding that a different product was obtained from each reagent. When benzoyl chloride was used there was isolated a stable crystalline compound, mp 94–95°, which analyzed correctly for $C_{22}H_{29}SiO_5P$ corresponding to a yield of 58% for reaction of 1 equiv of **1** with 2 equiv of benzoyl chloride. The product was more stable than expected for structure **13** to be correct¹⁰ and examination of its ir spectrum removed **13** from consideration. An intense absorption at 1750 cm^{-1} is too low in energy to arise from the carbonyl stretching of an aromatic ketone, but is consistent with that of a benzoyl ester and leads to the assignment of **14** for the compound.

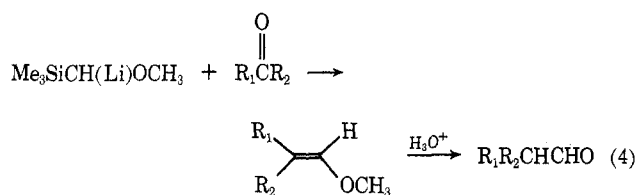


Formation of **14** by O-acylation of the initial intermediate is reasonable, since C-acylation is seriously hindered by the Me_3Si and $\text{P}(\text{O})(\text{OEt})_2$ substituents.¹¹

Monobenzoylation of **1** was effected by using methyl benzoate to afford a 56% yield of $\text{PhCOCH}_2\text{P}(\text{O})(\text{OEt})_2$ in what constitutes a useful alternative to the Arbusov reaction for the synthesis of β -ketophosphonates. This product may result from hydrolytic cleavage of $\text{PhCOCH}(\text{SiMe}_3)\text{P}(\text{O})(\text{OEt})_2$ during isolation. Reaction of **1** with *N,N*-dimethylbenzamide was less effective but interesting in that the unusual enamine **15** was isolated directly in 24% yield.



Synthesis of Vinyl Phenylthioethers.—The reagent $\text{Me}_3\text{SiCH}(\text{Li})\text{OCH}_3$ would be useful for extension of carbonyl chains *via* enol ethers according to eq 4.



Attempts to generate the required organolithium derivative by proton abstraction from $\text{Me}_3\text{SiCH}_2\text{OCH}_3$ (**16**)¹² were not successful. When *n*-butyllithium was used, **16** was cleaved to yield *n*-butyltrimethylsilane as the only identifiable product after quenching with D_2O .¹³ To minimize nucleophilic attack at silicon,

(10) C. R. Hauser and C. R. Hance, *J. Amer. Chem. Soc.*, **74**, 5091 (1952); W. K. Musker and G. L. Larson, *J. Organometal. Chem.*, **6**, 827 (1966).

(11) This reaction is similar to the O benzoylation of $\text{Me}_3\text{S}^+\text{CH}=\text{C}(\text{O}^-)\text{Ph}$ with benzoyl chloride reported by A. W. Johnson and R. T. Amel, *Tetrahedron Lett.*, 819 (1966). We thank a referee for bringing this reference to our attention.

(12) J. L. Speier, *J. Amer. Chem. Soc.*, **70**, 4142 (1948).

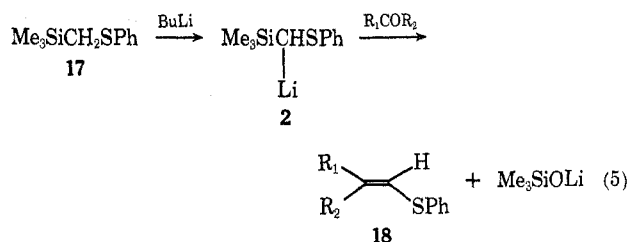
(13) A referee has pointed out that this cleavage is analogous to that which occurs in Schollkopf's procedure for preparation of methoxymethylithium.



See U. Schollkopf in E. Muller, Ed., "Methoden der Organischen Chemie," Vol. 13, Georg Thieme Verlag, Stuttgart, 1970, pp 87, 253.

tert-butyllithium was used as the base and was observed to abstract a proton from the Si-methyl group to give $\text{CH}_3\text{OCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Li}$ rather than $\text{CH}_3\text{OCH}(\text{Li})\text{Si}(\text{CH}_3)_3$. In this experiment methyl iodide was added to the organometallic and $\text{CH}_3\text{OCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ was isolated in 50% yield.

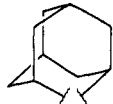
Extension of the carbonyl chain could also be accomplished by way of vinyl thioether intermediates which, however, suffer from the disadvantage of being more difficult to hydrolyze than enol ethers.^{14,15} Vinyl phenylthioethers (**18**) were readily prepared from a variety of aldehydes and ketones by reaction with **2** in tetrahydrofuran at 0–25° (eq 5). In contrast to the oxygen analog, **2** was generated quantitatively from phenylthiomethyltrimethylsilane (**17**)¹⁶ by metalation



with *n*-butyllithium at 0° at the methylene group without any evidence of cleavage.

The reactions of **2** with several aldehydes and ketones are summarized in Table II. The ease with which

TABLE II
REACTIONS OF **2** WITH ALDEHYDES AND KETONES

Carbonyl component	Product	R ₁	R ₂	Yield, ^a %
Benzaldehyde	18a	Ph	H	71 ^b
Benzophenone	18b	Ph	Ph	82 ^c
Acetone	18c	CH ₃	CH ₃	50
Cyclohexanone	18d	-(CH ₂) ₆ -		65
Pinacolone	18e	<i>tert</i> -Bu	CH ₃	55 ^d
Cyclohexenone	18f	-CH=CH(CH ₂) ₃ -		75
Adamantanone	18g			80

^a Isolated yields of product; not corrected for recovered starting material. The yield of **18c** is approximate since separation from **17** by distillation was difficult. ^b The cis:trans ratio was 2:1; see A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964), for nmr spectra of isomers. ^c E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966); H. K. Reimlinger, *Chem. Ind. (London)*, 1682 (1966). ^d Isomer ratio 3:2.

these reactions are carried out (see Experimental Section), the generally good yields obtained even with hindered ketones (55% from pinacolone), and 1,2 addition to an α,β -unsaturated ketone (cyclohexenone) make this method a highly desirable one for the synthesis of vinyl thioethers and as part of a general method for converting $\text{R}_1\text{R}_2\text{CO}$ to $\text{R}_1\text{R}_2\text{CHCHO}$. Alternative and analogous methods for preparing vinyl thioethers employing sulfur-substituted phosphonate

(14) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

(15) There has been much recent progress in the improvement of methods for hydrolysis of vinyl thioethers. See E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971); B. W. Erickson, Ph.D. Thesis, Harvard, 1970; T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, 3787 (1968); H. J. Bestmann and J. Angerer, *ibid.*, 3665 (1969).

(16) G. D. Cooper, *J. Amer. Chem. Soc.*, **76**, 3713 (1954).

carbanions have been reported,¹⁷ but these anions appear to be less reactive than 2 and, in some cases, tend to decompose under the reaction conditions.

Experimental Section

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in CDCl_3 and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr discs for solids and pressed films for liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV.

Microanalyses were performed by Alfred Bernhardt, Engelkirchen, West Germany.

Gas chromatographic analysis of product mixtures and purification of analytical samples were carried out on a Varian Aerograph A-90P3 instrument equipped with a thermal conductivity detector and disc integrator.

All reactions were carried out in an atmosphere of dry nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride. *n*-Butyllithium in *n*-hexane was purchased from Alfa Inorganics.

General Procedure for Synthesis of Diethyl Vinylphosphonates (6).—*n*-Butyllithium (25 mmol as a 23% solution in hexane) was added to a solution of 5.6 g (25 mmol) of diethyl trimethylsilylmethylphosphonate (6) in 10 ml of tetrahydrofuran and allowed to stir for 1.5 hr. To the yellow solution of 1 was added 25 mmol of the carbonyl compound and after 2 hr at 25° brine (25 ml) was added. The layers were separated, and the aqueous phase was extracted with ether, dried (MgSO_4), and evaporated. Distillation or recrystallization of the residue afforded the purified product. The nmr, ir, and uv spectra of 7a-c, 10, and 11 have been thoroughly discussed by Wysocki and Griffin. The spectral and analytical data for the previously unreported diethyl vinylphosphonates and related compounds follow.

Diethyl 1-Cyclohexenylmethylphosphonate (7).—The endocyclic olefin 7 was separated from its exocyclic isomer 6e by preparative glpc on a 10-ft 20% Carbowax 20M on firebrick column: retention time 21 (7), 26 min (6e); nmr (CDCl_3) δ 1.32 (t, 6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.6 (m, 4, ring CH_2), 2.1 (m, 4, allylic CH_2), 2.52 (d, 2, $J = 22$ Hz, CH_2P), 4.11 (q, 4, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{OP}$), 5.6 (m, 1, $\text{C}=\text{CH}$).

Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_3\text{P}$: C, 56.88; H, 9.11; P, 13.34. Found: C, 56.78; H, 9.28; P, 13.07.

Diethyl *cis*-3-Methyl-1-butenylphosphonate (6f).—The *cis* and *trans* products from reaction of isobutyraldehyde with 1 were separated by preparative glpc on a Carbowax column at 150°. The major product was eluted first and identified as 6f (*cis*) by its nmr spectrum (100 MHz) in CDCl_3 : δ 1.10 (d, 6, $J = 7$ Hz, CH_3CH), 1.4 (t, 6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 3.32 [m, 1, $(\text{CH}_2)_2\text{CH}$], 4.10 (q, 4, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 5.4 [d, d, 1, $J_{\text{HH}} = 12$, $J_{\text{HP}} = 20$ Hz, $\text{HC}(\text{=})\text{P}$], 6.2 [d, d, d, 1, $J_{\text{HH}} = 12$, $J_{\text{HP}} = 10$, $J_{\text{HP}} = 52$ Hz, $(\text{CH}_2)_2\text{CHC}=\text{CH}$].

Anal. Calcd for $\text{C}_9\text{H}_{19}\text{O}_3\text{P}$: C, 52.42; H, 9.28; P, 15.02. Found: C, 52.17; H, 9.10; P, 14.86.

Diethyl *trans*-3-Methyl-1-butenylphosphonate (6g).—The minor isomer isolated from the reaction described above was identified as 6g (*trans*) by its nmr spectrum (100 MHz, CDCl_3): δ 1.10 (d, 6, $J = 7$ Hz, CH_3CH), 1.36 t, [6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$], 4.10 (q, 4, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 5.58 [t, 1, $J_{\text{HH}} \cong J_{\text{HP}} \cong 18$ Hz, $\text{HC}(\text{=})\text{P}$], 6.8 (d, d, d, 1, $J_{\text{HH}} = 18$, $J_{\text{HH}} = 7$, $J_{\text{HP}} = 23$ Hz, $\text{HC}=\text{CP}$).

Anal. Calcd for $\text{C}_9\text{H}_{19}\text{O}_3\text{P}$: C, 52.42; H, 9.28; P, 15.02. Found: C, 52.43; H, 9.39; P, 14.94.

Methylation of 1-Lithio-1-trimethylsilylmethylphosphonate.—Methyl iodide (3.55 g, 25 mmol) was added slowly with cooling to a solution of 25 mmol of 1 in 10 ml of THF. The reaction mixture was worked up as previously described after 5.5 hr and the crude product was distilled to yield 5.1 g (86%) of diethyl 1-trimethylsilylethylphosphonate (8), bp 72–75° (1 mm).

Anal. Calcd for $\text{C}_9\text{H}_{23}\text{SiO}_3\text{P}$: C, 39.48; H, 8.61; P, 20.36. Found: C, 39.31; H, 8.74; P, 20.26.

A number of attempts to methylate 5 using sodium hydride in a variety of solvents did not yield useful results owing to formation of mixtures of di-, mono-, and nonmethylated products.

Hydrogen-Deuterium Exchange of 8.—To a solution of 4.1 g (18.5 mmol) of 8 in 10 ml of THF was added 5.1 g of butyllithium (23% in hexane). After 1 hr, D_2O was added, the solution was extracted with ether, and the product was distilled, yielding 3.3 g (80%) of 8 completely deuterated at the α position. This was evident from the nmr spectrum (CDCl_3): δ 0.15 [s, 9, $(\text{CH}_3)_3\text{Si}$], 1.21 (d, 3, $J_{\text{HP}} = 23$ Hz, CH_3CDP), 1.31 (t, 6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 4.10 (q, 4, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$). The presence of the molecular ion peak at m/e 239 in the mass spectrum confirmed deuterium incorporation.

Benzoylation of 1-Lithio-1-trimethylsilylmethylphosphonate.—To a solution of 25 mmol of 1 in tetrahydrofuran was added 3.5 g (25 mmol) of benzoyl chloride while cooling in ice. After 1 hr at 25° the reaction mixture was worked up according to the general procedure to yield 8.3 g of crude product which partially crystallized on standing. Recrystallization from ethanol gave 3.0 g (58%) of diethyl 1-trimethylsilyl-2-phenyl-2-benzoyloxyvinylphosphonate (14): mp 94–95°; ir (KBr) 1750, 1250, 1060, 1030, 970, 960, 930, 860, 805, 770, 710 cm^{-1} ; nmr (CDCl_3) δ 0.10 (s, 9, CH_3Si), 1.25 (t, 6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 4.10 (quintet, 4, $J = 7$ Hz, CH_3OP), 7.5 (m, 4, aromatic), 8.15 (m, 1, aromatic).

Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{SiO}_5\text{P}$: C, 61.09; H, 6.76; P, 7.16. Found: C, 61.28; H, 6.85; P, 7.12.

Reaction of 1 with Methyl Benzoate.—The preceding experiment was repeated employing methyl benzoate to afford, after distillation at 165° (1.8 mm), 3.6 g (56%) of diethyl benzoylmethylphosphonate, which was identical with authentic material prepared by reaction of triethyl phosphite with phenacyl bromide.

Reaction of 1 with *N,N*-Dimethylbenzamide.—Use of 25 mmol of *N,N*-dimethylbenzamide in a similar experiment yielded 1.68 g (24%) of diethyl 2-phenyl-2-dimethylaminovinylphosphonate: bp 163° (1 mm); ir (CCl_4) 3000, 1600, 1230, 1060, 1030, 950, 860, 700 cm^{-1} ; nmr (CDCl_3) δ 1.10 (t, 6, $J = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 2.78 (s, 6, CH_3N), 3.80 (quintet, 4, $J = 7$ Hz, CH_2OP), 4.21 (d, 1, $J = 10$ Hz, CCH), 7.41 (s, 5, aromatic).

Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3\text{P}$: C, 59.35; H, 7.83; N, 10.93; P, 4.94. Found: C, 59.20; H, 7.93; N, 11.08; P, 4.88.

Substantial amounts (19 mmol) of unreacted *N,N*-dimethylbenzamide were recovered.

Metalation of Methoxymethyltrimethylsilane (16) with *tert*-Butyllithium.—*tert*-Butyllithium (20 mmol) in pentane was added to a solution of 2.4 g (20 mmol) of 16 in 10 ml of tetrahydrofuran. After stirring for 30 min at 25°, the solution was cooled in an ice bath while 2.84 g (20 mmol) of methyl iodide was added. The ice bath was removed and the solution was allowed to stand for 2 hr at 25°, water was added, and the mixture was extracted thoroughly with ether. The ether solution was dried (MgSO_4) and distilled to yield 1.4 g (54%) of methoxymethylethyldimethylsilane: bp 109°; nmr (CDCl_3) δ 0.05 [s, 6, $(\text{CH}_3)_2\text{Si}$], 0.60 (2, CCH_2), 0.9 (3, CH_3C) (both multiplets distorted because $\nu/J \cong 3$), 3.1 (s, 2, SiCH_2O), 3.35 (s, 3, CH_3O).

Anal. Calcd for $\text{C}_8\text{H}_{18}\text{OSi}$: C, 54.48; H, 12.19; Si, 21.23. Found: C, 54.19; H, 12.01; Si, 21.23.

General Procedure for Synthesis of Vinyl Phenylthioethers (18).—To a solution of 3.92 g (20 mmol) of 17 in 10 ml of tetrahydrofuran at 0° was added 20 mmol of *n*-butyllithium in hexane. The resulting yellow solution was stirred for 15 min at 0°, a solution of 20 mmol of the carbonyl compound in 5 ml of tetrahydrofuran was added, and the reaction mixture was stirred for 15 min at 0°, then 15 min at 25°. Brine (15 ml) was added and the product was extracted with two 10-ml portions of ether, dried (MgSO_4), filtered, and evaporated to yield the crude product.

1-Phenylthio-2-phenylethylene (18a).—The crude product from 2.12 g of benzaldehyde and 2 was purified by distillation, bp 154° (0.8 mm), to yield 3.0 g (71%) of 18a as a mixture of *cis* and *trans* isomers along with 0.9 g (23%) of recovered 17. The *cis*:*trans* ratio was 2:1 as determined from the nmr spectrum of the mixture (see footnote b, Table II).

1-Phenylthio-2,2-diphenylethylene (18b).—Recrystallization of the crude residue from reaction of 2 with benzophenone from hexane gave 18b (82%), mp 66–68°. A further recrystallization from hexane raised the melting point to 71–73° [reported 71.5–73° (footnote c, Table II)].

1-Phenylthio-2-methyl-1-propene (18c).—Distillation of the crude product from reaction of acetone with 2 gave as a first fraction 1.5 g, bp 81° (1 mm), of product contaminated with ca. 20% of 17. Subsequent fractions were composed of 18c and 17

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in varying amounts. The analytical sample was obtained by preparative glpc on a 10-ft 20% SE-30 on Chromosorb column at 165°: nmr (CDCl₃) δ 1.90 (s, 6, CH₂), 5.92 (s, 1, =CH), 7.3 (s, 5, PhS).

Anal. Calcd for C₁₀H₁₂S: C, 73.11; H, 7.36. Found: C, 72.99; H, 7.31.

Phenylthiomethylenecyclohexane (18d).—Distillation of the residue afforded 2.62 g (65%) of 18d: bp 133° (1.1 mm); nmr (CDCl₃) δ 1.58 (br s, 6, CH₂), 2.3 (m, 4, allylic CH₂), 5.90 (s, 1, C=CH), 7.30 (s, 5, Ph).

Anal. Calcd for C₁₃H₁₆S: C, 76.41; H, 7.89. Found: C, 76.22; H, 7.74.

1-Phenylthio-2,3,3-trimethyl-1-butene (18e).—Fractional distillation of the crude product from reaction of pinacolone with 2 resulted in the recovery of 1.7 g (45%) of 17 and isolation of 2.1 g (55%) of 18e, bp 110° (1.2 mm), as a mixture of *cis* and *trans* isomers. The mixture was ca. 3:2 by nmr analysis of the crude product. No assignment is being made at present as to which isomer is the major component and which is the minor component. Major component: nmr (CDCl₃) δ 1.28 (s, 9, *tert*-Bu), 1.85 (s, 3, CH₃), 5.90 (m, 1, C=CH), 7.28 (m, 5, SPh). Minor component: nmr (CDCl₃) δ 1.13 (s, 9, *tert*-Bu), 1.82 (s, 3, CH₃), 6.03 (s, 1, C=CH), 7.28 (m, 5, SPh).

A sample of the mixture was purified by preparative glpc on Carbowax at 190°.

Anal. Calcd for C₁₃H₁₈S: C, 75.66; H, 8.79. Found: C, 75.51; H, 8.64.

3-Phenylthiomethylene-1-cyclohexene (18f).—Distillation of the crude product afforded 3.0 g (75%) of 18f as a mixture of *cis* and *trans* isomers: bp 131° (0.55 mm); nmr (CDCl₃) δ 1.75

(m, 2, CH₂), 2–2.7 (m, 4, allylic CH₂), 5.8–6.8 (m, 3, C=CH), 7.3 (m, 5, SPh).

The analytical sample of the mixture was obtained by preparative glpc on Carbowax at 190°.

Anal. Calcd for C₁₃H₁₄S: C, 77.17; H, 6.97. Found: C, 76.95; H, 6.87.

2-Phenylthiomethylenadamantane (18g).—The nmr of the crude product indicated an 80% yield of 18g. Recrystallization from absolute ethanol gave the analytical sample: mp 65°; nmr (CDCl₃) δ 1.90 (s, 12, CH₂ and bridgehead CH), 2.58 (br s, 1, allylic CH), 3.16 (br s, 1, allylic CH), 5.80 (s, 1, C=CH), 7.20 (s, 5, SPh).

Anal. Calcd for C₁₇H₂₀S: C, 79.63; H, 7.86. Found: C, 79.58; H, 7.69.

Registry No.—1, 33521-83-4; 2, 30536-77-7; 6f, 18689-34-4; 6g, 33536-50-4; 7, 33521-85-6; 8, 33521-86-7; 14, 33536-51-5; 18c, 13640-71-6; 18d, 33521-88-9; *cis*-18e, 33536-52-6; *trans*-18e, 33536-53-7; *cis*-18f, 33536-54-8; *trans*-18f, 33536-55-9; 18g, 33521-89-0; diethyl 2-phenyl-2-dimethylaminovinylphosphonate, 33521-90-3; methoxymethylethyldimethylsilane, 33521-91-4.

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The Lithium Salt Catalyzed Rearrangement of Epoxides. II. Glycidic Esters^{1,2}

BURR C. HARTMAN AND BRUCE RICKBORN*

Department of Chemistry, University of California, Santa Barbara, California 93106

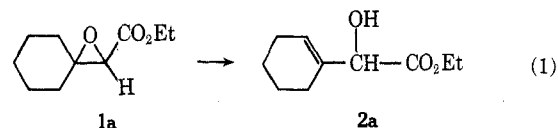
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The rearrangement of glycidic esters catalyzed by lithium salts and other Lewis acids has been explored. Lithium halide catalyst leads to a mixture of products derived from both α and β cleavage of the oxirane. Lithium perchlorate causes β cleavage of 3,3-disubstituted glycidic esters, with subsequent elimination yielding the 2-hydroxy-3-alkenoic acid ester product. Catalytic hydrogenation gives the glycolic ester, which on oxidation affords the corresponding glyoxylic ester. Attempted isomerization of a 2-hydroxy-3-alkenoate by ethanolic sodium ethoxide gave instead double bond reduction. The presumed intermediate glyoxylic ester is similarly reduced under these conditions.

The availability of glycidic esters from the Darzens condensation is an attractive feature for synthesis, and consequently we were interested in examining the behavior of these materials under the conditions of lithium salt catalyzed epoxide rearrangement.^{2,3} Simple alkyl-substituted epoxides rearrange to carbonyl compounds with these catalysts, *via* either hydrogen or alkyl migration. Glycidic esters can undergo epoxide scission at either the α or β carbon, and a sizable number of further products from these ring-opened intermediates can be envisioned.

Earlier studies using protic or Lewis acid catalysts have in fact led to a variety of rearrangement products. Boron trifluoride is an effective catalyst for phenyl-substituted glycidates, where, depending on the starting material structure, either α -keto ester⁴ products or products of carboethoxy migration⁵ may result. Hydrogen chloride at elevated temperature has been used to convert ethyl 3,3-diphenylglycidate to ethyl diphe-

nylgyoxylate,⁶ whereas sulfuric acid is reported⁷ to cause rearrangement of compound 1a to 2a as shown in



eq 1. A similar result using hydrochloric acid catalyst has been noted by Camps and coworkers.⁸ In contrast, ethyl dimethylglyoxylate was obtained in low yield in acid treatment of 3-methyl-2,3-epoxybutanoate.⁹

Also relevant to the present study is the report that Grignard reagents in reaction with glycidic esters yield exclusively α addition, α -hydroxy product,¹⁰ presumably by initial rearrangement to the glyoxylate ester followed by addition. This mechanism is supported by the fact that Darzens¹¹ has actually isolated the α -

(1) Supported in part by the National Science Foundation, GP-6043.

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