this unusual phosphorane (homocubyltriphenylphosphorane) is warmed to 75° or irradiated with ultraviolet light it fragments to give III. This is one of only few known fragmentations of a five-membered ring to two two-atom components and one one-atom component[3] and the only known cheleotropic reaction[4] of phosphorus.

Homocubyltriphenylphosphorane (II) is a white crystalline solid, mp 118–119°, is unaffected by water, and can be stored at room temperature in the atmosphere.[5] However when heated to 120°, just above its melting point, it decomposes in 85% yield to triphenylphosphine and a mixture of *syn*-tricyclo-$[4.2.0.0^{2,5}]$octa-3,7-diene (III, four parts)[7] and cyclooctatetraene (IV, one part).[8] In benzene solution the half-life[9] of II is about 7 hr at 75° and 50 hr at 60°. Photolyzed through Pyrex in C_6D_6 or CH_2Cl_2 it gives III (*ca.* 48% conversion after 6 hr in C_6D_6) and no IV. The hydrocarbon was isolated (15% yield) by glpc of the CH_2Cl_2 photolysate.

There are two possible reasons why the reaction of the phosphonium salt I with phenyllithium gives the pentavalent phosphorane rather than the ylide and why this pentavalent phosphorane is stable. Either (1) there is especial difficulty in the phenyllithium removing a proton from the carbon adjacent to phosphorus—although phenyllithium is known to be an effective reagent for forming many ylides,[2b] and the geometrical constraints of bridged ring systems have previously not inhibited ylide formation[10]—or (2) the formation of a pentavalent phosphorane is here especially favored. The latter is probably the true reason. In phosphonium salts the four groups attached to phosphorus should be tetrahedrally arranged,[11] and compound I must therefore be strained because the internal angle at phosphorus is close to, and probably less than, 90°.[12] This strain is unrelieved if the ylide is formed because the four groups should still be tetrahedrally arranged.[13] However if the pentavalent phosphorane forms, the strain is relieved because the trigonal-bipyramidal configuration normal for pentavalent phosphorus compounds[14] allows the ring to span without strain coordination positions separated by 90°.

It is probably for the same reason that the phosphonium salt I can be easily prepared by treating at −78° the corresponding phosphine oxide[15] in tetrahydrofuran with phenyllithium in benzene–ether (70:30),[16] followed by 20% aqueous HBr. (The salt melts at 310–311°, and the yield is 70%.)[17] Phosphonium salts are not usually prepared in this way[18] because phosphine oxides with α hydrogens usually give ylides instead,[19] and even when there are no α hydrogens the phosphonium salts form in only poor yield.[20]

The reason for the ease and efficiency with which the procedure gives the salt I is almost surely the reason II is so readily prepared: angle-strained tetravalent organophosphorus compounds react especially easily with nucleophiles to give their pentavalent derivatives. This is, of course, the reason given by Westheimer[6,21] why small-ring phosphate esters (and related substances) hydrolyze rapidly. The theory manifests itself in our experiments in the pentavalent derivative being isolable. We anticipate this to be a general phenomenon.[22]

Acknowledgments. We are grateful to the National Institutes of Health (MH-08912) for its support and Badische Anilin und Sodafabrik, A.G. for gifts of cyclooctatetraene.

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(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(5) The analyses for carbon, hydrogen, and phosphorus, the mass spectrum, and the proton nmr spectrum are all satisfactory. The proton nmr spectrum (100 MHz) in $CDCl_3$ at ambient temperature shows the resonances of the 15 aromatic protons and multiplets at τ 6.43, 6.71, and 7.04 of intensity 2, 2, and 4. The resonance at τ 6.43 is split into a doublet, $|J| = 13.0$ Hz, by coupling with ^{31}P, and this splitting is removed by irradiation at the phosphorus resonance frequency. The simplicity of the spectrum indicates that the molecule is pseudorotating rapidly.[6]

(6) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

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(8) Compound III is transformed by heating into cyclooctatetraene.[7] The half-life in benzene at 75° is about 7.5 hr.

(9) Proton nmr analysis.

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(16) From Alfa Inorganics, Inc., Beverly, Mass.

(17) The analyses for C, H, P, and Br and the proton nmr spectrum are satisfactory.

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(19) (a) J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963); (b) L. Horner, *et al.*, *Chem. Ber.*, **91**, 61 (1958); **94**, 1987 (1961); **95**, 536 (1962); (c) D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Amer. Chem. Soc.*, **86**, 1100 (1964).

(20) H. Gilman and G. E. Brown (*ibid.*, **67**, 824 (1945)), obtained no $(C_6H_5)_4P^+Br^-$ from $(C_6H_5)_3PO$ and C_6H_5Li, while Wittig and Rieber[1a] obtained some, but reported no yield. We obtained less than 10% yield.

(21) R. Kluger and F. H. Westheimer, *ibid.*, **91**, 4143 (1969).

(22) This probably accounts for the stability of the alkylbisbiphenylenephosphoranes.[23] Simple alkylphosphoranes are rapidly converted to a hydrocarbon and an ylide.[2a,24]

(23) (a) D. Hellwinkel, *Chem. Ber.*, **98**, 576 (1965); **102**, 548 (1969); (b) M. Schlosser, T. Kadibelban, and G. Steinhoff, *Angew. Chem., Int. Ed. Engl.*, **5**, 968 (1966).

(24) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 3467 (1965).

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Alkylation of the Dianion of β-Keto Esters

Sir:

Recently we required a method to substitute a β-keto ester at the γ carbon (eq 1). One method to

$$CH_3COCH_2CO_2R' \longrightarrow \underset{\mathbf{1}}{RCH_2COCH_2CO_2R'} \qquad (1)$$

$$\underset{\mathbf{2}}{\overset{-}{C}H_2CO\overset{-}{C}HCO_2R'} \qquad \underset{\mathbf{3}}{CH_3CO\overset{-}{C}HCO_2Me}$$

achieve this transformation is to alkylate the 1,3-dianion **2** at the γ carbon.[1] However, it has been reported that the yields for the alkylation of the dianion of ethyl acetoacetate (**2**, R′ = Et) were low or that the reaction failed.[2] This could be due to incomplete formation of dianion **2** under their conditions or to slow alkylation at the low reaction temperature, −33°.

Treatment of methyl acetoacetate[3] with 2 equiv of *n*-butyllithium yielded carbonyl addition products only. However, generation of the monoanion **3** and subsequent metalation was expected to surmount this difficulty since Hauser[4] had found that the dianion **4** was readily produced *via* the monoanion (eq 2).

$$C_6H_5CH_2COCH_3 \xrightarrow[NH_3]{M^+NH_2^-} C_6H_5\bar{C}HCOCH_3 \xrightarrow[THF]{n\text{-BuLi}} \underset{\mathbf{4}}{C_6H_5\bar{C}HCO\bar{C}H_2} \quad (2)$$

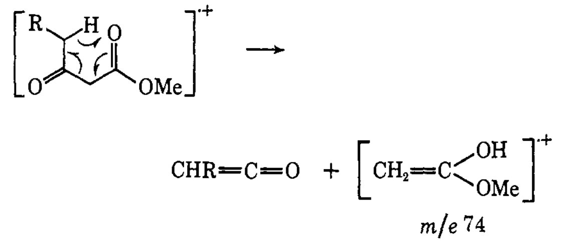
Treatment of methyl acetoacetate with sodium hydride in THF produced the monoanion **3** and subsequent metalation of **3** with *n*-butyllithium did generate the dianion **2** (R′ = Me). When **2** (R′ = Me) was quenched with D_2O and deuterated trifluoroacetic acid, the recovered methyl acetoacetate contained 0.96 ± 0.03 deuterium at the γ carbon.[5] Hence our method gave excellent yields of the dianion **2** (R′ = Me). When a solution of **2** (R′ = Me) in THF was treated with a variety of alkylating agents a facile reaction occurred. The monoalkylated products **1** were isolated in good yield (Table I). Yields have not been maximized. But we have found that alkylation of **2** was sluggish at −23° and no alkylation was observed at −78°. In addition, the dianion of ethyl acetoacetate was alkylated to yield **1** (R′ = Et).[3] For example, **1** (R′ = Et; R = $CH_2{=}CHCH_2$) was obtained in 77% yield.[6]

Table I. Alkylation of Dianion from Methyl Acetoacetate

R-X	Yield of **1**,[a,b] %	Bp of **1**, °C (R′ = Me) (*P*, mm)
MeI	81 (99)	70–71 (14)
EtBr	84 (96)	77–79 (14)
i-PrI	73 (90)	52–54 (2)
n-BuBr	72 (95)	53–54 (0.4)
$CH_2{=}CHCH_2Br$	83 (98)	99–100 (14)
$C_6H_5CH_2Cl$	81 (94)	102–103 (0.4)

[a] All products exhibited analytical and spectral data in accord with the assigned structures. [b] Yields refer to distilled products. The numbers in parentheses refer to vpc yields.

From the nmr spectra[3] of the products it was evident that alkylation occurred exclusively at the γ carbon. Furthermore, spectral analysis of the crude reaction mixtures failed to give any evidence of dialkylated or O-alkylated products. The nmr spectra of **1** have a *two-proton singlet at δ 3.4–3.5* due to the α-methylene protons.[7] The absence of a three-proton singlet at *ca.* δ 2.3[7] amplified the conclusion that alkylation occurred only on the γ carbon. Analysis of the mass spectrum of **1** corroborated this fact. There always was a significant peak at *m/e* 74 due to a McLafferty-type cleavage (eq 3)[8a] and there was also a large peak due to ion **5** (eq 4).[8b]



$$CHR{=}C{=}O + \left[CH_2{=}C\begin{matrix}OH\\ OMe\end{matrix}\right]^{\cdot+} \quad (3)$$

m/e 74

$$[RCH_2COCH_2CO_2Me]^{+} \longrightarrow {}^{\cdot}CH_2CO_2Me + \underset{\mathbf{5}}{[RCH_2CO]^{+}} \quad (4)$$

We have alkylated substituted β-keto esters also (eq 5). It is possible starting with methyl acetoacetate[3]

$$\underset{\mathbf{6}}{RCH_2COCH_2CO_2Me} \longrightarrow \underset{\mathbf{7}}{RR'CHCOCH_2CO_2Me} \quad (5)$$

to generate the dianion **2**, alkylate, generate the dianion of this alkylated product with a second equivalent of *n*-butyllithium, and add a second alkylating agent to yield **7**; for example, ester **7** (R = *n*-Bu; R′ = $C_6H_5CH_2$) was prepared in 48% yield[6] from methyl acetoacetate in this manner. However, we generally obtained higher yields of **7** if we isolated and purified the monoalkylated product **6** before proceeding with the second alkylation. Some typical results are given in Table II.

Table II. Alkylation of Dianion from $RCH_2COCH_2CO_2Me$

R	R-X	Yield of **7**,[a,b] %	Bp of **7**, °C (*P*, mm)
n-Bu	$CH_2{=}CHCH_2Br$	77	82–84 (0.6)
n-Bu	$C_6H_5CH_2Cl$	62	122–123 (0.4)
Me	$C_6H_5CH_2Cl$	76	103–104 (0.5)
$C_6H_5CH_2$	MeI	86	99–100 (0.3)

[a] All products exhibited analytical and spectral data in accord with assigned structures. [b] Yields are for distilled products.

The following experimental procedure is representative. Approximately 25 ml of dry THF was distilled into a 50-ml flask containing 0.54 g of sodium hydride (50% mineral oil). The flask was stoppered (septum cap), flushed with nitrogen, and cooled in ice. Methyl acetoacetate (10 mmol, 1.16 g) was added dropwise and the colorless solution was stirred at 0° for 10 min. Then 10.5 mmol (4.8 ml of 2.2 *M*) of *n*-butyllithium in hexane was added dropwise and the orange solution of **2** (R′ = Me) was stirred at 0° for an additional 10 min. Methyl iodide (11 mmol, 1.56 g) in 2 ml of dry THF was added and the reaction mixture was stirred at

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(1) (a) For a review of the alkylation of dianions and trianions, see T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969); (b) N. Sugiyama, M. Yamamoto, T. Takano, and C. Kashima, *Bull. Chem. Soc. Jap.*, **40**, 2909 (1967).

(2) J. F. Wolfe, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **29**, 3249 (1964).

(3) We chose methyl acetoacetate for most of our experimental work to simplify the spectra of the products; however ethyl acetoacetate gave comparable results.

(4) C. Mao, C. R. Hauser, and M. L. Miles, *J. Amer. Chem. Soc.*, **89**, 5303 (1967).

(5) Determined by nmr and mass spectrometry.

(6) This compound exhibited analtyical and spectral data in accord with the assigned structure.

(7) The nmr spectrum of methyl acetoacetate has the following signals: δ 3.74 (s, 3 H, OMe), 3.48 (s, 2 H, CH_2), and 2.27 (s, 3 H, MeCO).

(8) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967: (a) pp 190–192; (b) pp 134–135.

room temperature for 15 min. The color of the dianion faded immediately on addition of the methyl iodide. The mixture was quenched with 2 ml of concentrated hydrochloric acid plus 5 ml of water and diluted with 15 ml of ethyl ether. The organic phase was washed with water until the aqueous extracts were neutral pH, dried over magnesium sulfate, and filtered. The solvents were removed under reduced pressure and the crude product was distilled to yield 1.06 g (81%) of methyl 3-oxovalerate.[9]

(9) This research was supported by the Research Corporation and the National Research Council of Canada.

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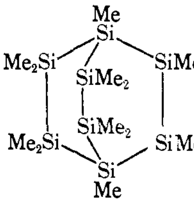
Cyclic Polysilanes. V. Tetradecylmethylbicyclo[2.2.2]octasilane, a Cage Polysilane[1]

Sir:

In continuing our studies of cyclic polysilanes, we have investigated the reaction of a mixture of Me_2SiCl_2 and $MeSiCl_3$ with sodium–potassium alloy. This reaction yields $Me_{14}Si_8$, the first fully characterized cage polysilane.[2,3]



Our assigned structure is based on spectral evidence. The exact molecular weight was determined by high-resolution mass spectrometry: calcd mass, 434.1440; found, 434.1439 ± 0.0043. The 100-MHz proton nmr taken in CCl_4 shows only two peaks, at −0.205 and −0.125 ppm (δ) with a relative intensity of 6:1, respectively.[4] The infrared spectrum of $Me_{14}Si_8$ is similar to those for the cyclosilanes $Me_{12}Si_6$ and $Me_{14}Si_7$ (Table I). It shows no absorption in the 3300-cm^{-1} or 1050-cm^{-1} region which would be indicative of Si–OH or Si–O–Si linkages, nor in the 2050–2300-cm^{-1} region characteristic of Si–H bonds. The ultraviolet spectrum in isooctane shows an inflection point at 245 nm (ε 7500). Tetradecylmethylbicyclo[2.2.2]octasilane is a white solid with mp >360°, but subliming readily at 100° and 0.3 Torr. It is air stable and soluble in organic solvents such as diethyl ether, chloroform, and carbon tetrachloride.

Table I. Infrared Spectra[a]

$Me_{14}Si_8$	$Me_{14}Si_7$	$Me_{12}Si_6$
2950 (s)	2950 (s)	2950 (s)
2890 (s)	2890 (m)	2885 (m)
2790 (w)	2790 (w)	2790 (w)
1400 (m)	1400 (m)	1400 (m)
1245 (s)	1250 (s)	1250 (s)
1240 (sh)	1240 (m)	1240 (m)
840 (m)	845 (m)	845 (m)
800 (vs)	830 (m)	830 (m)
725 (m)	795 (vs)	800 (vs)
685 (w)	735 (m)	735 (m)
670 (m)	690 (m)	690 (m)
650 (s)	655 (s)	655 (s)
630 (w)	630 (w)	630 (w)
390 (w)	362 (w)	383 (m)
375 (m)		

[a] Abbreviations used are: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

In a typical experiment 20 ml (0.165 mol) of Me_2SiCl_2 and 20 ml (0.18 mol) of $MeSiCl_3$ in 40 ml of THF were added dropwise over 4 hr to 3 g (0.023 mol) of naphthalene and 0.95 mol of sodium–potassium alloy (27 g of potassium and 6 g of sodium) in 500 ml of dry THF. The reaction was mechanically stirred and kept at reflux (65°) during the chlorosilane addition. At the completion of the reaction, methanol and water were added to destroy the excess sodium–potassium alloy. The solution was then extracted with 400 ml of diethyl ether, and the organic layer was separated and vacuum distilled. The fraction boiling between 160 and 180° at 0.3 Torr was collected and purified by preparative gas chromatography,[5] yielding $Me_{14}Si_8$. The compound can be purified further by recrystallization from ether–acetone (1:1) or by vacuum sublimation at 100° and 0.3 Torr.

The yield of $Me_{14}Si_8$ is 0.5%, with residue (50%), siloxanes (44%), $Me_{12}Si_6$ (5%), and $Me_{18}Si_{10}$[6] (0.5%) accounting for the remainder.

The monocyclic permethylpolysilanes are reducible to electron-delocalized anion radicals, $(Me_2Si)_n{}^{\cdot -}$.[1] We find that $Me_{14}Si_8$ is similarly reduced by sodium–potassium alloy in glyme–methyl THF (2:1) solvent at −90° to give an anion radical observable by esr. Work is

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(1) Previous paper in this series: E. Carberry, R. West, and G. E. Glass, *J. Amer. Chem. Soc.*, **91**, 5446 (1969).

(2) The reactions

$$SiBr_4 + Si(metal) \xrightarrow{1150^\circ} Si_{10}Br_{16}$$

and

$$Si_{10}Br_{16} + CH_3MgI \xrightarrow{\text{ether}} (CH_3)_{16}Si_{10}$$

have been reported, but no structural data on $Si_{10}Br_{16}$ or $Me_{16}Si_{10}$ have been published: M. Schmeisser (a) IUPAC Colloquium (Münster 1954), Silicium-Schwefel-Phosphate 28, 1955; (b) *Angew. Chem.*, **66**, 713 (1954).

(3) V. G. Schatt and R. Nagel (*J. Prakt. Chem.*, [4] 34, 158 (1966)) have reported the existence of $(C_6H_5)_{10}Si_{10}Br_6$. The compound was obtained as a by-product of the reaction of phenyltribromosilane with phenylmagnesium bromide. It could not be crystallized and was characterized only by elemental analysis and molecular weight determination.

(4) The chemical shift of the MeSi protons in $Me_{14}Si_8$ follows the pattern observed in $(Me_3Si)_3SiMe$, where the protons of the MeSi are at higher field, −0.05 ppm (δ), than the protons of Me_3Si, −0.14 ppm (δ). W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, **5**, 594 (1966).

(5) Good separation was obtained at 300° using a 3/8 in. × 10 ft column packed with 20% Apiezon L on Chromosorb W, and a helium flow rate of 160 ml/min. Retention time for $Me_{14}Si_8$ was 12.5 min.

(6) $Me_{18}Si_{10}$ shows four peaks in the proton nmr, −0.14, −0.15, −0.19, and −0.255 ppm (δ) in the ratio of 2:2:1:4, respectively. The molecular weight was determined by high-resolution mass spectrometry: calcd mass, 550.1918; found, 550.1955 ± 0.0050. Its infrared spectrum is similar to those for $Me_{14}Si_8$ and the permethylated cyclopolysilanes. We suspect it to have either the decalin- or the bicyclo-[3.3.2], or -[4.2.2] (suggested by the referee) decane-type structure. If the nmr cannot differentiate between the methyl groups syn and anti to the 4 bridge and 2 bridge in the bicyclo[4.2.2] and -[3.3.2], respectively, then four peaks, as observed, would appear in the nmr. However if the syn and anti positions are sufficiently different, then six peaks for the bicyclo[3.3.2] structure and five peaks for the bicyclo[4.2.2] structure should be observed. Likewise the decalin-type structure would exhibit three peaks if no distinction between the axial and equatorial methyl groups is observable, but five peaks if the difference in chemical shift is large enough. The nmr spectra were recorded on a Varian XL100-MHz instrument at a sweep width of 25 cycles.