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A Rapid Method of Preparation of Phospholanium Perchlorates via Intramolecular Cyclizations of 4-Hydroxybutylorganophosphines[1]

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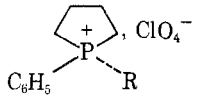
A rapid synthetic procedure for the preparation of phospholanium perchlorates in high yield has been developed. The process involves the cleavage of tetrahydrofuran by lithium organophosphides, affording 4-hydroxybutylorganophosphines, which are then intramolecularly cyclized in an aqueous solution. The following phospholanium salts (very tediously prepared by other methods) have been obtained by this procedure: methylphenyl-, ethylphenyl-, *n*-propylphenyl-, *n*-butylphenyl-, and diphenylphospholanium perchlorate. Evidence is also presented to show that cleavage of THF by diethylphenylphosphine and lithium metal afforded not only the expected diethyl-4-hydroxybutylphosphine, but also ethyl-4-hydroxybutylphenylphosphine. Confirmation of this was obtained in the form of subsequent intramolecular cyclization of these phosphines to the corresponding diethylphospholanium perchlorate and ethylphenylphospholanium perchlorate. Extension of this synthetic procedure to tetrahydropyran also afforded the desired phosphorinanium perchlorate in good yield.

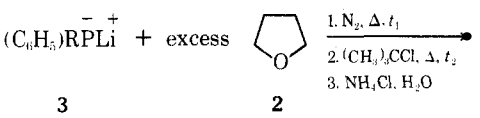
Historically, phospholanium salts have been prepared by quaternization of a selected phospholane with an alkyl halide.[3] Although the quaternization procedures generally afforded the desired salts in high yield, major drawbacks to this approach have been centered around the synthesis of the initial phospholanes,[4] which have been recently reviewed.[3,5,6] In order to alleviate this necessity of first preparing the phospholane, we have developed a process involving the cleavage of a cyclic ether by lithium organophosphides to yield γ-hydroxyalkylorganophosphines, which were intramolecularly cyclized to the desired alkylphenylphospholanium salts **1** in high yield. The initial step



1

R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_5

in the synthetic sequence involved the cleavage of tetrahydrofuran **2** by a lithium alkylphenylphosphide **3**, generated in situ from the corresponding diphenylalkylphosphines and lithium metal,[7] to yield the necessary alkyl-4-hydroxybutylphenylphosphines **4**.



3 **2**

$(C_6H_5)RP(CH_2)_4OH$

4

R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, C_6H_5

This cleavage of cyclic ethers **5** by alkali organophosphides **6** has been previously shown to afford the corresponding γ-hydroxyalkylorganophosphines **7**, although the yields reported were quite variable.[8-15] A variety of substituted cyclic ethers such as propylene oxide, styrene oxide, and cyclohexene oxide have also been utilized.[8] Most of the alkali organophosphides **6** studied have been symmetric, i.e., the organic substituents of the phosphide have been dimethyl,[13] diethyl,[8] diphenyl, etc.[8,11] In the present work, the lithium organophosphides **3** have been *dissymmetric*, except in the case of the diphenyl derivative, and have afforded the dissymmetric 4-hydroxybutylalkylphenylphosphines **4** (Table I). The cleavage of tetrahydrofuran by

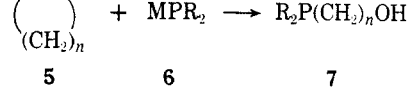
Table I
Preparation of 4-Hydroxybutylalkylphenylphosphines 4 via Lithium Organophosphides and Tetrahydrofuran

$(C_6H_5)RP(CH_2)_4OH$

4

R	t_1, hr[a]	t_2, hr[b]	Bp, °C (mm)	Yield, %	Registry no.
CH_3	12	12	87–89 (0.10)	86	55759-63-2
C_2H_5	12	24	121–124 (0.15)	86	54807-90-8
n-C_3H_7	48	12	126–128(0.35)	73	55759-64-3
n-C_4H_9	48	12	135–137 (0.10)	78	55759-65-4
C_6H_5	48	12	160–164 (0.20)	73	7526-70-7

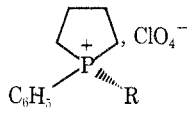
[a] Time of reflux before addition of $(CH_3)_3CCl$. [b] Time of reflux after addition of $(CH_3)_3CCl$.



5 **6** **7**

n = 2, 3, 4, 5 M = Li, K
R = dialkyl or diaryl

Table II
Preparation of Phospholanium Salts 1 via Intramolecular Cyclizations of 4-Hydroxybutylorganophosphines 4

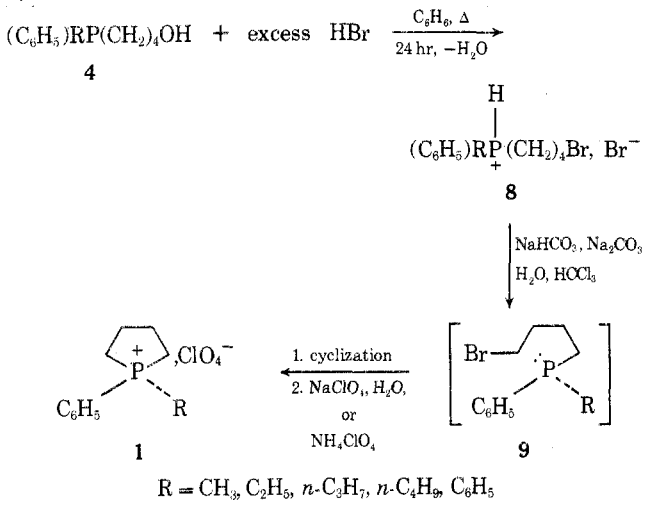


R	Mp, °C	Yield, %[a]	Molecular formula	Anal., % P	Registry no.
CH_3	75–77	74	$C_{11}H_{16}ClO_4P$	Calcd 11.11 Found 10.88	55759-67-6
C_2H_5	81–83	90	$C_{12}H_{18}ClO_4P$	Calcd 10.58 Found 10.78	55759-69-8
n-C_3H_7	96–97	81	$C_{13}H_{20}ClO_4P$	Calcd 10.10 Found 10.08	55759-71-2
n-C_4H_9[b]	54–55.5	75	$C_{14}H_{22}ClO_4P$	Calcd 9.66 Found 9.41	55759-73-4
C_6H_5	112–113.5[c]	71	$C_{16}H_{18}ClO_4P$	Calcd 9.09 Found 9.04	55759-75-6

[a] Overall yields for the reactions based on the amount of initial 4-hydroxybutylorganophosphine 4. Mass spectral data (determined with a CEC Model 21 HR unit) are available upon request. [b] See ref 26. [c] Lit. mp 114–115° (ref 27).

the bulkier (R = n-C_3H_7, n-C_4H_9) lithium organophosphides or the resonance-stabilized lithium diphenylphosphide was found to be very dependent upon the length of time of the reflux. If shorter reaction times comparable to the methyl and ethyl derivatives were employed, a considerable amount of the unreacted phosphide remained as noted by the isolation of a mixture of the corresponding secondary phosphines $(C_6H_5)RPH$, secondary phosphine oxides, and phosphinic acids. With lithium diphenylphosphide, a large quantity of diphenylphosphine was isolated after reaction times comparable to the methyl and ethyl derivatives. This observation is in agreement with earlier work in which after only 7 hr of boiling in THF, lithium diphenylphosphide afforded only 22% of the 4-hydroxybutyldiphenylphosphine along with diphenylphosphine and diphenylphosphinic acid.[11] Although the cleavage of THF by the phenyllithium coproduct is not expected under normal conditions,[16] it was deemed necessary in the present study to selectively remove this product by the addition of *tert*-butyl chloride[17] owing to the requirements of vigorous reflux and extended reaction times for the phosphide–ether cleavage reaction to occur.

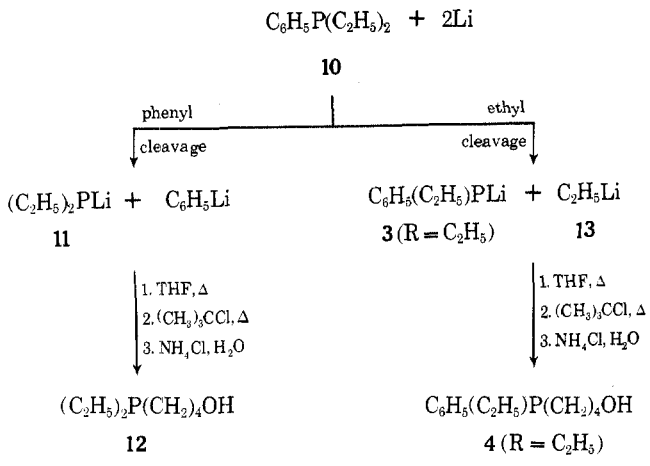
Once the 4-hydroxybutylorganophosphines **4** had been obtained, the next step involved the conversion of these phosphine alcohols to 4-halobutylorganophosphonium hydrobromides **8**, which were then *intramolecularly cyclized* via generation in situ of the 4-halobutylorganophosphines **9**, to the desired phospholanium salts **1**. The conversion of



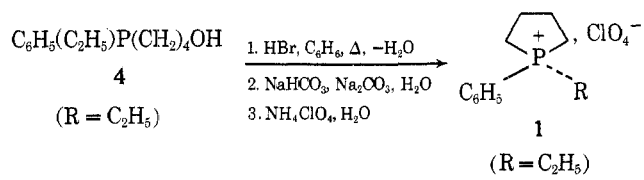
4 to the haloalkylphosphonium hydrobromide **8** was markedly facilitated by the continual removal of the water formed. The hydrobromides **8**, although isolated, were not characterized, since they were generally found to be very hygroscopic. Rather **8** was quickly dissolved in a minimum of chloroform and treated with a dilute solution of aqueous sodium bicarbonate and sodium carbonate.[18] Surprisingly the cyclization occurred in the *aqueous layer* in all cases. Confirmation of this was obtained by the observation that after mixing the solutions for 15 min, separation of the layers was effected. Upon standing at room temperature for 48 hr, the aqueous layer was treated with a saturated sodium or ammonium perchlorate solution and **1** precipitated (Table II). In every case <10% of **1** was obtained from the chloroform layer upon work-up. Intramolecular cyclizations of this type are rare but not unknown.[19–23] However, the application of this technique for the preparation of phospholanium salts **1** via the 4-hydroxybutylorganophosphines has *not* been previously reported. Examination of Table II reveals the procedure to be superior, since the yields recorded were for the overall multistep sequence of **4** to **1** and were based upon the initial quantity of **4**.

Earlier reports have indicated that cleavage of diethylphenylphosphine (**10**) by lithium metal resulted in formation of lithium diethylphosphide (**11**), whereas cleavage by potassium afforded potassium ethylphenylphosphide.[15,24] Thus, if applied to the cleavage of THF, diethylphenylphosphine (**10**) and lithium metal would be expected to give diethyl-4-hydroxybutylphosphine (**12**). Upon treatment of diethylphenylphosphine with lithium metal in THF, a dark green color developed which was considered an indication that lithium diethylphosphide (**11**) formed (Scheme I). This tentative conclusion was based on the earlier literature results[15,24] and the observations that with the diphenylalkylphosphines, formation of the lithium alkylphenylphosphides **3** produced a dark red color. The resulting dark-colored solution was vigorously boiled for 96 hr with subsequent treatment of *tert*-butyl chloride. However, the isolation of the products afforded the expected diethyl-4-hydroxybutylphosphine (**12**, 33.3%), recovered diethylphenylphosphine (**10**, 20.3%), *plus* ethyl-4-hydroxybutylphenylphosphine (**4**, R = C_2H_5, 26.3%). The latter product apparently resulted from the cleavage of diethylphenylphosphine (**10**) by lithium to form C_2H_5Li (**13**) and $C_6H_5(C_2H_5)PLi$ (**3**, R = C_2H_5). Besides the spectral analyses, additional confirmation that **4** (R = C_2H_5) had been

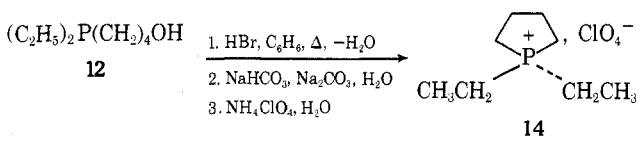
Scheme I



formed was afforded when a portion of this fraction was subjected to the intramolecular cyclization procedure to yield ethylphenylphospholanium perchlorate (**1**, R = C_2H_5, 84%). Treatment of the diethyl-4-hydroxybutylphosphine

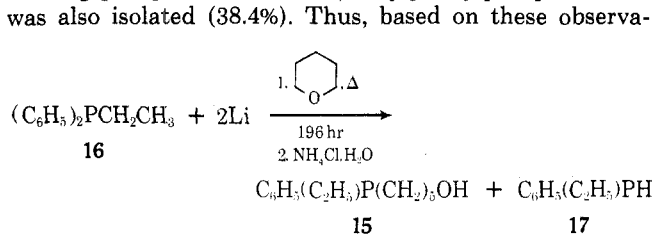


(**12**) by a similar procedure afforded the desired diethylphospholanium perchlorate (**14**, 85%). Thus, although the

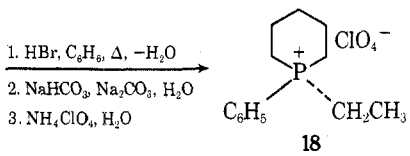


initial partial cleavage of diethylphenylphosphine by lithium afforded predominantly lithium diethylphosphide (**11**) based on the earlier reports[15,24] and our initial color observations, apparently a competitive reaction of ethyl–P vs. phenyl–P bond cleavage resulted under the conditions of vigorous reflux and long reaction time.

This synthetic procedure has also been extended to another ether system, tetrahydropyran (THP). Treatment of THP with diphenylethylphosphine and lithium under an extended reflux period (196 hr) did afford the desired ethyl-5-hydroxypentylphenylphosphine (**15**) but only in a yield of 13.4%. Besides a considerable amount of recovered starting phosphine **16** (38.8%), ethylphenylphosphine (**17**) was also isolated (38.4%). Thus, based on these observa-



tions, the initial C–P cleavage in phosphine **16** by lithium to afford the lithium ethylphenylphosphide (**3**) did not occur as readily in THP as compared to THF (almost 40% recovered phosphine in THP case). Apparently, the phosphide, once formed, is not sufficiently basic and/or nucleophilic in THP to facilitate ether cleavage (appreciable amount of secondary phosphine isolated). This latter point may be more dependent upon the coordination ability of THP with the lithium ethylphenylphosphide as compared with that of THF, rather than the reactivity of the phosphide itself. Our results appear in good agreement with the previous report that, after 13.5 hr of vigorous boiling, lithium diphenylphosphide cleaved THP in a low yield (4%).[11] The ethyl-5-hydroxypentylphenylphosphine (**15**), however, was subjected to our intramolecular cyclization procedure and *did afford* the desired ethylphenylphosphorinanium perchlorate (**18**, 50.4%).



This study has revealed a convenient and rapid procedure for the preparation of cyclic phosphonium salts in high yield based on the cleavage of cyclic ethers, THF and THP, by lithium organophosphides. The intermediate γ-hydroxyalkylorganophosphines can be isolated and subsequently cyclized to the desired salts. Work is continuing in this area.

Experimental Section

General Procedure. Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5A unit as thin films for **4** and as KBr pellets for **1**. ^1H NMR and ^{31}P NMR spectra were obtained with a XL-100(15) Varian spectrometer with Me_4Si as internal standard unless otherwise indicated. Anhydrous THF and tetrahydropyran were obtained fresh for each cleavage reaction by distillation from NaH immediately before use.

Starting Materials. The initial starting phosphines $(C_6H_5)_2PR$ were easily prepared via the appropriate Grignard reaction on $(C_6H_5)_2PCl$.[25] Triphenylphosphine was from a commercially available source. Diethylphenylphosphine was prepared by the reaction of ethylmagnesium bromide on $C_6H_5PCl_2$.[25]

Since the procedures for the preparation of the 4-hydroxybutylalkylphenylphosphines **4** [derived from $(C_6H_5)_2PR$] were identical except for the time of reaction as indicated in Table I, only the preparation of ethyl-4-hydroxybutylphenylphosphine will be described in detail. A similar approach will be used for the description of the preparation of the phospholanium salts **1** given in Table II.

Ethyl-4-hydroxybutylphenylphosphine (4, R = C_2H_5). Diphenylethylphosphine (21.4 g, 0.10 mol) and lithium shavings (1.4 g, 0.02 g-atom) in 200 ml of anhydrous THF were stirred at room temperature under N_2 until the dark-red color persisted (~1 hr). The mixture was heated at vigorous reflux for 12 hr with the disappearance of the lithium shavings. After cooling to room temperature, *tert*-butyl chloride (9.3 g, 0.10 mol) was added, and the mixture was boiled for an additional 24 hr with a color change to a reddish-orange. This mixture was then cooled, hydrolyzed (5.9 g, 0.11 mol, NH_4Cl in 50 ml of H_2O), saturated (NaCl), and extracted (3 × 150 ml) with benzene. The organic extracts were dried ($MgSO_4$) and evaporated to an oil on a rotary evaporator. Distillation of the residual oil under reduced pressure through a short-path Vigreux column afforded 18.0 g (86%) of ethyl-4-hydroxybutylphenylphosphine (**4**, R = C_2H_5): bp 121–124° (0.15 mm); ir (film) ν 3283 (OH), 1583 (C_6H_5), 1050 (C–O), 733 and 695 cm^{-1} (C_6H_5); ^1H NMR ($DCCl_3$) δ 0.98 (d of t, J_{PCCH} = 16, J_{HCCH} = 7 Hz, 3 H, CH_3CH_2P), 1.22–1.84 (m, 8, $CH_3CH_2PCH_2CH_2CH_2CH_2OH$), 3.20 (s, broad, 1, OH), 3.50 (t, J_{HCCH} = 6 Hz, 2, CH_2OH), and 7.20–7.60 (m, 5, ArH). The data of other 4-hydroxybutylalkylphenylphosphines **4** prepared by a similar procedure are given in Tables I and III.

Ethylphenylphospholanium Perchlorate (1, R = C_2H_5). A solution of 5.65 g (0.027 mol) of ethyl-4-hydroxybutylphenylphosphine (**4**, R = C_2H_5) in 50 ml of benzene was added to 75 ml of a saturated benzene solution of anhydrous HBr with immediate formation of a white slurry. This mixture was vigorously boiled for 12 hr with continual removal of the H_2O (ca. 0.5 ml) formed (Dean-Stark trap). After resaturation of the mixture with HBr (bubbling in at 20 ml/min for 10 min), the boiling was continued for an additional 12 hr. The benzene was concentrated via distillation to a volume of ~25 ml. Upon cooling to room temperature, the residual slurry was triturated with 75 ml of hexane and resulted in the formation of a white precipitate. This very hygroscopic solid was col-

Table III
Spectral Properties of 4-Hydroxybutylalkylphenylphosphines 4[a]
$(C_6H_5)RP(CH_2)_4OH$

R	Ir absorption spectra, selected bands, cm^{-1} [b]	^1H NMR spectral assignments, chemical shifts, δ, ppm
CH_3[c]	3300 (OH), 1059 (C–O), 737 and 693 (C_6H_5)	1.19 (d, J_{PCH} = 3 Hz, 3, CH_3P), 1.30–1.80 [m, broad, 6, $(CH_2)_3$-P], 3.53 (t, broad, 2, CH_2OH), 4.42 (s, broad, 1 OH), 7.12–7.60 (m, 5, ArH)[d]
n-C_3H_7[e]	3285 (OH), 1577 (C_6H_5), 1065 (C–O), 749 and 696 (C_6H_5)	0.94 [t, J_{HCCH} = 6 Hz, $CH_3(CH_2)_2P$], 1.10–1.82 [m, 10, CH_3-$(CH_2)_2P$ and $P(CH_2)_3$-CH_2OH], 3.10 (s, broad, 1, OH), 3.51 (t, J_{HCCH} = 6 Hz, 2, CH_2OH), 7.16–7.60 (m, 5, ArH)[f]
n-C_4H_9[c]	3276 (OH), 1584 (C_6H_5), 1066 (C–O), 744 and 702 (C_6H_5)	0.83 [t, J_{HCCH} = 7 Hz, 3, $CH_3(CH_2)_3P$], 1.10–1.86 [m, 12, $CH_3(CH_2)_3P$ and P-$(CH_2)_3CH_2OH$], 3.22 (s, 1, OH), 3.50 (t, J_{HCCH} = 6 Hz, 2, CH_2OH), 7.20–7.62 (m, 5, ArH)[f]
C_6H_5[g]	3259 (OH), 1584 (C_6H_5), 1067 (C–O), 741 and 700 (C_6H_5)	1.10–1.80 (m, 4, PCH_2-$CH_2CH_2CH_2OH$), 2.04 (m, 2, PCH_2), 2.52 (s, 1, OH), 3.51 (t, J_{HCCH} = 6 Hz, CH_2-OH), 7.14–7.52 (m, 10, ArH)[f]

[a] Other properties in addition to yields are found in Table I. [b] The spectra were obtained as thin films between NaCl plates. [c] Cleavage reaction conducted on a scale of 0.10 mol of phosphine. [d] This spectrum was obtained on a neat sample with Me_4Si as internal standard. [e] Cleavage reaction conducted on a scale of 0.052 mol of phosphine. [f] Spectrum was obtained as a solution in $DCCl_3$ with Me_4Si as internal standard. [g] Cleavage reaction conducted on a scale of 0.05 mol of phosphine.

lected by vacuum filtration, dissolved in 75 ml of chloroform, transferred to a separatory funnel, and treated with 75 ml of a 5% $NaHCO_3$ solution (with 5 g of Na_2CO_3 added) for 15 min under N_2 in the standard manner, and the layers were separated. After reextraction of the aqueous layer (2 × 100 ml) with chloroform, the aqueous layer was stoppered and set aside at room temperature for 48 hr.[18] Combination of the chloroform extracts, drying ($MgSO_4$), and boiling for 12 hr under N_2 afforded, after removal of solvent and trituration with a saturated $NaClO_4$ solution, 0.1 g of the desired product.

Treatment of the aqueous layer with 50 ml of a saturated $NaClO_4$ solution gave the desired product as a white precipitate.[26] Recrystallization from absolute C_2H_5OH–$(C_2H_5)_2O$ (1:3) yielded 7.1 g (90%) of the phospholanium salt 1 (R = C_2H_5): mp 81–83°; ir (KBr pellet) ν 1588 (C_6H_5), 1068 (ClO_4^-), 739 and 687 cm^{-1} (C_6H_5); ^1H NMR ($DCCl_3$) δ 1.23 (d of t, J_{PCCH} = 20, J_{HCCH} = 8 Hz, 3, CH_3CH_2P), 2.23 (m, 4, β-CH_2CH_2 of ring), 2.71 (m, 6, CH_3CH_2P and CH_2PCH_2 of ring), 7.50–8.06 (m, 5, ArH); ^{31}P NMR (40.5 MHz, 12% in $HCCl_3$) δ −51.39 ppm relative to 85% H_3PO_4. Additional analytical data are given in Table II. The data of other phospholanium perchlorates prepared by a similar procedure are given in Tables II and IV.

Cleavage of THF with Diethylphenylphosphine and Lithium Metal. Diethylphenylphosphine (12.3 g, 0.074 mol) and lithium shavings (1.05 g, 0.15 g-atom) in 200 ml of anhydrous THF were stirred at room temperature under N_2 with the appearance of a dark green color (~1 hr). The mixture was heated at reflux for 96 hr, cooled to room temperature, treated with *tert*-butyl chloride (6.85 g, 0.074 mol), and boiled for an additional 12 hr with formation of a white slurry. This mixture was then cooled, hydrolyzed (4.0 g, 0.074 mol, NH_4Cl in 50 ml of H_2O), and extracted (3 × 100 ml) with benzene. The organic extracts were dried ($MgSO_4$) and the solvents were removed via distillation under N_2. Distillation of the resultant oil under reduced pressure on an 18-in. stainless steel spinning band afforded four fractions: (1) bp 62–65° (3.0 mm), 2.5 g (20.3%) of recovered diethylphenylphosphine (**10**); ^1H NMR ($DCCl_3$) δ 0.95 (d of t, J_{PCCH} = 16, J_{HCCH} = 7 Hz, 6, CH_3CH_2P), 1.62 [m, 4, $(CH_3CH_2)_2P$], 7.10–7.62 (m, 5, ArH); (2) bp 75–78° (3.3 mm), 4.0 g (33.3%) of diethyl-4-hydroxybutylphosphine (**12**); ir (film) ν 3300 (OH), 2925 (CH), 1040 cm^{-1} (C-O); ^1H NMR ($DCCl_3$) δ 1.03 (d of t, J_{PCCH} = 14, J_{HCCH} = 7 Hz, 6, CH_3CH_2P), 1.25–1.90 [m, 10, $(CH_3CH_2)_2P$ and $PCH_2CH_2CH_2CH_2OH$], 3.58 (t, 2, CH_2OH), 3.68 (s, 1, OH); (3) bp 98–100° (0.05 mm), 4.1 g (26.3%) of ethyl-4-hydroxybutylphenylphosphine (**4**, R = C_2H_5); ir (film) ν 3290 (OH), 1586 (C_6H_5), 1049 (C–O), 735 and 695 cm^{-1} (C_6H_5); ^1H NMR ($DCCl_3$) δ 0.95 (d of t, J_{PCCH} = 16, J_{HCCH} = 7 Hz, 3, CH_3CH_2P), 1.15–2.0 (m, 8, CH_3CH_2P and $PCH_2CH_2CH_2OH$), 3.55 (t, 2, CH_2OH), 4.37 (s, 1, OH), 7.10–7.78 (m, 5, ArH); (4) bp 110–115° (0.05 mm), 2.0 g of a mixture tentatively identified as diethyl-4-hydroxybutylphosphine oxide (major) and diethylphenylphosphine oxide (minor).

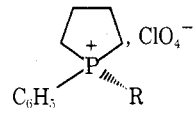
Diethylphospholanium Perchlorate (14). A solution of 2.5 g (0.0154 mol) of diethyl-4-hydroxybutylphosphine in 50 ml of benzene was added to 100 ml of a saturated benzene solution of anhydrous HBr with formation of a white slurry. This mixture was boiled for 12 hr with the continual removal of H_2O (ca. 0.3 ml) (Dean-Stark trap). After resaturation of the mixture with HBr (bubbling in at 20 ml/min for 10 min), the boiling was continued for an additional 12 hr. After the benzene was evaporated via distillation to a volume of ~25 ml and the mixture was cooled to room temperature, the resultant slurry was triturated with 125 ml of hexane with formation of a white precipitate. After decantation of the solvents, this solid was treated with 125 ml of a 5% $NaHCO_3$ solution (with 3 g of Na_2CO_3 added) for 12 hr under N_2 at ~80°. This clear aqueous solution was cooled to room temperature and treated with 75 ml of a saturated NH_4ClO_4 solution with the appearance of some turbidness. This mixture was concentrated in vacuo to a volume of ~50 ml and extracted (5 × 100 ml) with chloroform.[28] The combination of chloroform extracts were dried ($MgSO_4$) and then concentrated in vacuo to afford a white solid. Recrystallization from absolute C_2H_5OH–$(C_2H_5)_2O$ (2:1) yielded 3.2 g (85%) of diethylphospholanium perchlorate (**14**): mp 248–250°; ir (KBr pellet) ν 2950 (CH), 1077 (ClO_4^-), also bands at 1453, 1403, 858, 787, and 754 cm^{-1}; ^1H NMR ($DCCl_3$ + 3 drops of F_3CCO_2H) δ 1.29 (d of t, J_{PCCH} = 20, J_{HCCH} = 7 Hz, 6, CH_3CH_2P), 1.88–2.54 (m, 12, $CH_2CH_2PCH_2CH_2$ and CH_3CH_2P); ^{31}P NMR (40.5 MHz, 12% in $HCCl_3$–F_3CCO_2H) δ −58.75 ppm relative to 85% H_3PO_4.

Anal. Calcd for $C_8H_{18}ClO_4P$: P, 12.66. Found: P, 12.35.

Ethylphenylphospholanium Perchlorate (1, R = C_2H_5). Confirmation of Ethyl-4-hydroxybutylphenylphosphine Isolated in Diethylphenylphosphine–THF Cleavage Reaction. The procedure was as described above for diethylphospholanium perchlorate with 2.5 g (0.0119 mol) of ethyl-4-hydroxybutylphenylphosphine (fraction 3 of diethylphenylphosphine–THF cleavage reaction) in 150 ml of a saturated benzene solution of HBr. With work-up identical with that previously described, treatment of the aqueous layer with 75 ml of a saturated NH_4ClO_4 solution gave a turbid mixture. The aqueous mixture was concentrated in vacuo to ~75 ml and extracted with 4 × 100 ml of chloroform. The chloroform extracts were combined and dried ($MgSO_4$), and the solvent was removed in vacuo to afford a white solid. Recrystallization from absolute C_2H_5OH–$(C_2H_5)_2O$ (1:3) yielded 2.9 g (84%) of ethylphenylphospholanium perchlorate (1, R = C_2H_5): mp 81–83°; mmp [with authentic sample of 1 (R = C_2H_5) as prepared previously] 80.5–82.5°; ir (KBr pellet) ν 1588 (C_6H_5), 1070 (ClO_4^-), 740 and 687 cm^{-1} (C_6H_5); ^1H NMR ($DCCl_3$) δ 1.23 (d of t, J_{PCCH} = 20, J_{HCCH} = 8 Hz, 3, CH_3CH_2P), 2.22 (m, 4, β-CH_2CH_2 of ring), 2.70 (m, 6, CH_2PCH_2 and PCH_2CH_3), 7.50–8.06 (m, 5, ArH).

Ethyl-5-hydroxypentylphenylphosphine (15). Diphenylethylphosphine (21.4 g, 0.10 mol) and lithium shavings (1.4 g, 0.20 g-atom) in 100 ml of anhydrous tetrahydropyran were stirred at room temperature under N_2 until the dark red color persisted (~1

Table IV
Spectral Data of Phospholanium Perchlorates 1[a]



R	Ir absorption spectra, selected bands, cm^{-1} [b]	^1H NMR spectral assignments, chemical shifts, δ, ppm	$^{31}P_{(\delta)}$ [c]
CH_3[d]	1617 (C_6H_5), 1092 (ClO_4^-), 717 and 687 (C_6H_5)	2.23 (d, J_{PCH} = 14 Hz, 3, CH_3P), 2.26 (m, 4, β-CH_2CH_2 of ring), 2.62 (m, 4, CH_2PCH_2), 7.70 (m, 5, ArH)[e]	−44.26
n-C_3H_7[f]	1588 (C_6H_5), 1090 (ClO_4^-), 740 and 693 (C_6H_5)	1.06 [t, J_{HCCH} = 7 Hz, 3, $CH_3(CH_2)_2P$], 1.57 (m, 2, $CH_3CH_2CH_2$), 2.15 (m, 4, β-CH_2CH_2 of ring), 2.66 (m, 6, CH_2-PCH_2 and $PCH_2CH_2CH_3$), 7.48–8.02 (m, 5, ArH)[g]	−49.09
n-C_4H_9[h]	1575 (C_6H_5), 1070 (ClO_4^-), 748 and 790 (C_6H_5)	0.87 [t, J_{HCCH} = 7 Hz, 3, $CH_3(CH_2)_4P$], 1.48 (m, 4, $CH_3CH_2CH_2CH_2P$), 2.21 (m, 4, β-CH_2CH_2 of ring), 2.66 [m, 6, CH_2PCH_2 and $PCH_2(CH_2)_2CH_3$], 7.50–8.10 (m, 5, ArH)[g]	−49.22
C_6H_5[i]	1587 (C_6H_5), 1089 (ClO_4^-), 730 and 694 (C_6H_5)	2.30 (m, 4, β-CH_2CH_2 of ring), 3.01 (m, 4, CH_2PCH_2), 7.48–7.98 (m, 10, ArH)[g]	−44.34

[a] Additional analytical data are given in Table II. [b] The spectra were obtained on samples (4 mg) with KBr (400 mg) pellets. [c] The spectra were obtained at 40.5 MHz on 12% solutions in $HCCl_3$ with resonance positions given in parts per million relative to 85% H_3PO_4. [d] Cyclization procedure conducted on a scale of 0.028 mol of 4 (R = CH_3) with recrystallization from absolute C_2H_5OH-$(C_2H_5)_2O$ (1:3). [e] Spectrum was obtained as a solution in $DCCl_3$ with 3 drops of F_3CCO_2H added and Me_4Si as internal standard. [f] Cyclization procedure conducted on a scale of 0.022 mol of 4 (R = n-C_3H_7) with recrystallization from absolute C_2H_5OH-$(C_2H_5)_2O$ (1:3). [g] Spectrum was obtained as a solution in $DCCl_3$ and Me_4Si as internal standard. [h] Cyclization procedure conducted on a scale of 0.021 mol of 4 (R = n-C_4H_9) with recrystallization from absolute C_2H_5OH-$(C_2H_5)_2O$ (1:4). [i] Cyclization procedure conducted on a scale of 0.018 mol of 4 (R = C_6H_5) with recrystallization from absolute C_2H_5OH-$(C_2H_5)_2O$ (1:3).

hr). The mixture was heated at vigorous reflux for 24 hr, cooled to room temperature, treated with 9.3 g (0.10 mol) of *tert*-butyl chloride, and boiled for an additional 172 hr with formation of a reddish-orange slurry. This mixture was then cooled, hydrolyzed [5.9 g (0.11 mol) of NH_4Cl in 50 ml of H_2O], and extracted (3 × 150 ml) with diethyl ether. The ether extracts were dried ($MgSO_4$) and the solvents were removed via distillation under N_2. Distillation of the residual oil under reduced pressure on an 18-in. stainless steel spinning band afforded three fractions: (1) bp 43–45° (1.5 mm), 5.3 g (38.4%) of ethylphenylphosphine (**17**); ^1H NMR ($DCCl_3$) δ 0.98 (d of t, J_{PCCH} = 13, J_{HCCH} = 8 Hz, CH_3CH_2P), 1.60 (m, 2, CH_3CH_2P), 4.02 (d of t, J_{PH} = 204, J_{HPCH} = 7 Hz, 1, PH), 7.02–7.60 (m, 5, ArH);[29] (2) bp 88–91° (0.1 mm) [lit.[30] bp 108–111° (0.3 mm)], 8.1 g (38.8%) of recovered diphenylethylphosphine (**16**), ^1H NMR ($DCCl_3$) δ 0.96 (d of t, J_{PCCH} = 16, J_{HCCH} = 7 Hz, 3, CH_3CH_2P), 1.90 (m, 2, CH_3CH_2P), 7.0–7.56 (m, 10, ArH); (3) bp 120–122° (0.2 mm), 3.0 g (13.4%) of **15**; ir (film) ν 3283 (OH), 1588 (C_6H_5), 1045 (C–O), 735 and 694 cm^{-1} (C_6H_5); ^1H NMR (C_6D_6) δ 0.92 (m, 3, CH_3CH_2P), 1.2–2.0 (m, 10, CH_3CH_2P and $PCH_2CH_2CH_2CH_2CH_2OH$), 3.16 (s, broad, 1, OH), 3.50 (t, broad, 2, CH_2OH), 7.0–7.80 (m, 5, ArH).

Ethylphenylphosphorinanium Perchlorate (18). A solution of 2.5 g (0.011 mol) of ethyl-5-hydroxypentylphenylphosphine in 50 ml of benzene was added to 150 ml of a saturated benzene solution of anhydrous HBr. This mixture was vigorously boiled for 24 hr with continual removal of the H_2O (ca. 0.2 ml) formed. After resaturation of the mixture with HBr, the boiling was continued for an additional 24 hr. The benzene mixture was concentrated via distillation to ~25 ml, cooled to room temperature, and triturated with 125 ml of hexane with formation of a white precipitate. After decantation of the solvents, the solid was treated with 125 ml of a 5% $NaHCO_3$ solution (with 3 g of Na_2CO_3 added) and the resulting solution was boiled for 24 hr under N_2. This solution was cooled to room temperature, treated with 50 ml of a saturated NH_4ClO_4 solution (turbidness developed), and extracted (3 × 150 ml) with chloroform. The chloroform extracts were dried ($MgSO_4$) and solvent was removed in vacuo, affording a white solid. Recrystallization from absolute C_2H_5OH-$(C_2H_5)_2O$ (1:2) yielded 1.7 g (50.4%) of **18**: mp 143.5–144.5°; ir (KBr pellet) ν 1590 (C_6H_5), 1076 (ClO_4^-), 743 and 693 cm^{-1} (C_6H_5); ^1H NMR ($DCCl_3$) δ 1.12 (d of t, J_{PCCH} = 20, J_{HCCH} = 7 Hz, 3, CH_3CH_2P), 1.46–2.34 (m, 6, β- and γ-CH_2 of the ring), 2.34–3.06 (m, 6, CH_2PCH_2 and CH_3CH_2P), 7.56–8.08 (m, 5, ArH); ^{31}P NMR (40.5 MHz, 12% in $HCCl_3$) δ −21.74 ppm relative to 85% H_3PO_4.

Anal. Calcd for $C_{13}H_{20}ClO_4P$: P, 10.10. Found: P, 10.16.

Registry No.—**10**, 1605-53-4; **12**, 55759-76-7; **14**, 55759-78-9; **15**, 55759-79-0; **16**, 607-01-2; **17**, 3619-88-3; **18**, 55759-81-4.

References and Notes

(1) We gratefully acknowledge support of this work by the USPHS, NIH, National Cancer Institute, CA 11967.
(2) Research Associate, 1973–1975.
(3) For a discussion on the synthetic aspects involved in the preparation of phospholanium salts, see P. Beck in "Organic Phosphorus Compounds", Vol. 2, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 4, and references cited therein. Additional insight may be obtained by examining the brief discussions of the preparation of phospholanes, phospholenes, and phospholene oxides (all potential precursors of phospholanium salts). For the former two, see L. Maier in "Organic Phosphorus Compounds", Vol. 1, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 1, and references cited therein. For the latter, see H. R. Hays and D. J. Peterson in "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 6, and references cited therein.
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(26) These phospholanium salts are slightly hygroscopic and have a tendency to precipitate as an oil. In those cases, the precipitates were dissolved in $HCCl_3$ and the aqueous layer was also extracted (3 × 100 ml) with $HCCl_3$. The $HCCl_3$ extracts were combined, dried ($MgSO_4$), and evaporated in vacuo to afford the solid products.
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Synthesis and Solvolysis of Tricyclo[4.3.2.0^{2,5}]undeca-3,8,10-trien-7-ol. An Unusual $[CH]_{11}^+$ Rearrangement[1]

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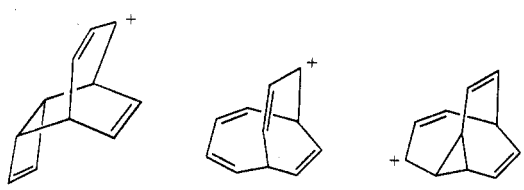
Synthesis of the title compound (**11**) has been achieved by two routes, the cycloaddition of cyclobutadiene to tropone and addition of tetrachlorocyclopropene to an appropriate bicyclo[4.2.0]diene (**6**) and subsequent transformations. Acetolysis of esters of **11** afforded a rearranged allylic acetate (**15**) and dihydroindenylenol acetate (**20**). Deuterium-labeling studies indicate that **20** derives from **15** via a bicyclo[2.1.0]pentane (**25**) and subsequent thermal fission. Activation parameters for this process ($\Delta H^\ddagger$ = 31.2 kcal/mol, $\Delta S^\ddagger$ = −6.2 eu) are in accord with the proposed mechanism.

Interest in the preparation and reorganization of $[CH]_n$ hydrocarbons and ions has been aroused by the surprising variety of rearrangements observed in these systems and by attempts to correlate experimental evidence regarding these energy surfaces to theoretical prediction. Particularly, the concepts of homoaromaticity,[2] bicycloaromaticity,[3] and spiroaromaticity[4] have served at least to focus attention on structures of importance. We were led to synthesize precursors of **1** in view of its relationship to the interesting ions **2** and **3**. Our expectations that **1** might lead to **2** or **3**



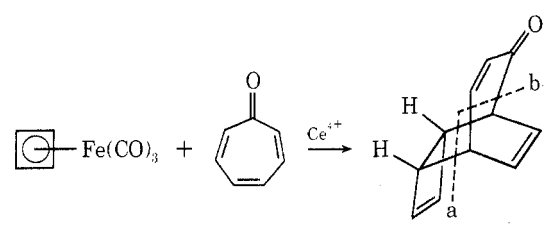
1 **2** **3**

were based upon the known σ participation of appropriately positioned cyclobutenes[5] and predictions regarding the stabilization of **2**.[3]

At the outset of this work no derivatives of the $[CH]_{11}$–X family of valence tautomers had been described. Since that time we[6] and others[7] have reported six other members of this series and a number of rearrangements relating them. We report here two independent synthetic approaches to the alcohol corresponding to **1** and evidence bearing on the mechanism of its unusual rearrangement to an enol acetate by thermal fission of a bicyclo[2.1.0]pent-2-yl intermediate.

Results and Discussion

Synthesis. Inspection of **4** suggested two attractive synthetic approaches, the annulation of a cyclobutene ring onto tropone (a) and the elaboration of an enone bridge onto an appropriate bicyclo[4.2.0]octane precursor (b). We have investigated both routes.



4

When cyclobutadiene was generated in situ[8] in the presence of freshly distilled tropone, only one volatile product was detected by analytical GLC. After column chromatography, a 14% yield of a 1:1 adduct was isolated. Of several possible isomers only **4** was consistent with the spectral data.

The presence of a single α,β-unsaturated carbonyl unit was indicated by the ^1H NMR spectrum (δ 7.0, 1 H, dd, J = 11, 8 Hz; δ 5.7, 1 H, dd, J = 11, 2 Hz) and an accordant ir spectrum (1680, 1640 cm^{-1}). A sharp singlet at δ 6.0 and an ir band at 1560 cm^{-1} were assigned to a cyclobutene. The spin-decoupled ^1H NMR spectrum revealed that the β carbon of the enone unit was adjacent to a bridgehead proton. Both the coupling constants and chemical shifts found in the ^1H NMR spectrum of enone **4** were in excellent agreement with those found in appropriate model compounds.[9]

While the direct, one-step approach to this ring system was successful, the yields of enone **4** remained uneconomical since excess cyclobutadieneiron tricarbonyl was used. In another approach (Scheme I) we have applied the known