(22) Disproportionation of organic ligands as presented in eq 18 and 19 may also proceed between two iron nuclei and is not required by the data to be intramolecular.

(23) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **92**, 1426 (1970); G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *ibid.*, **94**, 232 (1972); M. Tamura and J. K. Kochi, *ibid.*, **93**, 1483 (1971); *J. Organomet. Chem.*, **42**, 205 (1972); **29**, 111 (1971); G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Am. Chem. Soc.*, **94**, 5251 (1972).

(24) The absence of crossover products reported earlier[1,2] when a pair of different organic bromides are employed also poses some difficult questions for the mechanism in Scheme I.

(25) For example, it is possible that three or more organic ligands are present on the iron(III) intermediates to form ferrate(III) complexes.

(26) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 9269 (1972).

(27) D. D. Perrin, W. L. Armaego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, Elmsford, N.Y., 1966.

(28) O. Kamm and C. S. Marvel, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 25.

(29) A. Tsolis, P. P. Hunt, J. K. Kochi, and S. Seltzer, *J. Am. Chem. Soc.*, in press.

(30) Taken in part from the B.S. Thesis of R. Scott Smith submitted to Indiana University, 1975.

A Study of the Chemistry of Lithiotriphenylphosphineacetylmethylene[1]

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Treatment of triphenylphosphineacetylmethylene (**3**) with 1.2 equiv of *n*-butyllithium in THF–hexane at −78° resulted in abstraction of a methyl proton to form the ylide anion, lithiotriphenylphosphineacetylmethylene (**4**, M = Li). Reactions of **4** with several alkyl halides, aldehydes, saturated and α,β-unsaturated ketones, and benzoate esters occurred at the terminal carbanion site to afford β-ketophosphonium ylides **9**, δ-hydroxy-β-keto ylides **14**, and the β,δ-diketo ylide **17**, respectively. Sequential treatment of **4** with *n*-butyl iodide and benzaldehyde or with allyl bromide and 3,4-dichlorobenzaldehyde gave 1-phenyl-1-octen-3-one (**13a**) and 1-(3,4-dichlorophenyl)-1,6-heptadien-3-one (**13b**), respectively. Reaction of **4** with *o*-phthaldehyde afforded 4,5-benzotropone (**16**). Triphenylphosphine(3-phenylpropanoyl)methylene (**9a**) was converted into ylide anion **10** by means of *n*-butyllithium as shown by alkylation with benzyl chloride and allyl bromide to give triphenylphosphine(2-benzyl-3-phenylpropanoyl)methylene (**11a**) and triphenylphosphine(2-allyl-3-phenylpropanoyl)methylene (**11b**). Attempted formation of **4** (M = K) by means of potassium amide in liquid ammonia lead to cleavage of **3** with formation of diphenylacetonylphosphine oxide (**5**) and diphenylphosphinic amide (**6**).

The synthetic utility of 1,3-dicarbanions[2] of type **1** where A may be a ketone,[3a–c] aldehyde,[4a–c] or ester[5a–f] group, and A′ is a ketone function, was discovered and exploited by

$$\underset{\mathbf{1}}{\mathrm{A{-}\overset{-}{C}H{-}A'{-}\overset{-}{C}H_2}} \xrightarrow{\text{electrophiles}} \underset{\mathbf{2}}{\mathrm{A{-}CH_2{-}A'{-}CH_2R}}$$

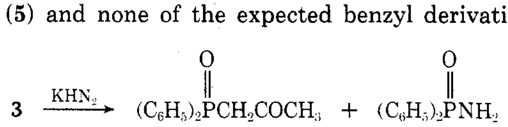
Hauser and his co-workers.[2,6] The major preparative value of these intermediates lies in the fact that they undergo regiospecific reactions with electrophilic reagents at the more nucleophilic carbanion site to form compounds of type **2**, where R corresponds to the moiety furnished by the electrophile. When we began the present study, dianions of type **1** had been used primarily to elaborate the structure of their precursors, e.g., in the synthesis of new β-diketones from various β-diketone dianions.[3–c] It occurred to us that the synthetic utility of intermediates of type **1** might be expanded in an interesting new direction if activating group A could be easily removed or altered in several ways after introduction of appropriate R groups adjacent to A′. Thus, A would act as a control element[7] and its subsequent replacement could give rise to compounds differing significantly from the original dianion precursor.[8]

The ability of the triphenylphosphonium function to stabilize an adjacent carbanion center, its propensity toward cleavage[9] and participation in carbonyl olefination reactions,[9,10] and the fact that no compounds possessing a phosphorus containing activating function had been converted to 1,3-dianions, prompted us to test the above hypothesis with triphenylphosphineacetylmethylene[11] (**3**) as the precursor to ylide anion **4**. The present paper represents an expanded account of our preliminary findings[12] concerning the chemistry of lithiotriphenylphosphineacetylmethylene (**4**, M = Li). Following our communication, Cooke[13] reported on the alkylation of **4** and hydrolysis of the resulting β-keto phosphonium ylides to afford methyl ketones in good yields. Cooke and Goswami[14] also used an ylide dianion related to **4** in the synthesis of an eight-membered-ring diketo ylide. Grieco and Pogonowski have recently made elegant use of dianions containing an expendable activating-control unit in cases involving 1,3-dianions of β-keto phosphonates[15a–b] and β-keto sulfoxides.[16a–b] Kuwajima and Iwasawa[17] have also investigated the chemistry of dianions derived from β-keto sulfoxides.

$$\underset{\mathbf{3}}{\mathrm{(C_6H_5)_3\overset{+-}{P}CHCOCH_3}} \longrightarrow \underset{\mathbf{4}}{\mathrm{[(C_6H_5)_3\overset{+-}{P}CHCO\overset{-}{C}H_2]M^+}}$$

Results and Discussion

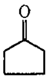
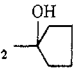
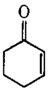
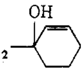
Initially, formation of ylide anion **4** (M = K) from **3** was attempted using potassium amide in liquid ammonia. However, we were unable to obtain evidence for the desired proton abstraction. Instead, reaction of **3** with 2 equiv of potassium amide in liquid ammonia followed by benzyl chloride afforded a 57% yield of acetonyldiphenylphosphine oxide (**5**) and none of the expected benzyl derivative **9a**.



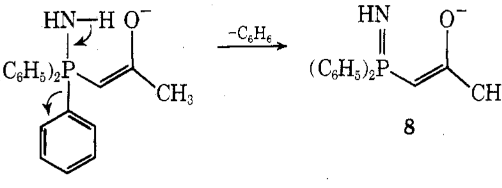
$$\mathbf{3} \xrightarrow{\mathrm{KNH_2}} \underset{\mathbf{5}}{\mathrm{(C_6H_5)_2\overset{\overset{\displaystyle O}{\|}}{P}CH_2COCH_3}} + \underset{\mathbf{6}}{\mathrm{(C_6H_5)_2\overset{\overset{\displaystyle O}{\|}}{P}NH_2}}$$

This reaction was repeated several times using potassium amide, but no benzyl chloride. In each case **5** was again produced, along with varying amounts of diphenylphosphinic amide (**6**). Apparently amide ion preferentially attacks the electrophilic phosphorus of **3** to form a pentavalent intermediate such as **7**, which then decomposes with loss of benzene to form iminophosphorane anion **8**. This series of

Table I
Reactions of Lithiotriphenylphosphineacetylmethylene (4)

Electrophile	Registry no.	Product (no.)	Mp, °C	% yield
$C_6H_5CH_2Cl$	100-44-7	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2CH_2C_6H_5$ (**9a**)	147.5–149.5[a,b]	47
$C_6H_5CH_2Br$	100-39-0	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2CH_2C_6H_5$ (**9a**)	149–151[a,b]	44
$CH_2{=}CHCH_2Br$	106-96-7	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2CH_2CH{=}CH_2$ (**9b**)	94–96.5[c]	52
$C_6H_5CH_2Cl$, $C_6H_5CH_2Cl$		$(C_6H_5)_3\overset{+-}{P}CHCOCH(CH_2C_6H_5)_2$ (**11a**)	177–177.5[d]	37
$C_6H_5CH_2Cl$, $CH_2{=}CHCH_2Br$		$(C_6H_5)_3\overset{+-}{P}CHCOCH(CH_2CH{=}CH_2)(CH_2C_6H_5)$ (**11b**)	127.5–130[e]	50
$Br(CH_2)_3Br$	109-64-8	$(C_6H_5)_3\overset{+-}{P}CHCO(CH_2)_5CO\overset{-}{C}H\overset{+}{P}(C_6H_5)_3$ (**12**)	200–207[d]	59
CH_3CHO	75-07-0	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2CH(OH)CH_3$ (**14a**)	160–161[d]	43
C_6H_5CHO	100-52-7	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2CH(OH)C_6H_5$ (**14b**)	163[d]	50
$(C_6H_5)_2CO$	119-61-9	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2C(OH)(C_6H_5)_2$ (**14c**)	180–182[f]	81
$C_6H_5COCH_3$	98-86-2	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2C(OH)(CH_3)C_6H_5$ (**14d**)	187–187.5[d]	66
CH_3COCH_3	67-64-1	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2C(OH)(CH_3)_2$ (**14e**)	185–187[d]	63
	120-92-3	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2$  (**14f**)	154–155[d]	59
	930-68-7	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2$  (**14g**)	124–126[d]	52
$C_6H_5CH{=}CHCOC_6H_5$	94-41-7	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2C(OH)(C_6H_5)CH{=}CHC_6H_5$ (**14h**)	148–150[d]	63
$C_6H_5COOC_6H_5$	93-99-2	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2COC_6H_5$ (**17**)	158–160[a]	58
$C_6H_5COOCH_3$	93-58-3	$(C_6H_5)_3\overset{+-}{P}CHCOCH_2COC_6H_5$ (**17**)	158–160[a]	60

[a] Recrystallized from ethyl acetate–hexane. [b] Lit.[9] mp 148–150°. [c] Recrystallized from hexane. [d] Recrystallized from ethyl acetate. [e] Recrystallized from benzene–petroleum ether. [f] Recrystallized from acetone.



7

8

steps is analogous to the mechanisms for decomposition of phosphonium salts by organolithium reagents[18] and hydrolysis of phosphonium salts and ylides.[19] In the case of basic hydrolysis of β-keto phosphonium ylides, the leaving group is normally the relatively stable enolate ion derived from the carbonyl portion of the ylide.[11,13] Under the present conditions, loss of phenyl anion from **7** may be favored since expulsion of the acetonyl moiety would require its departure as a dianion. Formation of **5** and/or **6** could then arise from protonation and hydrolysis of **8** during work-up.[20] Thus, hydrolytic loss of ammonia from protonated **8** would give phosphine oxide **5**, while competitive loss of acetone from the same intermediate could yield amide **6**. Attempts to isolate an intermediate corresponding to **8** by omitting the final hydrolysis step were unsuccessful. However, benzene was shown to be formed in these experiments, thereby lending support to the proposed mechanism for formation of **5** and **6**.

Formation of ylide anion **4** (M = Li) proceeded smoothly and without appreciable nucleophilic attack at phosphorus when **3** was treated with 1.2 equiv of *n*-butyllithium in THF–hexane at −78°.[21] Initial evidence for the formation of **4** was obtained by quenching with deuterium oxide followed by ^{1}H NMR analysis, which revealed incorporation of 0.9 deuterium atom at the methyl group of recovered **3**.

Alkylation of **4** with benzyl chloride, benzyl bromide, and allyl bromide afforded β-keto ylides **9a,b** (Table I). Surprisingly, **4** failed to undergo C-alkylation with trimethylchlorosilane, and methyl iodide functioned poorly as an alkylating agent. In our preliminary account of this work we reported that alkylations of **4** were best carried out at −68°. Subsequent examinations of these reactions by us and others[13] have revealed that alkylations occur satisfactorily at temperatures from −78 to 0° depending on the reactivity of the halide. Since Cooke[13] had thoroughly investigated the alkylations of **4** with primary and secondary halides, we did not attempt to extend this line of investigation or optimize our yields of **9a,b**. However, we found that **9a** could be converted into secondary ylide anion **10** by means of *n*-butyllithium, and that **10** underwent alkylation with benzyl chloride and allyl bromide to give disubstituted ylides **11a** and **11b** in yields of 37 and 50%, respectively. This procedure could presumably be carried through

$$[(C_6H_5)_3\overset{+-}{P}CHCO\overset{-}{C}HCH_2C_6H_5]Li^+ \xrightarrow{RX} (C_6H_5)_3\overset{+-}{P}CHCOCH(R)CH_2C_6H_5$$

10 **11**

a hydrolysis step[13] to yield various methyl secondary alkyl ketones. Attempts to alkylate **11a** via its ylide anion were unsuccessful.

Reaction of **4** (2 equiv) with 1 equiv of 1,3-dibromopropane gave bis ylide **12** in 59% yield. Alkylations of **4** could also be followed by Wittig-type reactions without extensively purifying the initial alkylation products. Thus, treatment of **4** with butyl iodide followed by benzaldehyde gave **13a** (63%). Similarly, the combination of allyl bromide and

$$(C_6H_5)_3\overset{+-}{P}CHCO(CH_2)_5CO\overset{-}{C}H\overset{+}{P}(C_6H_5)_3$$

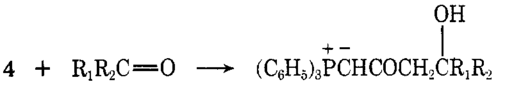
12

$ArCH{=}CHCOCH_2R$

13a, Ar = C_6H_5; R = nC$_4$H$_9$
b, Ar = 3,4-$Cl_2C_6H_3$;
R = $CH_2{=}CHCH_2$

3,4-dichlorobenzaldehyde afforded **13b** (59%). This reaction sequence provides a convenient method for the synthesis of α,β-unsaturated ketones of type **13** within the limitations associated with alkylations of 4.[13]

Next, we examined the reactions of 4 (M = Li) with a series of aldehydes and ketones. In all instances involving both aliphatic and aromatic aldehydes and ketones, condensations occurred exclusively at the terminal carbanion site of 4 to form **14a–h.** No evidence for Wittig products



$$4 + R_1R_2C{=}O \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCOCH_2\overset{OH}{\overset{|}{C}}R_1R_2$$

14

was obtained in any of the cases examined. The results of these experiments are presented in Table I. Structural assignments were verified by analytical and ^{1}H NMR data (Table II). In particular the methyl signal of **3**, which appeared at 2.06 ppm, was replaced by a resonance for the methylene protons adjacent to the carbonyl group of **14a–h.** The diastereotopic methylene and the methinyl protons of **14a** and **14b** appeared as ABX patterns while the methylene protons of **14d, 14g,** and **14h** gave rise to AB patterns (Table II).

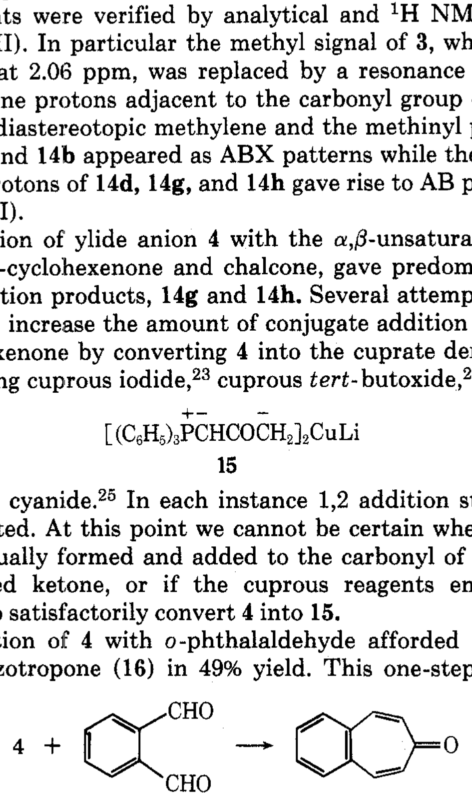
Reaction of ylide anion 4 with the α,β-unsaturated ketones, 2-cyclohexenone and chalcone, gave predominantly 1,2-addition products, **14g** and **14h.** Several attempts were made to increase the amount of conjugate addition with 2-cyclohexenone by converting 4 into the cuprate derivative **15**[22] using cuprous iodide,[23] cuprous *tert*-butoxide,[24a,b] and

$$[(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCO\overset{-}{C}H_2]_2CuLi$$

15

cuprous cyanide.[25] In each instance 1,2 addition still predominated. At this point we cannot be certain whether **15** was actually formed and added to the carbonyl of the unsaturated ketone, or if the cuprous reagents employed failed to satisfactorily convert 4 into **15.**

Reaction of 4 with *o*-phthalaldehyde afforded directly 4,5-benzotropone (**16**) in 49% yield. This one-step procedure compares favorably with more complex previous methods[26] for the preparation of **16,** and could conceivably be used for the synthesis of 2-alkyl-4,5-benzotropones from ylide anions such as **10.**



16

Acylation of 4 was accomplished with methyl benzoate and phenyl benzoate to give diketo ylide **17** (Table I). The ^{1}H NMR spectrum of this compound, which was consistent with the assigned structure, revealed that **17** existed as ca. 50% of one or more β-dicarbonyl enol tautomers in CDCl$_3$.

In summary, ylide anion 4 has been found to react satisfactorily with a representative series of electrophilic compounds including alkyl halides, aldehydes, ketones, and benzoate esters. Among the electrophiles examined we found that cyclohexene oxide and styrene oxide failed to react with 4, even after 24 hr at 25°.

Table II
^{1}H NMR Absorptions of Products Obtained from Lithiotriphenylphosphineacetylmethylene (4)[p]

Product no.	Types of hydrogen and chemical shifts, δ			
	Aromatic	$-\overset{+}{P}\overset{-}{C}H-$	$-CH_2-$	Other
9a	7.44 (m)	3.64 (d, broad)	2.84 (m)	
9b	7.52 (m)	3.80 (s, broad)	2.44 (m)	5.96 (m)[a] 5.04 (t)[b]
11a	7.16 (s)[c] 7.44 (m)	3.36 (s, broad)	2.86 (m)	2.86 (m)[d]
11b	7.2 (s)[c] 7.48 (m)	3.52 (d, broad)	2.6 (m)	5.92 (m)[a] 5.02 (t)[b] 2.6 (m)[d]
12	7.52 (m)	3.6 (s, broad)	2.36 (t)[e] 1.68 (m)[f]	
14a	7.7 (m)	3.8 (broad)	2.59 (m)[g] 2.32 (m)[g]	4.2 (m) 1.2 (d)[h]
14b	7.56 (m)	3.68 (d, broad)	2.79 (m)[i] 2.65 (m)[i]	5.1 (m)
14c	7.52 (m)	3.72 (d, broad)	3.28 (s)	
14d	7.44 (m)	3.6 (s, broad)	2.99[j] 2.71[j]	1.48 (s)[h]
14e	7.52 (m)	3.78 (d, broad)	2.46 (s)	1.24 (s)[h]
14f	7.56 (m)	3.8 (s, broad)	2.6 (s)	1.74 (m)[k]
14g	7.64 (m)	3.82 (d, broad)	2.57[l] 2.49[l]	1.92 (m)[m] 5.78 (s)[n]
14h	7.46 (m)	3.74 (d)	3.06[o] 2.98[o]	6.72 (q)[n]
17	7.8 (m) 8.52 (q)	4.00 (d, broad)	4.14 (d)	6.11 (s)[a]

[a] CH=C. [b] CH$_2$=C. [c] CH$_2$C$_6$H$_5$. [d] Methine proton. [e] –COCH$_2$–. [f] –(CH$_2$)$_3$–. [g] Calculated values for AB protons of an ABX system with J_{AB} = 15, J_{AX} = 9.43, and J_{BX} = 2.57 Hz. [h] –CH$_3$. [i] Calculated values for AB protons of an ABX system with J_{AB} = 15, J_{AX} = 11.57, and J_{BX} = 3.43 Hz. [j] Calculated values for an AB system with J_{AB} = 14 Hz. [k] Cyclopentyl group. [l] Calculated chemical shift values for an AB system with J_{AB} = 14 Hz. [m] Methylene protons of the cyclohexenyl group. [n] CH=CH. [o] Calculated chemical shift values for an AB system with J_{AB} = 14.5 Hz. [p] Satisfactory analytical data (±0.4% for C, H) for all compounds were submitted for review.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed in this department, by T. E. Glass, using a Perkin-Elmer 24 Elemental Analyzer. Infrared (ir) spectra were taken on a Beckman IR 20A-X infrared spectrophotometer using 10% chloroform solutions or liquid films. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL JHM-PS-100 spectrometer, using deuteriochloroform (CDCl$_3$) or deuteriodimethyl sulfoxide (Me$_2$SO-d_6) as solvents. Tetramethylsilane (Me$_4$Si) was used as internal standard. Chemical shifts were measured to the center of a singlet or multiplet and are given in δ units, parts per million (ppm). In all ^{1}H NMR descriptions, s = singlet, d = doublet, t = triplet, and m = multiplet. Mass spectra were taken by F. Battrel using a Hitachi Perkin-Elmer RMU-7 spectrometer. Thin layer chromatography (TLC) was carried out using Eastman Chromatogram sheets (silica gel) type 6060 with fluorescent indicator. Acetone–benzene (1:1) was generally used as the developing solvent. Spots were visualized with ultraviolet light. The yield of 4,5-benzotropone (**16**) was determined on a Varian Aerograph Model 90-P gas chromatograph, equipped with a 6-ft column, packed with 6.3% Carbowax 20M on a Gas-Chrom Z 30/60, at a column temperature of 200°. *n*-Butyllithium, as a 2.04 *M* solution in hexane, was purchased from Ventron Co., Alfa Products, Beverly, Mass. Liquid ammonia, obtained from the Matheson Co., E. Rutherford, N.J., was dried prior to use by distillation from potassium metal. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride immediately prior to use. Triphenylphosphineacetylmethylene (**3**) was prepared as described previously.[11]

Attempted Formation and Benzylation of Potassiotriphenylphosphineacetylmethylene (4, M = K). In a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer and a dry ice condenser was prepared 0.032 mol of potassium amide from 0.032 g-atom of potassium metal and a catalytic amount of Fe(NO$_3$)$_3$·9H$_2$O in 250 ml of anhydrous liquid ammonia. To this amide suspension was added 5.0 g (0.016 mol) of solid triphenylphosphineacetylmethylene (**3**) and the reaction mixture was stirred for 1 hr to ensure complete dissolution of **3** and its conversion into the anticipated ylide anion. Then 5.13 g (0.045 mol) of benzyl chloride in 30 ml of anhydrous ether was added. The purple color associated with stilbene formation[27] was observed, indicating the presence of excess potassium amide. The reaction mixture was stirred for 1 hr before neutralization with excess solid ammonium chloride. The liquid ammonia was evaporated and replaced with 250 ml of anhydrous ether. The resulting suspension was poured over a slurry of 15 ml of 12 *N* HCl and 150 g of ice and stirred until dissolution was complete. The ethereal layer was separated and the acidic aqueous solution was extracted twice with 150-ml aliquots of ether. The combined ethereal fractions were dried ($MgSO_4$) and concentrated to leave 4.1 g of recovered benzyl chloride. The acidic aqueous solution was then adjusted to pH 11 with 10% aqueous potassium hydroxide and extracted three times with 150-ml portions of chloroform. The combined chloroform extracts were dried ($MgSO_4$) and concentrated to give 2.4 g (57%) of acetonyldiphenylphosphine oxide (**5**). The analytical sample, recrystallized from benzene–heptane, had mp 127.5–129° (lit.[28] 127–129°); ^1H NMR ($CDCl_3$) δ 7.76 (m, 10, phenyl) 3.64 (d, 2, CH_2), and 2.32 (s, 3, CH_3); ir ($CHCl_3$) 5.84 (C=O) and 8.25 μ (P=O).

A reaction similar to that described above was repeated except that benzyl chloride was omitted. The reaction mixture was processed in the same manner to afford a 42% yield of **5**.

Attempted Isolation of an Iminophosphorane Intermediate. Treatment of **3** (0.008 mol) with 0.016 mol of potassium amide in 150 ml of liquid ammonia for 1 hr was followed by replacement of the liquid ammonia with 150 ml of anhydrous ether. This ethereal suspension was filtered, and the ether evaporated. The ^1H NMR spectrum of the resulting ether-soluble solid showed the presence of acetonyldiphenylphosphine oxide (**5**) along with diphenylphosphinic amide (**6**). Recrystallization of this solid from benzene afforded 0.31 g of amide **6**. The solid remaining after filtering the ethereal suspension was digested in chloroform. The chloroform solution was concentrated and the resulting crude solid was recrystallized from benzene to give an additional 0.47 g of **6**, bringing the total yield of **6** to 0.78 g (44%): mp 163.5–164.5° (lit.[29a–e] values vary between 160 and 168°); ^1H NMR ($CDCl_3$) δ 7.76 (m, 10, phenyl) and 3.84 (s, 2, NH_2).

Anal. Calcd for $C_{12}H_{12}NOP$: C, 66.36; H, 5.57; N, 6.45. Found: C, 66.41; H, 5.66; N, 6.56.

General Procedure for Formation of Ylide Anion 4 (M = Li) and Reactions with Various Electrophiles. A 5.00-g (0.016 mol) sample of **3** was dissolved in 300 ml of anhydrous THF under a nitrogen atmosphere. The solution was cooled by means of a dry ice–acetone bath and then 9.23 ml (0.019 mol) of *n*-butyllithium in hexane was added. The red-brown ylide anion solution was stirred for 20 min before addition of 0.019 mol of the appropriate electrophile as a solution in anhydrous THF. The reaction mixture was stirred for 1 hr at −78° and then allowed to warm to room temperature. The dark ylide anion color was discharged either at −78° or during the warm-up period. The resulting orange-yellow solution was poured into 300 ml of water–ether (2:1) and stirred for 5 min. The ethereal layer was separated and the basic aqueous solution was extracted three times with 150-ml portions of chloroform. All the ethereal and chloroform extracts were combined, washed with 10% aqueous sodium chloride, dried ($MgSO_4$), and concentrated to give usually an oil, which solidified upon standing or when triturated with ether or ether–hexane. The crude products were recrystallized from appropriate solvents (Table I).

Reaction of **4** (0.019 mol) with 0.02 mol of methyl iodide produced 6.71 g of light yellow solid, mp 165–209°. Several recrystallizations afforded 6.0 g of solid consisting of starting ylide **3**, the desired C-methylated ylide, and O-methylated phosphonium iodide as evidenced by ^1H NMR spectroscopy.

Treatment of **4** (0.019 mol) with 0.02–0.04 mol of trimethylchlorosilane failed to discharge the ylide anion color after 2 hr at 25°. When the reaction employing the lesser amount of silyl halide was processed, ylide **3** was recovered in 64% yield. When 0.04 mol of halide was used, there was isolated 48% of acetonyltriphenylphosphonium chloride, mp 234–237° (lit.[11] 237–238°). The ^1H NMR spectrum of this material was identical with that of an authentic sample.

Formation and alkylation of ylide anion **10** was carried out in a manner essentially identical with that described for **4**.

In the reactions of **4** with 2-cyclohexenone and chalcone, ^1H NMR analysis of the crude product mixtures indicated that only minor amounts (<10%) of conjugate addition products may have been present.

Attempts to convert **4** into cuprate derivative **15** were carried out by first preparing 7 mmol of **4** in 150 ml of THF and then adding 7 mmol of cuprous iodide, cuprous *tert*-butoxide,[24a,b] or cuprous cyanide at −78°. After 2–4 hr a 7-mmol sample of 2-cyclohexone was added via syringe and the reaction allowed to warm to 25° and stir for 2 hr. The reaction mixtures were processed as above and the crude products analyzed by TLC and ^1H NMR. In each case the major product was the 1,2 adduct **14g**.

Elemental analyses and ^1H NMR spectra of all products (Table II) were consistent with the assigned structures.

1-Phenyl-1-octen-3-one (13a) and 1-(3,4-Dichlorophenyl)-1,6-heptadien-3-one (13b). Ylide anion **4** (0.016 mol) was alkylated as described above with 3.88 g (0.021 mol) of *n*-butyl iodide to give, after concentration of the organic extracts, 6.0 g (98%) of crude triphenylphosphinehexanoylmethylene as an oil: ^1H NMR ($CDCl_3$) δ 7.60 (m, 15, phenyl), 3.80 (d, 1, $-P^+C^-H-$) and 1.60 (m, 11, *n*-C_5H_{11}). A 3.8-g (0.010 mol) sample of this crude product and 1.06 g (0.010 mol) of benzaldehyde in 30 ml of Me_2SO was stirred at 50–55° (oil bath) for 19 hr under a nitrogen atmosphere. After cooling, the reaction mixture was poured into 150 ml of cold water and a white solid separated. To this suspension was added 100 ml of hexane, the mixture was stirred for 10 min, and undissolved solid was collected by suction filtration. Recrystallization of this solid from acetone–heptane gave 1.42 g of triphenylphosphine oxide. The hexane layer was separated and the aqueous solution extracted once with 100 ml of hexane. The combined hexane extracts were dried ($MgSO_4$) and concentrated to give a red oil which was vacuum distilled at 145–150° (0.55 mm) to give a yellow distillate which partially crystallized. This semisolid was recrystallized from methanol–water to give 1.28 g (63% based on **4**) of predominantly *trans*-1-phenyl-1-octen-3-one (**13a**): mp 44.5–46.5° (lit.[30] 47°); ^1H NMR ($CDCl_3$) δ 7.45 (m, 6, $=CHC_6H_5$), 6.70 (d, 1, $=CHCO$, $J_{\text{trans}} = 16$ Hz), 2.64 (t, 2, $COCH_2$), 1.45 [m, 6, $-(CH_2)_3-$], and 0.91 (t, 3, CH_3); ir ($CHCl_3$) 5.93 (s-cis C=O), 6.05 (s-trans C=O), and 6.19 μ (conjugated C=C).

Alkylation of **4** (0.032 mol) with 0.036 mol of allyl bromide produced, after concentration of the organic extracts, a quantitative yield of crude triphenylphosphine(4-pentenoyl)methylene (**9b**) as a light brown oil. A solution of 7.38 g (0.020 mol) of this crude product and 3.50 g (0.020 mol) of 3,4-dichlorobenzaldehyde in 35 ml of Me_2SO was stirred at 55° for 18 hr under a nitrogen atmosphere. Following the same procedure as described above, 2.79 g of triphenylphosphine oxide was isolated. The original hexane layer was separated, and the aqueous solution was then extracted four times with 100-ml aliquots of ether. The combined organic extracts were dried ($MgSO_4$) and concentrated to give 5.34 g of yellow oil, which was vacuum distilled at 145–150° (0.15 mm) to give 3.03 g (59% based on **4**) of predominantly *trans*-1-(3,4-dichlorophenyl)-1,-6-heptadien-3-one (**13b**). The ^1H NMR spectra of this material indicated the presence of ca. 10% of triphenylphosphine oxide as a contaminant: ^1H NMR ($CDCl_3$) δ 7.50 (m, 6.55, $=CHC_6H_5$), 6.70 (d, 1, $C=CHCO$, $J_{\text{trans}} = 16$ Hz), 5.90 (m, 1, $=CH$), 5.10 (m, 2, $C=CH_2$), and 2.6 (m, 4, $-CH_2CH_2-$); ir (neat), 5.90 (s-cis C=O), 6.00 (s-trans C=O), and 6.19 μ (conjugated C=C).

4,5-Benzotropone (16). A solution of 0.008 mol of **4** was prepared as described above and a solution of 1.23 g (0.009 mol) of *o*-phthalaldehyde in THF was added. The reaction mixture was stirred for 1 hr at −78°, then allowed to warm to room temperature. The resulting dark orange solution was poured into 150 ml of water–ether (2:1) and stirred. The organic phase was separated and the aqueous solution was extracted twice with 75-ml portions of chloroform. The organic extracts were combined, washed with 10% aqueous sodium chloride, dried ($MgSO_4$), and concentrated to give a dark yellow oil. TLC analysis [acetone–benzene (1:1)] of the reaction mixture indicated the presence of four products. The presence of triphenylphosphine oxide, *o*-phthalaldehyde, and phthalic acid was detected by comparison of their R_f values with those of authentic samples. The reaction mixture was chromatographed on silica gel to afford 0.12 g of pure 4,5-benzotropone: mp 66–67° (lit.[31] 65–66°); ^1H NMR ($CDCl_3$) δ 7.66 (m, 4, phenyl), 7.44 (d, 2, H_2 and H_7), and 6.7 (d, 2, H_3 and H_6).

Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.63; H, 5.15.

The above reaction was repeated and the yield of 4,5-benzotropone in the resulting crude product mixture was shown to be 49% by VPC using chalcone as the internal standard.

Registry No.—**3** charged form, 29942-64-1; **3** uncharged form, 1439-36-7; **4** (M = Li) charged form, 38938-34-0; **4** (M = Li) uncharged form, 38938-46-4; **5**, 1733-52-4; **6**, 5994-87-6; **9a** charged form, 57362-41-1; **9a** uncharged form, 16640-69-0; **9b** charged form, 38938-47-5; **9b** uncharged form, 38938-35-1; **11a** charged form, 57362-42-2; **11a** uncharged form, 57362-43-3; **11b** charged form, 57362-44-4; **11b** uncharged form, 57362-45-5; **12** charged form, 57362-46-6; **12** uncharged form, 57362-47-7; **13a**, 29478-39-5; **13b**, 57362-48-8; **14a** charged form, 57362-49-9; **14a** uncharged form, 57362-50-2; **14b** charged form, 57362-51-3; **14b** uncharged form, 57362-52-4; **14c** charged form, 38938-48-6; **14c** uncharged form, 38938-36-2; **14d** charged form, 57362-53-5; **14d** uncharged form, 57362-54-6; **14e** charged form, 57362-55-7; **14e** uncharged form, 57362-56-8; **14f** charged form, 57362-57-9; **14f** uncharged form, 57362-58-0; **14g** charged form, 57362-59-1; **14g** uncharged form, 57362-60-4; **14h** charged form, 57362-61-5; **14h** uncharged form, 57362-62-6; **16,** 4443-91-8; **17** charged form, 57362-63-7; **17** uncharged form, 57362-64-8; potassium amide, 17242-52-3; *n*-butyllithium, 109-72-8; methyl iodide, 74-88-4; trimethylchlorosilane, 75-77-4; *n*-butyl iodide, 542-69-8; trihhenylphosphinehexanoylmethylene charged form, 57362-65-9; triphenylphosphinehexanoylmethylene uncharged form, 33803-58-6; *o*-phthalaldehyde, 643-79-8.

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Atomic Oxygen. V. Reactions of Enol Ethers with Oxygen (^{3}P) Atoms[1]

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The products of the gas-phase reactions of ground state (^{3}P) oxygen atoms with methyl vinyl ether, ethyl vinyl ether, 2-methoxypropene, 1-methoxy-2-methylpropene, 2,3-dihydrofuran, and dihydropyran are reported. The oxygen atoms were generated by the mercury photosensitized decomposition of nitrous oxide. The reactions produced alkoxyoxiranes, α-alkoxycarbonyl compounds, esters, and fragmentation products. Novel alkoxy radical rearrangements and a reinvestigation of the acid-catalyzed reaction between 3-hydroxy-3-methyl-2-butanone and methanol are reported.

The reactions of atomic oxygen are of continuing interest because of their application to mechanisms of photochemical air pollution,[2] upper atmosphere chemistry,[3] and combustion. Oxygen atom reactions have also been applied to the synthesis of new or labile organic compounds. For example, 3-butenal is produced by reaction of 1,3-butadiene with oxygen (^{3}P) atoms.[4]

Ground state (^{3}P) oxygen atoms react with olefins of formula C_nH_{2n} to produce epoxides, aldehydes, and ketones of formula $C_nH_{2n}O$. Cvetanovic[5] has proposed that O(^{3}P) atoms add to olefins to form short-lived carbon–oxygen 1,3-biradicals. These biradicals can either close to epoxides or rearrange to aldehyde and ketones. The 1,2 migration of a hydrogen atom is intramolecular, but alkyl groups become at least partially detached during rearrangement. The rearrangement of hydrogen atoms and alkyl radicals in 1,3-biradicals is significant, because these groups do not commonly migrate in monoradical systems.

It was expected that reaction of atomic oxygen with enol ethers would produce enol ether epoxides (or alkoxyoxiranes). Four methods have been applied to the synthesis of simple enol ether epoxides: (a) reaction of diazomethane with esters,[6] (b) epoxidation of enol ethers with peracids,[7,8] (c) reaction of α-halocarbonyl compounds with sodium methoxide,[9] and (d) base-induced ring closure of alkoxy-substituted chlorohydrins.[10] Each of these alkoxyoxirane syntheses has disadvantages.

Reaction Conditions. In this study, conditions for the gas-phase production and reaction of atomic oxygen were derived from the pioneering work of Cvetanovic and coworkers.[5] Ground state (^{3}P) oxygen atoms were produced by the mercury photosensitized decomposition of nitrous