*Anal.* Calcd for $C_{13}H_{11}BrO$: C, 59.4; H, 4.18. Found: C 59.7; H, 4.08.

*endo*-7-Methyl-*exo*-7-phenoxybicyclo[3.2.0]hept-2-en-6-one (V).—V was prepared in 69% yield: bp 118° (0.2 mm); ir 1776 (C=O) and 1597 $cm^{-1}$ (C=C).

*Anal.* Calcd for $C_{14}H_{14}O_2$: C, 78.5; H, 6.54. Found: C, 78.68; H, 6.85.

Bromine was added slowly, cautiously, and dropwise from a small syringe to a 30% solution of V in $CCl_4$ in an nmr tube. This addition was done intermittently and continued until the nmr spectrum revealed no resonance for the vinyl protons. During the addition, the methyl singlet at $\delta$ 1.26 began to decrease in intensity and a new singlet at $\delta$ 1.56 began to appear. Eventually, only the new methyl singlet was present.

*endo*-7-Phenoxybicyclo[3.2.0]hept-2-one (VI).—Concentration of the filtrate and recrystallization from hexane afforded a 65% yield of VI: mp 55–56°; ir 1789 (C=O) and 1597 $cm^{-1}$ (C=C).

*Anal.* Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Found: C, 78.12; H, 6.06.

**Cycloadditions of Phenylmethyl- and Phenylethylketenes with Cyclopentadiene.**—A 0.2-mol portion of the ketene in 50 ml of dry hexane was added dropwise to a 0.8-mol portion of fresh cyclopentadiene in 200 ml of hexane. After the addition was complete, the reaction mixture was heated to reflux until the yellow color of the ketene disappeared (6–10 hr). Concentration and recrystallization from ether afforded the pure cycloadducts.

*exo*-7-Methyl-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (III).—III was obtained in 85% yield: mp 26–30°; ir 1773 (C=O) and 1603 $cm^{-1}$ (C=C).

*Anal.* Calcd for $C_{14}H_{14}O$: C, 84.85; H, 7.13. Found: C, 84.9; H, 7.16.

Bromination in an nmr tube of III, as described above, resulted in the disappearance of the vinyl proton resonance but produced no change in the methyl singlet. However, on an expanded portion of the spectrum, the methyl resonance at $\delta$ 1.61 could be seen to disappear and a new singlet appear at $\delta$ 1.63.

*exo*-7-Ethyl-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (IV).—An 83% yield of IV was obtained with mp 43.5–44°; ir 1761 (C=O) and 1592 $cm^{-1}$ (C=O).

*Anal.* Calcd for $C_{15}H_{16}O$: C, 84.9; H, 7.55. Found: C, 85.2; H, 7.67.

**General Procedure for Phenylmethylketene Cycloadditions.**—A solution of 0.06 mol of phenylmethylketene in 0.5 mol of olefin was refluxed overnight. The unreacted olefin was removed on a rotoevaporator. The isomer distribution was determined by nmr and vpc after mixing the reactants during the reflux period and after concentration of the reaction solution. The isomer distributions were the same in all three determinations in every instance. The concentrated reaction solution was fractionally distilled under reduced pressure. The yields were based on the total *endo*- and *exo*-methyl isomers.

2-Methyl-2-phenyl-3-ethoxycyclobutanone (VII).—An 82% yield was obtained at 95° (0.6 mm): ir 1780 $cm^{-1}$ (C=O): nmr ($CCl_4$) (both isomers) $\delta$ 0.8 (t, 2.1 H), 1.15 (t, 0.9 H), 1.39 (s, 1 H), 1.4 (s, 2 H), 3.0 (m, 4 H), 3.8 (t, 0.7 H), 4.1 (t, 0.3 H), and 6.95 (m, 5 H).

*Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.5; H, 7.84: Found: C, 76.37; H, 7.79.

8 Methyl-8-phenyl-2-oxabicyclo[4.2.0]octan-7-one (VIII).—A 77% yield was obtained at 110° (at 0.3 mm): ir 1765 $cm^{-1}$ (C=O); nmr ($CCl_4$) (both isomers) $\delta$ 1.5 (m, 7 H), 1.4 and 1.55 (two singlets out of multiplet corresponding to *endo*- and *exo*-methyl isomers respectively; 1.7 *exo*-/*endo*-methyl ratio), 3.4 (m, 3 H), 4.2 (d, 0.6 H), 4.35 (d, 0.4 H), and 7.1 (m, 5 H).

*Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.8; H, 7.42. Found: C, 77.67; H, 7.67.

8-Methyl-8-phenylbicyclo[4.2.0]octan-7-one (IX).—A 43% yield was obtained at 115° (0.3 mm): ir 1780 $cm^{-1}$ (C=O); nmr ($CCl_4$) (both isomers) $\delta$ 1.3 (s, *endo*-methyl, 1 H), 1.6 (s, *exo*-methyl, 2 H), 1.45 (m, 11 H, the two methyl singlets were a part of this multiplet), 2.5 (m, 1 H), 3.55 (m, 1 H), and 7.2 (m, 5 H).

*Anal.* Calcd for $C_{15}H_{18}O$: C, 83.7; H, 8.84. Found: C, 83.92; H, 8.34.

10-Methyl-10-phenylbicyclo[6.2.0]decan-9-one (X).—A 41% yield was obtained at 120° (0.35 mm): ir 1780 $cm^{-1}$ (C=O); nmr ($CCl_4$) (both isomers) $\delta$ 1.4 (s, *endo*-methyl, 1.4 H), 1.6 (s, *exo*-methyl, 1.6 H), 1.45 (m, 16 H, the two methyl singlets were a part of this multiplet), 3.3 (m, 1 H), and 7.3 (m, 5 H).

*Anal.* Calcd for $C_{17}H_{22}O$: C, 84.3; H, 9.46. Found: C, 84.1; H, 9.58.

**Registry No.**—I, 27849-05-4; II, 28291-19-2; III, 27849-04-3; IV, 28538-79-6; V, 28538-80-9; VI, 28538-81-0; VII (ethoxy/methyl-*cis*), 28538-82-1; VII (ethoxy/methyl-*trans*), 28538-89-8; VIII (*endo*-methyl), 28538-83-2; VIII (*exo*-methyl), 28538-90-1; IX (*endo*-methyl), 28607-65-0; IX (*exo*-methyl), 28538-91-2; X (*endo*-methyl), 28538-84-3; X (*exo*-methyl), 28607-67-2.

**Acknowledgment.**—Support for this investigation by the Robert A. Welch Foundation, the National Science Foundation (GP-14016), and a North Texas State University Faculty Research Grant is gratefully acknowledged.

# Reactions of Phosphorus Compounds. XXIV.[1] Preparation and Reactions of Phosphonium Betaines

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*Received October 28, 1970*

A number of active methylene species (dibenzoylmethane, ethyl benzoylacetate, benzoylacetone, dimedon, ethyl acetoacetate, acetylacetone, and diethyl malonate) have been phosphonioethylated with vinyltriphenylphosphonium bromide. A correlation was observed between acidity of the active methylene moiety and ease of di- *vs.* monophosphonioethylation. The monophosphonioethylated salts obtained were converted into the corresponding betaines, on treatment with base, and isolated. Methylation of the betaines was accomplished. Fusion of the betaines produced 1,1-disubstituted cyclopropanes and/or 2,3-disubstituted 4,5-dihydrofurans.

In 1964 phosphonioethylation reactions were accomplished for the first time[3,4] by allowing compounds with replaceable protons to react with vinylphosphonium bromides (1).

$$ZH + CH_2{=}CH\overset{+}{P}R_3\ Br^- \longrightarrow ZCH_2CH_2\overset{+}{P}R_3\ Br^-$$
$$\text{1a, R = } n\text{-Bu} \quad \text{b, R = Ph} \qquad \text{2}$$

Although the adducts from acetoacetic ester and diethyl malonate were prepared and isolated as their

(1) Previous paper in this series: E. E. Schweizer and A. T. Wehman, *J. Chem. Soc. C*, in press.

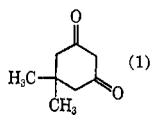
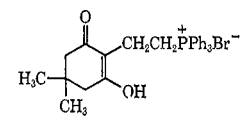
(2) From the Ph.D. Dissertation of C. M. Kopay.

(3) P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

(4) E. E. Schweizer and R. D. Bach, *ibid.*, **29**, 1746 (1964).

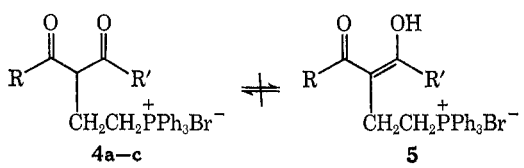
TABLE I

PHOSPHONIOETHYLATION WITH VINYLTRIPHENYLPHOSPHONIUM BROMIDE

| | Addendum (mol) | Solvent | Temp, °C | Time, hr | Adduct | Yield, % |
|---|---|---|---|---|---|---|
| 3a | $PhCOCH_2COPh$ (1) | *tert*-BuOH | 30 | 48 | $(PhCO)_2CHCH_2CH_2\overset{+}{P}Ph_3Br^-$ **4a** | 97 |
| 3b | $PhCOCH_2CO_2Et$ (3) | DMF | 25 | 16 | $\begin{matrix}PhCO\\EtO_2C\end{matrix}>CHCH_2CH_2\overset{+}{P}Ph_3Br^-$ **4b** | 95 |
| 3c | $PhCOCH_2COCH_3$ (3) | DMF | 28 | 20 | $\begin{matrix}PhCO\\CH_3CO\end{matrix}>CHCH_2CH_2\overset{+}{P}Ph_3Br^-$ **4c** | 76 |
| 3d |  (1) | *tert*-BuOH | 30 | 40 |  **4d** | 81 |
| 3e | $CH_3COCH_2CO_2Et$ (1) | $Et_2O$–$CH_3CN$ (9:1) | 25 | 16 | $\begin{matrix}CH_3CO\\EtO_2C\end{matrix}>C(CH_2CH_2\overset{+}{P}Ph_3Br^-)_2$ **4e** | 95 |
| 3f | $CH_3COCH_2COCH_3$ (1) | DMF | 25 | 18 | $(CH_3CO)_2C(CH_2CH_2\overset{+}{P}Ph_3Br^-)_2$ **4f** | 76 |
| 3g | $EtO_2CCH_2CO_2Et$ (1) | Glyme | 25 | 24 | $(EtO_2C)_2C(CH_2CH_2\overset{+}{P}Ph_3Br^-)_2$ **4g** | 73 |

tetraphenylborate derivatives, no further reactions were undertaken with these reagents.[3] We wish to report the reactions of a number of $\beta$ diketones and $\beta$-keto esters with vinyltriphenylphosphonium bromide (**1b**) and the synthetic utility of the phosphonium betaines produced from the initially formed phosphonioethylated species.

Phosphonioethylation of dibenzoylmethane (**3a**), ethyl benzoylacetate (**3b**), benzoylacetone (**3c**), and dimedon (**3d**) with **1b** and a catalytic amount of $K^+O^-$-*tert*-Bu gave good yields of 1:1 adducts (**4a–d**) (Table I). The $^1H$ nmr spectra of phosphonium salts (**4a–c**) in $CDCl_3$ exhibited a characteristic triplet ($\delta$ 5.8–6.3 ppm, $J$ = 7.0 Hz) assigned to the methine proton (>CH-$\overset{+}{C}H_2CH_2PPh_3$). The presence of any enol tautomer was not detected.[5] The enol tautomer **5** would be a nonplanar, tetrasubstituted ethylene unsuitable for intramolecular hydrogen bonding.[6] The adduct of dimedon (**4d**) was completely in the enol form as shown by $^1H$ nmr. The ir spectrum showed a low carbonyl stretching frequency (1590 $cm^{-1}$), attributed to an $\alpha,\beta$-unsaturated ketone and a hydroxyl stretching frequency (3430 $cm^{-1}$).



**4a–c** **5**

Ethyl acetoacetate (**3e**), acetylacetone (**3f**), and diethyl malonate (**3g**) when treated with **1b** gave good yields of 2:1 adducts (Table I). All attempts to prepare 1:1 adducts failed or gave complex mixtures of 1:1 adducts, 2:1 adducts, and starting material.

It appears that the inability to readily isolate 1:1 adducts from the reactions of active methylene species with the vinyl salt **1b** may be predictable from the acidity[7] of the active methylene precursors employed. Compounds **3e–g** all have $pK_a$'s equal to or greater than acetylacetone (**3f**) and thus the stabilized anion produced after monophosphonioethylation is nucleophilic enough to undergo ready diphosphonioethylation. The anion of the monophosphonioethylated species produced from active methylene reagents whose original $pK_a$'s are less than (or equal to) benzoylacetone (**3c**) is of such low nucleophilicity that the reaction is stopped readily at the monoadduct.

When the phosphonium salts **4a** and **4b** were treated with 1 equiv of butyllithium in DMF, nearly quantitative yields of phosphonium betaines **6a** and **6b** were obtained. The benzoylacetone adduct **4c** was found to undergo cleavage in the presence of BuLi, and considerable amounts of 1-(3-benzoyl)-*n*-propyltriphenylphosphonium bromide, arising from attack of butyllithium at the acetyl carbonyl, were isolated. To obviate this cleavage, the base used for the conversion of **4c** to **6c** was sodium hydride. The dimedon adduct **4d**, upon conversion to its betaine, yielded only a gummy oil which could not be crystallized or purified (Table II). The ir spectra of the betaines showed a shift in the carbonyl stretching frequency of ~200 $cm^{-1}$. The 60-MHz $^1H$ nmr indicated the loss of the low field proton, previously assigned to the methine proton of the phosphonium salts, and the $^{31}P$ nmr showed phosphorus resonance at −20 ppm (relative to 85% phosphoric acid) which is indicative of an open betaine

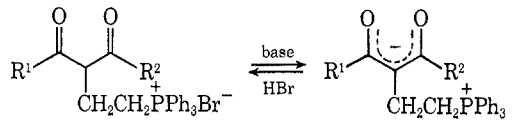
(5) The phosphonium salts were insoluble in nonpolar solvents, and spectra in DMF, DMSO, $CHCl_3$, $AsCl_3$, and $F_3CCO_2H$ did not reveal the presence of any **5**.

(6) P. Rumpf and R. L. Riviere, *C. R. Acad. Sci.*, **244**, 902 (1957).

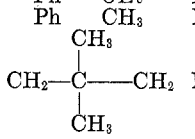
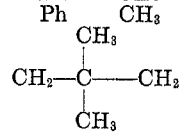
(7) J. F. King, "Technique of Organic Chemistry," Vol. VI, K. W. Bentley, Ed., Interscience, New York, N. Y., 1963, p 357.

TABLE II

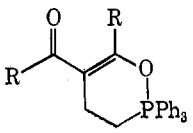
CONVERSION OF PHOSPHONIUM SALTS TO PHOSPHONIUM BETAINES



4 6

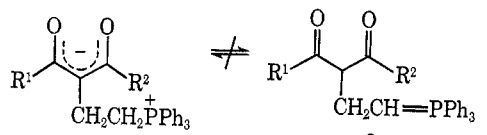
| | R¹ | R² | Base-solvent | | R¹ | R² |
|---|---|---|---|---|---|---|
| 4a | Ph | Ph | BuLi-DMF | 6a | Ph | Ph |
| 4b | Ph | OEt | BuLi-DMF | 6b | Ph | OEt |
| 4c | Ph | $CH_3$ | NaH-Benzene | 6c | Ph | $CH_3$ |
| 4d |  | | NaH-$CH_3CN$ | 6d |  | |

structure, rather than a pentacovalent phosphorus species such as **7**.[8]



7

When the betaines **6a–d** were acidified with 10% aqueous HBr, they reverted quantitatively to their respective phosphonium salts **4a–d**. To determine whether there existed an equilibrium between betaine and the tautomeric ylide **8**, betaines **6a–d** were treated with $D_2O$ and examined by $^1H$ nmr for deuterium exchange in the position $\alpha$ to phosphorus. After 96 hr at 25° no exchange had taken place, which excludes the possibility of the existence of the ylide tautomer **8**.



8

Alkylation of betaines **6a–d** with $CH_3I$ gave good yields of only O- or only C-alkylated products; only in the case of **9d** was there observed any mixture of C- and O-alkylation products (Table III).

In light of the work of Denney and Smith[9] on the pyrolysis of phosphonium carboxylates and that of Freeman[10] on the conjugate addition of the Wittig reagent, phosphonium betaines **6a–d** appeared to be potential precursors to 4,5-dihydrofurans or 1,1-disubstituted cyclopropanes (Scheme I).

Fusion pyrolysis of **6a** gave a complex mixture of products, 2-phenyl-3-benzoyl-4,5-dihydrofuran (**11a**), dibenzoylmethane (**3a**), phenacyltriphenylphosphorane (**14**), and triphenylphosphine (Table IV). The formation of **11a**, pathway a, may be envisioned as the attack of the oxygen enolate anion in an SNi displacement of $Ph_3P$. By pathway b, the oxygen enolate would abstract the proton $\alpha$ to phosphorus forming the phosphorane intermediate **15**. $\beta$ elimination of the phosphorane would give **3a**. Intramolecular benzoylation of **15** to **16**, followed by $\beta$ elimination, would account

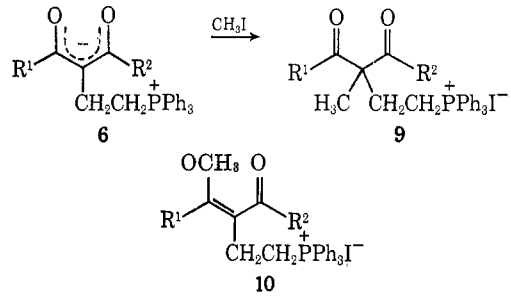
(8) J. R. Van Wazer and J. A. Letcher in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffin, Ed., Interscience, New York, N. Y., 1967, p 169.

(9) D. B. Denney and T. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).

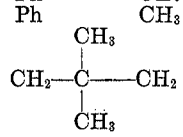
(10) J. P. Freeman, *ibid.*, **31**, 538 (1966).

TABLE III

ALKYLATION OF PHOSPHONIUM BETAINES WITH $CH_3I$



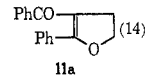
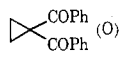
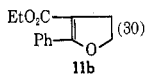
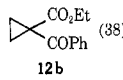
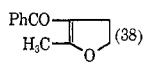
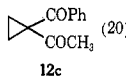
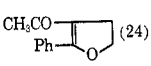
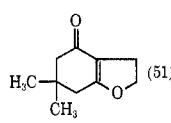
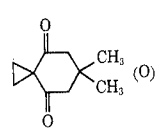
6 9 10

| | R¹ | R² | | % yield | | % yield |
|---|---|---|---|---|---|---|
| 6a | Ph | Ph | 9a | 0 | 10a | 87[a] |
| 6b | Ph | OEt | 9b | 100[a] | 10b | 0 |
| 6c | Ph | $CH_3$ | 9c | 78[a] | 10c | 0 |
| 6d |  | | 9d | 82[b] | 10d | 18[b] |

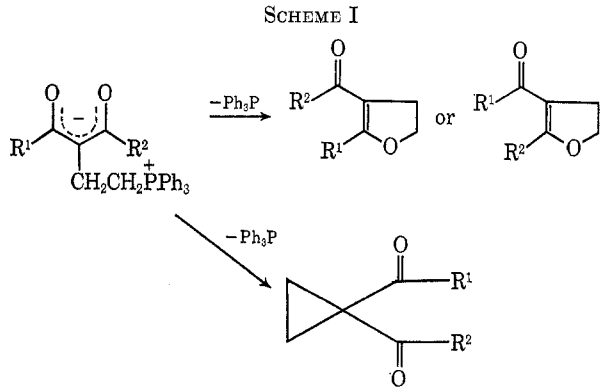
[a] Overall isolated yield. [b] Isolated yield was 78%.

TABLE IV

PYROLYSIS OF BETAINES BY FUSION

| Betaine | Temp, °C (mm) | Dihydrofuran (%) | Cyclopropane (%) | Other products (%) |
|---|---|---|---|---|
| 6a | 280 (0.1) |  (14) 11a |  (0) 12a | $PhCOCH_2COPh$ (10) 3a; $PhCOCHPPh_3$ (6) 14 |
| 6b | 200 (0.1) |  (30) 11b |  (38) 12b | |
| | |  (38) 11c | | |
| 6c | 200 (0.1) | |  (20) 12c | |
| | |  (24) 11c′ | | |
| 6d | 220 (0.1) |  (51) 11d |  (0) 12d | |

SCHEME I

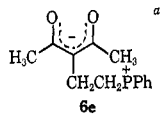
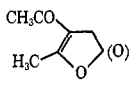
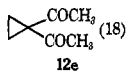
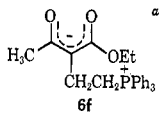
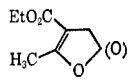
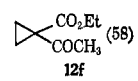


for phosphorane **14**. The acrylophenone was not isolated (Scheme II).

The fusion pyrolysis of **6b** gave a mixture of 2-phenyl-3-carboethoxy-4,5-dihydrofuran (**11b**) and ethyl ben-

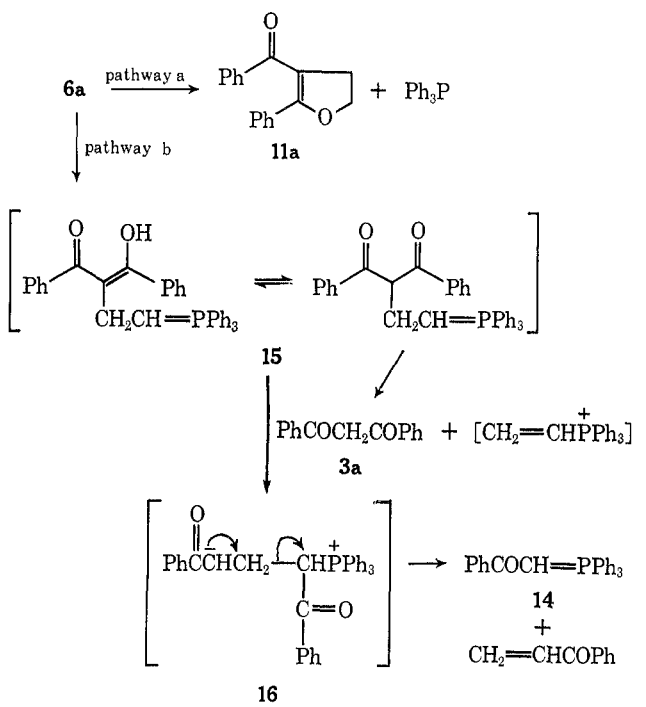
TABLE V

PYROLYSIS OF BETAINES

| Betaine | Method of pyrolysis (temp) | Dihydrofuran (%) | Cyclopropane (%) |
|---|---|---|---|
| 6a | Vpc (300) | 11a (41) | 12a (0) |
| 6b | Vpc (300) | 11b (0) | 12b (84) |
| 6c | Vpc (300) | 11c (0) | 12c (72) |
| 6d | Vpc (300) | 11d (74) | 12d (0) |
|  6e [a] | Benzene (80) |  11e |  12e |
|  6f [a] | Toluene (111) |  11f |  12f |

[a] These betaines were never isolated but prepared from the reaction of the sodium salt of the 1,3 diketone or β-keto ester with 1 equiv of **1b**.

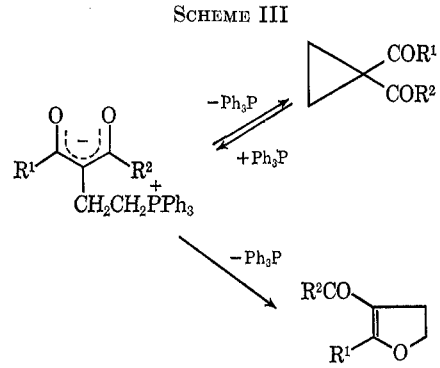
SCHEME II



zoylcyclopropane carboxylate (**12b**) in a total yield of 68%. In this and the subsequent pyrolyses no fragmentation products were observed. Likewise, the pyrolysis of **6c** gave a mixture of dihydrofurans (**11c**, **11c′**) and cyclopropane (**12c**). The mixture of isomeric dihydrofurans (**11c**, **11c′**) were not separable by either vpc or tlc. These dihydrofurans were identified by C and H analysis, molecular weight by mass spectrum, and their characteristic nmr spectrum. The 2-methylfuran **11c** exhibited a methyl resonance (triplet, $J$ = 1.2 Hz) being coupled to the 4-methylene protons, whereas the methyl resonance of **11c′** showed no such coupling. The thermolysis of **11d** gave only dihydrofuran in 51% yield (Table IV).

In an attempt to maximize the yields, the thermolysis of the stable betaines was undertaken in the heated inlet of a gas chromatographic column. The results of these pyrolyses show an increase in the yields of **11a** and **11d**. More striking, however, is the fact that **6b** and **6c** gave only cyclopropanes and no furans as observed previously by the fusion pyrolysis (Table V). This may be accounted for by the fact the cyclopropanes are kinetically controlled products and the furans are the more stable thermodynamically controlled products. This interpretation implies the reversible equilibrium between cyclopropane and betaine. Since pyrolysis by vpc afforded an immediate separation of cyclopropane from $Ph_3P$, there would be little chance for the reverse reaction (cyclopropane to betaine) to occur. In the pyrolysis by fusion $Ph_3P$ was not removed and the reverse reaction (cyclopropane to betaine) could occur, and the thermodynamically more stable furan formed (Scheme III).

SCHEME III



The results of the pyrolysis of the phosphonium betaines in a kinetically controlled process (*i.e.*, vpc pyrolysis–cyclopropane formation) are parallel to and in complete agreement with the results obtained by demercuration of mercurial chlorides[11,12] and our selective alkylations of the betaines (Table III).

In a previous communication[13] we reported on the Lewis base catalyzed isomerization of cyclopropanes to dihydrofurans. It was found that electrophilically 1,1-disubstituted cyclopropanes underwent the isomerization in quantitative yields (Table VI). These results in addition to the isolation and characterization of the phosphonium betaines confirmed the previous speculation on the cyclopropane–betaine equilibrium

(11) K. Ichikawa, O. Itah, T. Kawamura, M. Fujiwara, and T. Ueno, *J. Org. Chem.*, **31**, 447 (1966).

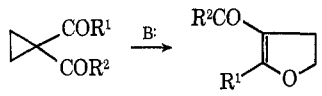
1240 (1968).

(12) K. Ichikawa, O. Itoh, and T. Kawamura, *Bull. Chem. Soc. Japs.*, **41**, 1240 (1968).

(13) E. E. Schweizer and C. M. Kopay, *Chem. Commun.*, 677 (1970).

TABLE VI

ISOMERIZATION OF CYCLOPROPANES TO DIHYDROFURANS



| | R¹ | R² | Base (mol %) | Time,[c] hr | Temp, °C | Product (% yield)[a] |
|---|---|---|---|---|---|---|
| 12b | Ph | OEt | $Ph_3P$ (20) | 7.0 | 200 | 11b (>95) |
| | | | $Et_3N$ (20) | 32.0 | 200 | |
| 12c | Ph | $CH_3$ | $Ph_3P$ (20) | 1.0 | 200 | 11c, 11c′ (57, 43[b]) |
| | | | $Et_3N$ (20) | 28.0 | 200 | 11c, 11c′ (56, 44[b]) |
| 12e | $CH_3$ | $CH_3$ | $Ph_3P$ (20) | 1.0 | 200 | 11e (>95) |
| | | | $Et_3N$ (20) | 30.0 | 200 | 11e (>95) |
| 12f | $CH_3$ | OEt | $Ph_3P$ (20) | 1.0 | 200 | 11f (>95) |

[a] All yields were determined by nmr and checked by vpc. [b] 57 and 56 are the yields of 9c and 43 and 44 the yields of 9c′. [c] The large time differences between $Ph_3P$ and $Et_3N$ do not reflect the relative nucleophilicity of $Ph_3P$ and $Et_3N$, since at 200° the concentration of $Et_3N$ in solution was considerably lower than 20 mol %.

in the formation of 4,5-dihydrofurans from cyclopropanes.

## Experimental Section

**General.**—Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. The proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. The chemical shifts in parts per million ($\delta$) are followed by the splitting pattern (m = multiplet, q = quartet, t = triplet, d = doublet, s = singlet), the number of protons, the coupling constant ($J$), and the assignment of the resonance signal. The $^{31}P$ nmr spectra were obtained on a Varian HR-60 with phosphoric acid (85%) used as an external standard.

Vapor phase chromatography was performed on an F & M Model 700 instrument using a 10% UC-W98 (silicone) on Chromosorb W (60–80 mesh, 12 ft × 0.25 in.) column. Preparative vpc was performed on a Wilkens Aerograph Model A-90P instrument using a 10% UC-W98 (silicone) on Chromosorb W (60–80 mesh, 10 ft × 3/8 in.) column. The internal standard procedure was used in yield determinations. Thin layer chromatography (tlc) was performed with 2 × 8 in. glass plates coated with silica gel G; the coatings thickness was 0.25 mm. The solvents used in tlc were 20% methanol in chloroform (for phosphonium salts), ethyl acetate (for phosphine oxides), and hexane (for phosphines). An iodine chamber was used for developing the spots. Melting points were determined on a Fisher-Johns or a Thomas-Hoover melting point apparatus and are uncorrected.

**1-(3,3-Dibenzoyl)propyltriphenylphosphonium Bromide (4a).**—To a slurry of 35 g (0.094 mol) of vinyltriphenylphosphonium bromide (**1b**) and 21 g (0.094 mol) of 1,3-diphenyl-1,3-propanedione in 400 ml of dry *tert*-BuOH was added 0.5 ml of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. The pasty reaction mixture was stirred vigorously at 30° for 48 hr. The milky white slurry was then poured slowly into 2 l. of anhydrous ether. The solid was filtered and air-dried. Recrystallization from MeOH–$Et_2O$ afforded 54.5 g (97%) of small colorless prisms, mp 265–267°. An analytical sample was obtained by recrystallization from MeOH three times: mp 266–268°; $\nu^{KBr}$ 1680 (s, >=O), 1115 $cm^{-1}$ (s, PC); nmr ($CF_3CO_2H$) 2.37–3.00 (m, 2, $CH_2CH_2P^+Ph_3$), 3.42–4.00 (m, 2, $CH_2CH_2P^+Ph_3$), 6.30 (t, 1, $J$ = 5.5 Hz, >H), 7.1–8.0 (m, 25, $C_6H_5$).

*Anal.* Calcd for $C_{35}H_{30}O_2PBr$: C, 70.83; H, 5.10. Found: C, 70.67; H, 5.26.

**1-(3-Benzoyl-3-carbethoxy)propyltriphenylphosphonium Bromide (4b).**—To a slurry of 27.6 g (0.075 mol) of **1b** and 44.0 g of ethyl benzoylacetate in 50 ml of dry DMF was added 0.5 ml of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. A pale green solution resulted and was stirred at room temperature for 16 hr. The pale green solution was then rapidly poured into 1 l. of anhydrous ether. The ether was decanted from the resulting oil, and the pale yellow oil was dissolved in 100 ml of $CH_2Cl_2$ followed by dropwise addition to a vigorously stirred benzene solution. The resulting solid was filtered and recrystallized from $CH_2Cl_2$–$C_6H_6$, 38 g (95%), mp 104–106°. The solid was found to contain benzene of crystallization, and all attempts to crystallize the compound from a different solvent system only resulted in gummy oils: $\nu^{KBr}$ 1730 (s, ester >=O), 1675 (s, >=O), 1115 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.03 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$), 1.86–2.70 (m, 2, $CH_2CH_2P^+Ph_3$), 3.61–4.70 (m, 2, $CH_2CH_2P^+Ph_3$), 4.08 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 5.88 (t, 1, $J$ = 7.0 Hz, >H), 7.0–7.9 (m, 26, $C_6H_5$).

*Anal.* Calcd for $C_{31}H_{30}O_3PBr \cdot C_6H_6$: C, 69.48; H, 5.67. Found: C, 69.23; H, 5.71.

**1-(3-Acetyl-3-benzoyl)propyltriphenylphosphonium Bromide (4c).**—To a solution of 31.0 g (0.18 mol) of benzoylacetone and 22.1 g (0.06 mol) of **1b** in 50 ml of dry DMF was added 0.5 ml of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. The yellow solution was stirred at room temperature for 20 hr and then quickly poured into 2 l. of anhydrous ether. A gummy oil resulted which was dissolved in 200 ml of $CH_2Cl_2$. The $CH_2Cl_2$ solution was brought to boiling and benzene added until the solution was slightly turbid. The hot solution was allowed to cool slowly to room temperature. The resulting white solid that had crystallized was filtered and washed with 100 ml of cold benzene. Recrystallization from $CH_2Cl_2$–$C_6H_6$ afforded 26.0 g (81%) of a powdery white solid: mp 176–177°; $\nu^{Nujol}$ 1710 (s, >=O), 1660 (s >=O), 1108 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.75–2.67 (m, 2, $CH_2CH_2P^+Ph_3$), 2.25 (s, 3, $COCH_3$), 3.67–4.42 (m, 2, $CH_2CH_2P^+Ph_3$), 6.20 (t, 1, $J$ = 6.5 Hz, >H), 7.1–8.4 (m, 20, $C_6H_5$).

*Anal.* Calcd for $C_{30}H_{28}O_2PBr$: C, 67.82; H, 5.27. Found: C, 68.11; H, 5.40.

**2-(2,6-Dioxo-4,4-dimethylcyclohexyl)ethyltriphenylphosphonium Bromide (4d).**—To a slurry of 14.0 g (0.10 mol) of dimedon and 36.9 g (0.10 mol) of **1b** in 300 ml of dry *tert*-BuOH was added 11.3 g (0.10 mol) of $K^+O^-$-*tert*-Bu. The solution was stirred at 30° for 40 hr and then poured into 2.5 l. of distilled water. The weakly basic solution was made strongly acidic with 48% HBr. Vigorous stirring afforded colorless prisms which were filtered and washed with two 250-ml portions of distilled water. Recrystallization from $CH_2Cl_2$–EtOAc furnished 37.5 g (76%) of small colorless needles: mp 174–175°; $\nu^{KBr}$ 1590 (s, $\alpha,\beta$-unsaturated >=O), 1115 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.03 (s, 6, iso-$CH_3$), 2.17–3.53 (m, 5, $CH_2CH_2P^+Ph_3$ and OH), 2.43 (broad s, 4, $CH_2CO$), 7.5–7.9 (m, 15, $C_6H_5$).

*Anal.* Calcd for $C_{28}H_{30}O_2PBr$: C, 66.01; H, 5.93. Found: C, 66.19; H, 6.27.

**3-Acetyl-3-carbethoxypentane-1,5-bistriphenylphosphonium Bromide (4e).**—To a suspension of 1.30 g (10 mmol) of ethyl acetoacetate and 3.69 g (10 mmol) of vinyltriphenylphosphonium bromide in 10 ml of acetonitrile and 90 ml of anhydrous ether was added 5 drops of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. After being stirred at room temperature for 1 hr, the suspension became gummy, and continuous stirring for 16 hr afforded a fluocculent solid. The white solid was filtered and washed with 100 ml of anhydrous ether. Recrystallization from $CH_2Cl_2$–EtOAc afforded 4.10 g (95%) of small flocculent needles: mp 167–168°; $\nu^{KBr}$ 1725 (s, ester >=O), 1680 (s, >=O), 1105 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.13 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$, 2.14 (s, 3, $COCH_3$), 2.29–2.95 (m, 4, $CH_2CH_2P^+Ph_3$), 3.45–4.47 (m, 4, $CH_2CH_2P^+Ph_3$), 4.12 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 7.5–8.3 (m, 30, $C_6H_5$).

*Anal.* Calcd for $C_{46}H_{46}O_3P_2Br_2$: C, 63.66; H, 5.34. Found: C, 64.02; H, 5.37.

**3,3-Diacetylpentane-1,5-bistriphenylphosphonium Bromide (4f).**—To a solution of 1.00 g (10 mmol) of acetylacetone and

3.69 g (10 mmol) of vinyltriphenylphosphonium bromide in 10 ml of dry DMF was added 5 drops of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. The solution was stirred for 18 hr and then triturated with EtOAc under vigorous stirring. The white powder was filtered and washed with 100 ml of dry ether. Recrystallization from $CH_2Cl_2$–EtOAc afforded 3.10 g (76%) of a white powder: mp 284–286°; $\nu^{KBr}$ 1660 (s, >=O), 1104 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 2.13 (s, 6, $COCH_3$), 2.49–3.28 (m, 4, $CH_2CH_2P^+Ph_3$), 3.28–4.19 (m, 4, $CH_2CH_2P^+Ph_3$), 7.4–8.3 (m, 30, $C_6H_5$).

*Anal.* Calcd for $C_{45}H_{44}O_2P_2Br_2$: C, 64.45; H, 5.29. Found: C, 64.59; H, 5.37.

**3,3-Dicarbethoxypentane-1,5-bistriphenylphosphonium Bromide (4g).**—To a slurry of 1.85 g (10 mmol) of vinyltriphenylphosphonium bromide and 1.30 g (10 mmol) of diethyl malonate in 10 ml of glyme and 5 ml of *tert*-BuOH was added 5 drops of 10% $K^+O^-$-*tert*-Bu-*tert*-BuOH. The slurry was stirred at room temperature, and after 0.5 hr all of the solid had dissolved. After 4 hr, a solid began to precipitated from solution, and stirring was continued for a total of 24 hr. The white solid was filtered and washed with 100 ml of anhydrous ether. Recrystallization from $CH_2Cl_2$–EtOAc afforded 1.80 g (73%) of small flocculent needles: mp 155–157°; $\nu^{KBr}$ 1720 (s, ester >=O), 1105 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.12 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$), 2.17–2.83 (m, 4, $CH_2CH_2P^+Ph_3$), 3.58–4.42 (m, 4, $CH_2CH_2P^+Ph_3$), 4.08 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 7.5–8.2 (m, 30, $C_6H_5$).

*Anal.* Calcd for $C_{47}H_{48}O_4P_2Br_2$: C, 62.82; H, 5.28. Found: C, 62.57; H, 5.26.

**General Procedure for the Preparation of Phosphonium Betaines (6).**—To a solution of 16.8 mmol of phosphonium salt **3** in 50 ml of dry solvent was added 1 equiv of base (Table II). The solution was stirred under a nitrogen atmosphere for 15 min. The yellow solution was then poured into 600 ml of distilled water. Immediately a pale yellow solid formed which was filtered, washed with 200 ml of distilled water, and then washed with 400 ml of anhydrous ether. The pale yellow solid was dried *in vacuo* and then recrystallized from $CH_2Cl_2$–benzene.

**1-(3,3-Dibenzoyl)propyltriphenylphosphonium betaine (6a)**: mp 188–189°; $\nu^{KBr}$ 1570 (w), 1450 (s, CO), 1110 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 2.91–3.83 (m, 4, $CH_2CH_2P^+Ph_3$), 6.6–8.1 (m, 25, $C_6H_5$); $^{31}P$ nmr ($CHCl_3$) −20.1 ppm.

*Anal.* Calcd for $C_{35}H_{29}O_2P$: C, 82.01; H, 5.70. Found: C, 82.03; H, 5.52.

**1-(3-Benzoyl-3-carbethoxy)propyltriphenylphosphonium betaine (6b)**: mp 113–114°; $\nu^{KBr}$ 1600 (s, ester CO), 1470 (s, CO), 1100 $cm^{-1}$ (m, PC); nmr ($CDCl_3$) 0.77 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$), 2.67–4.21 (m, 4, $CH_2CH_2P^+Ph_3$), 3.80 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 7.1–8.2 (m, 20, $C_6H_5$); $^{31}P$ nmr ($CHCl_3$) −21.6 ppm.

*Anal.* Calcd for $C_{39}H_{29}O_3P$: C, 77.48; H, 6.08. Found: C, 77.38; H, 6.30.

**1-(3-Acetyl-3-benzoyl)propyltriphenylphosphonium betaine (6c)**: mp 181–182° dec; $\nu^{Nujol}$ 1550 (m, CO), 1440 (s, CO), 1105 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.77 (s, 3, $COCH_3$), 2.67–3.67 (m, 4, $CH_2CH_2P^+Ph_3$), 7.1–8.0 (m, 20, $C_6H_5$); $^{31}P$ nmr ($CHCl_3$) −21.6 ppm.

*Anal.* Calcd for $C_{30}H_{27}O_2P$: C, 79.97; H, 6.04. Found: C, 79.99; H, 6.18.

**General Procedure for the Treatment of Phosphonium Betaines 6 with HBr.**—To a solution of 100 mg of betaine in 2.0 ml of methanol was added 1.0 ml of 10% HBr. The yellow solution turned colorless immediately. The addition of 20 ml of distilled water, scratching, and chilling furnished the corresponding phosphonium salt.

**General Procedure for the Treatment of Phosphonium Betaines 6 with $CH_3I$.**—A solution of 300 mg of betaine in 10 ml of $CH_3I$ was refluxed for 0.5 hr. The solution had changed from yellow to colorless. The $CH_3I$ solution was then concentrated *in vacuo* and triturated with EtOAc. The white solid was filtered and recrystallized from $CH_2Cl_2$–EtOAc. All filtrates were examined by nmr and tlc for other products and in all cases none were found.

**1-(3-Benzoyl-4-methoxy-4-phenyl)-3-butenyltriphenylphosphonium iodide (10a)**: yield 325 mg (87%); mp 216–218°; $\nu^{KBr}$ 1600 (s, $\alpha,\beta$-unsaturated >=O), 1100 $cm^{-1}$ (s, PO); nmr ($CDCl_3$) 2.51–3.14 (m, 2, $CH_2$ $CH_2CH_2P^+Ph_3$), 3.59 (s, 3, $OCH_3$), 3.33–4.08 (m, 2, $CH_2CH_2P^+Ph_3$), 6.9–8.2 (m, 25, $C_6H_5$).

*Anal.* Calcd for $C_{36}H_{32}O_2PI$: C, 65.63; H, 4.72. Found: C, 65.82; H, 4.76.

**1-(3-Benzoyl-3-carbethoxy)butyltriphenylphosphonium iodide (9b)**: yield 380 mg (100%); mp 85–95°; $\nu^{KBr}$ 1715 (s, ester >=O), 1660 (s, >=O), 1100 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 0.96 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$), 1.73 (s, 3, $CCH_3$), 1.91–2.55 (m, 2, $CH_2CH_2P^+Ph_3$), 3.19–3.92 (m, 2, $CH_2CH_2P^+Ph_3$), 4.08 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 7.2–8.0 (m, 20, $C_6H_5$).

*Anal.* Calcd for $C_{32}H_{32}O_3PI$: C, 61.74; H, 5.18. Found: C, 61.70; H, 5.27.

**1-(3-Acetyl-3-benzoyl)butyltriphenylphosphonium iodide (9c)**: yield 300 mg (78%); mp 168–170°; $\nu^{Nujol}$ 1665 (s, >=O), 1105 $cm^{-1}$ (s, PC); nmr ($CDCl_3$) 1.77 (s, 3, $CCH_3$), 1.78–2.50 (m, 2, $CH_2CH_2P^+Ph_3$), 2.17 (s, 3, $COCH_3$), 2.75–3.72 (m, 2, $CH_2CH_2P^+Ph_3$), 7.2–8.0 (m, 20, $C_6H_5$).

*Anal.* Calcd for $C_{31}H_{30}O_2PI$: C, 62.85; H, 5.10. Found: C, 63.10; H, 5.12.

**2-(1-Methyl-2,6-dioxo-4,4-dimethylcyclohexyl)ethyltriphenylphosphonium iodide (9d) and 2-(2-methoxy-6-oxo-4,4-dimethylcyclohex-1-enyl)ethyltriphenylphosphonium iodide (10d)**: $\nu^{Nujol}$ 1710 (s), 1680 (s), 1590 (w, >=O), 1110 $cm^{-1}$ (s, PC); nmr ($COCl_3$) 0.88 (s, 3, $CCH_3$), 1.13 (s, 3, $CCH_3$), 1.29 (s, 3, $CCH_3$), 1.8–3.5 (m, 16, $CH_2CH_2P^+Ph_3$, $CH_2CO$), 3.98 (s, 3, $OCH_3$), 7.5–8.0 (m, 30, $C_6H_5$).

*Anal.* Calcd for $C_{29}H_{32}O_2PI$: C, 61.06; H, 5.66. Found: C, 61.17; H, 5.60.

**Pyrolysis of 6a.**—In a short-path distillation apparatus 3.40 g (6.65 mol) of 1-(3,3-dibenzoyl)propyltriphenylphosphonium betaine (**6a**) was slowly evacuated to 0.10 mm. The flask was then immersed in a Wood's metal bath at 260° and the distillate was collected in a receiver cooled by Dry Ice. A yellow oil (2.05 g) collected. The oil was chromatographed on Florisil and eluted with benzene. Fraction one afforded a colorless oil. The colorless oil was refluxed overnight with 30 ml of anhydrous $Et_2O$ and 2.0 ml of methyl iodide. Filtration of the white solid and washing with 20 ml of cold $Et_2O$ afforded 450 mg of methyltriphenylphosphonium iodide: mp 193–194°; ir and nmr were identical with those of an authentic sample.

The solvent was then changed to 20% EtOAc–$C_6H_6$. The second fraction collected was concentrated *in vacuo* to 240 mg (14%) of a pale yellow oil. Preparative vpc afforded an analytical sample of 2-phenyl-3-benzoyl-4,5-dihydrofuran (**11a**): $\nu^{neat}$ 1600 (s, >=O), 1220 $cm^{-1}$ (m, vinyl ether); nmr ($CDCl_3$) 3.23 (t, 2, $J$ = 10.5 Hz, $OCH_2CH_2$), 4.55 (t, 2, $J$ = 10.5 Hz, $OCH_2CH_2$), 7.3–8.1 (m, 10, $C_6H_5$); mass spectrum $m/e$ 250.

*Anal.* Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 81.76; H, 5.71.

Elution was continued and the third fraction upon concentration and crystallization from methanol afforded 140 mg (10%) of dibenzoylmethane: mp 72–73°; mixture melting point with an authentic sample showed no depression.

Elution was then started with methanol and the fourth and final fraction was collected. Concentration and treatment with HBr afforded 173 mg (6%) of phenacyltriphenylphosphonium bromide: mp 281–282°; ir and nmr identical with that of an authentic sample. In a separate experiment the phenacyltriphenylphosphorane was isolated and shown to be identical with an authentic sample. Examination of the distillation residue by tlc showed the presence of a small amount of triphenylphosphine and mostly polymeric material.

**General Procedure for the Pyrolysis of Betaines 6b–d.**—In a short-path distillation apparatus betaine was slowly evacuated to 0.10 mm, the flask was then immersed in a Wood's metal bath at 200°, and the distillate was collected in a receiver cooled by Dry Ice. The cyclopropane and dihydrofuran were separated by preparative vpc and analytical samples obtained.

**Ethyl 1-benzoylcyclopropanecarboxylate (12b) and 2-phenyl-3-carbethoxy-4,5-dihydrofuran (11b) spectra** were identical with those of authentic samples.[14]

**1-Acetyl-1-benzoylcyclopropane (12c)**: $\nu^{neat}$ 1680 (s, >=O), 1660 (s, >=O), 1010 $cm^{-1}$ (m, cyclopropyl); nmr ($CDCl_3$) 1.55 (dd, 4, $J$ = 4.0, 1.0 Hz, cyclopropyl H's), 2.07 (s, 3, $COCH_3$), 7.3–8.1 (m, 5, $C_6H_5$); mass spectrum $m/e$ 188.

*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.46; H, 6.42.

**2-Methyl-3-benzoyl-4,5-dihydrofuran (11c′) and 2-phenyl-3-acetyl-4,5-dihydrofuran (11c′)**: $\nu^{neat}$ 1680 (m, >=O), 1660 (s, >=O), 1220 (s, COC), 885 $cm^{-1}$ (m); nmr ($CDCl_3$) 1.84 (t, 3, $J$ = 1.2 Hz, $CH_3CO$), 1.97 (s, 3, $COCH_3$), 3.10 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$), 3.14 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$), 4.45 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$), 4.53 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$), 7.2–8.0 (m, 10, $C_6H_5$); mass spectrum $m/e$ 188.

(14) W. H. Perkin, *J. Chem. Soc.*, **47**, 838 (1885).

*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.35.

**4-Oxo-6,6-dimethyl-4,5,6,7-tetrahydrocoumaran (11d).**—Spectra were identical with that reported by Ichikawa, *et al.*[12]

**Preparation of 1,1-Diacetylcyclopropane (12e).**—To a solution of 3.00 g (30 mmol) of acetylacetone in 200 ml of anhydrous ether was added 1 equiv of $K^+O^-$-*tert*-Bu. The reaction mixture was stirred for 2 hr, 11.10 g (30 mmol) of vinyltriphenylphosphonium bromide added, and the mixture stirred overnight. The solid was filtered and washed with 200 ml of ether. The solid was transferred to a Soxhlet and extracted with benzene for 24 hr. The benzene solution was concentrated *in vacuo* and the residue dissolved in ether. The ether solution was refluxed overnight with 5 ml of $CH_3I$. The white methyltriphenylphosphonium iodide was filtered. The ether filtrate was concentrated *in vacuo* and distilled to give 650 mg of **12e**.[11]

**Preparation of 1-Acetyl-1-carbethoxycyclopropane (12d).**—To a solution of 2.60 g (0.02 mol) of ethyl acetoacetate in 300 ml of anhydrous ether was added 2.26 g (0.02 mol) of $K^+O^-$-*tert*-Bu. The reaction mixture was stirred at room temperature for 1 hr. To the white flocculent solid was added 7.38 g of vinyltriphenylphosphonium bromide, and the reaction mixture stirred for an additional 2 hr. The yellow solid was filtered and washed with 200 ml of anhydrous $Et_2O$. The yellow solid was placed in a Soxhlet extractor and extracted with toluene for 24 hr. The yellow toluene solution was concentrated *in vacuo* and the residue dissolved in 100 ml of ether and refluxed overnight with 5 ml of $CH_3I$. The white methyltriphenylphosphonium iodide was filtered, 4.96 g; melting point and spectra were identical with that of an authentic sample. The ether filtrate was concentrated *in vacuo* and distilled to give 1.84 g (58%) of **12d**; vpc retention time and spectra were identical with those of an authentic sample prepared by the method of Perkin.[15]

**General Procedure for the Base-Catalyzed Rearrangement of Cyclopropanes.**—In a sealed nmr tube was placed 80 mol % of cyclopropane and 20 mol % of triphenylphosphine or triethylamine. The tube was heated in a silicone oil bath at 200 ± 5°. The reaction was monitored by nmr for the appearance of 4,5-dihydrofuran and the disappearance of cyclopropane. The yield was determined by nmr and then checked by vpc upon completion of the reaction. All cyclopropane samples were heated at 200° without base present for the same period of time to determine whether or not the furan arose by a thermal pathway. None of the cyclopropanes showed any change after the heating period.

**2-Phenyl-3-carbethoxy-4,5-dihydrofuran (11b).**—Spectra and vpc retention time were identical with those of a previous sample of **11b**.

**2-Methyl-3-benzoyl-4,5-dihydrofuran (11c) and 2-Phenyl-3-acetyl-4,5-dihydrofuran (11c').**—Spectra and vpc retention time were identical with those of a previous sample of **11c** and **11c'**.

**2-Methyl-3-acetyl-4,5-dihydrofuran (11e):** $\nu^{neat}$ 1660 (m, >=O), 1230 $cm^{-1}$ (s, COC); nmr ($CDCl_3$) 2.21 (s, 6, $COCH_3$ and $CH_3C(O)$=), 2.93 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$), 4.40 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$); mass spectrum $m/e$ 126.

*Anal.* Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.56; H, 7.94.

**2-Methyl-3-carbethoxy-4,5-dihydrofuran (11f):** $\nu^{neat}$ 1700 (s, $\alpha,\beta$-unsaturated >=O), 1650 (s, >=O), 1200 $cm^{-1}$ (s, COC); nmr ($CDCl_3$) 1.23 (t, 3, $J$ = 7.0 Hz, $OCH_2CH_3$), 2.18 (t, 3, $J$ = 1.2 Hz, $CH_3$), 2.81 (t, 2, $J$ = 10.0 Hz, $OCH_2CH_2$, 4.18 (q, 2, $J$ = 7.0 Hz, $OCH_2CH_3$), 4.33 (t, 2, $J$ = 10.0 Hz, $OCH_2$-$CH_2$); mass spectrum $m/e$ 156.

*Anal.* Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.71. Found: C, 61.86; H, 7.63.

**Registry No.**—**4a**, 28638-64-4; **4b**, 28638-65-5; **4c**, 28638-66-6; **4d**, 28638-67-7; **4e**, 28638-68-8; **4f**, 28638-69-9; **4g**, 28638-70-2; **6a**, 28638-71-3; **6b**, 28638-72-4; **6c**, 28638-73-5; **9b**, 28638-74-6; **9c**, 28638-75-7; **9d**, 28638-76-8; **10a**, 28638-77-9; **10d**, 28638-78-0; **11a**, 28638-79-1; **11c**, 28638-80-4; **11c'**, 28638-81-5; **11e**, 5831-64-1; **11f**, 2986-03-0; **12c**, 5186-09-4.

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(15) T. R. Marshall and W. H. Perkin, *J. Chem. Soc.*, **59**, 880 (1891).

# Double-Bond Migration in 1-Methyl-4-(carbethoxymethylene)phosphorinane[1]

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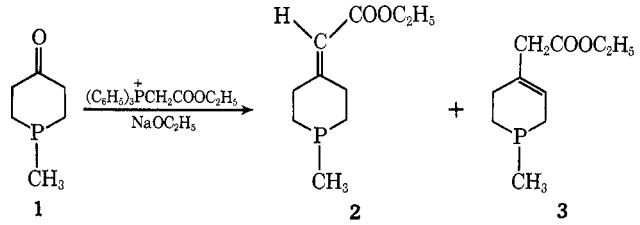
The product from the Wittig reaction of 1-methyl-4-phosphorinanone with carbethoxymethylenephosphorane was unexpectedly a mixture of 1-methyl-4-(carbethoxymethylene)phosphorinane (**2**) and 1-methyl-4-carbethoxymethyl-1,2,5,6-tetrahydrophosphorin (**3**). However, reaction of the ketone with the carbanion of triethylphosphonoacetate gave only **2**. This compound was found to be readily isomerized to **3** under basic or thermal conditions, accounting for the formation of the isomer mixture in the Wittig procedure. The same conditions were without effect on ethyl cyclohexylideneacetate, although the thermal treatment did cause extensive rearrangement of *N*-methyl-4-(carbethoxymethylene)piperidine. The pronounced tendency for the phosphine and the amine to rearrange was attributed to intramolecular catalysis of enolization by the basic centers.

One of the valuable features of the Wittig olefin synthesis is the specificity with which the product is obtained; isomer formation is not known to occur in this process. However, we found that 1-methyl-4-phosphorinanone (**1**), on reaction with the phosphorane prepared *in situ* from carbethoxymethyltriphenylphosphonium bromide and sodium ethoxide, gave an unsaturated product consisting of almost equal amounts of two isomers, **2** and **3**. This observation prompted an investigation of the factors responsible for the formation of isomer **3** and a comparison of the behavior of ketone **1** with that of cyclohexanone and of *N*-methyl-4-piperidone in this reaction.




**1** **2** **3**

The study was facilitated by the obtention of pure **2** in 55% yield when the ketone was reacted with the carbanion of triethylphosphonoacetate.[2] The structure of the product was easily established by its spectral features. The uv spectrum was that of an $\alpha,\beta$-unsaturated

(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961). This reagent is preferred for introducing the carbethoxymethylene group into cyclic ketones.[3]

(3) (a) S. Sugasawa and H. Matsuo, *Chem. Pharm. Bull.*, **8**, 819 (1960); (b) S. Trippett and D. W. Walker, *Chem. Ind. (London)*, 990 (1961).