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PRELIMINARY NOTE

Facile Transformation of 1-Substituted F-1-Alkenyl Phosphates into Polyfluorinated 1,3-Dienes by Use of Phosphonium Ylides

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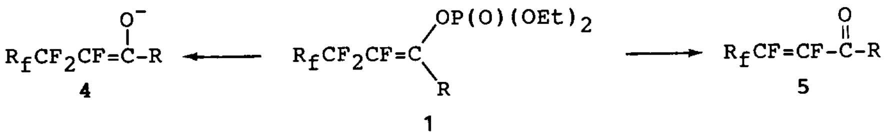
SUMMARY

1-Substituted F-1-alkenyl phosphates, easily prepared from F-alkyl ketones and the sodium salt of diethyl phosphite, were allowed to react with various phosphonium ylides in tetrahydrofuran or hexane at room temperature or at the reflux temperature of the solvent to lead to the corresponding polyfluorinated 1,3-diene derivatives in moderate to good yields.

It is an important subject in organofluorine chemistry to extend the chemistry of fluorine-containing carbonyl compounds. We have been studying the reactions and synthetic applications of fluorinated enol phosphates (**1**) [1-5], derived from F-alkyl ketones and sodium diethyl phosphite [4], on the basis of the idea that these enol phosphates would be usable as good precursors for the generation of α-F-alkylated ketone enolates (**4**) and F-1-alkenyl ketones (**5**) (Scheme 1). As part

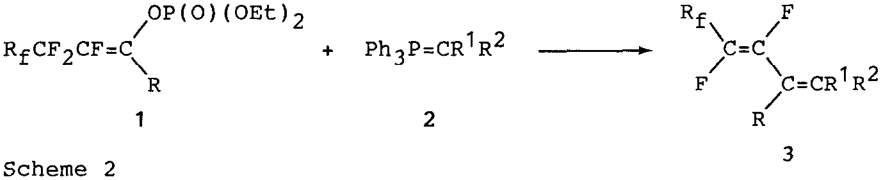


$$\underset{\mathbf{4}}{R_fCF_2CF{=}\overset{O^-}{\overset{|}{C}}{-}R} \longleftarrow \underset{\mathbf{1}}{R_fCF_2CF{=}C\begin{smallmatrix}OP(O)(OEt)_2\\R\end{smallmatrix}} \longrightarrow \underset{\mathbf{5}}{R_fCF{=}CF{-}\overset{O}{\overset{\|}{C}}{-}R}$$

Scheme 1

0022-1139/88/$3.50

of our studies on this line, we have examined the reaction of **1** with several carbon nucleophiles and have now found that 1-substituted *F*-1-alkenyl phosphates 1 may easily be transformed into the corresponding polyfluorinated 1,3-dienes (**3**) in moderate to good yields by the treatment with various phosphonium ylides (**2**) (Scheme 2).



Scheme 2

The reaction (Run 1 or 2) was performed in the following manner. To a suspension of hexyltriphenylphosphonium bromide (3 mmol) in anhydrous tetrahydrofuran (THF) or hexane (15 mL) was added dropwise a solution (1.5 M) of butyllithium (3 mmol) in hexane at -10 to 0 °C under argon. After stirring for 1 h, diethyl 1-hexyl-*F*-1-butenyl phosphate (1 mmol) was added to the resultant mixture via a syringe at 0 °C. The whole mixture was refluxed for 20 h. The reaction was quenched with an aqueous solution of ammonium chloride and the mixture was subjected to extraction with ether. The ethereal extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated. The residue was chromatographed on silica gel to give the product 3 in 70-88% yield. The results of the reaction are summarized in Table 1.

The reaction between 1-alkyl-substituted *F*-1-alkenyl phosphates and triphenylphosphonium alkylide (R^1 = *n*-C_5H_{11}, R^2 = H) required high reaction temperature (Runs 1, 2, and 9), but 1-phenyl-substituted phosphate reacted cleanly rather at room temperature (Runs 5 and 6). The reaction of **1** with triphenylphosphonium benzylide (R^1 = Ph, R^2 = H) smoothly proceeded at room temperature in THF (Runs 3, 7, and 10). Triphenylphosphonium dichloromethylide (R^1 = R^2 = Cl), generated from triphenylphosphine, chloroform and a slight excess of potassium *tert*-butoxide in hexane at 0 °C [6], also reacted with the enol phosphates 1 at room temperature to give the corresponding 1,3-dienes **3** in moderate yields (Runs 4, 8 and

TABLE 1
The reaction between F-1-alkenyl phosphates **1** and phosphonium ylides **2**

Run	R_f	R	R^1	R^2	Solvent	Temp °C	Yield[a] of **3**[b] (%)
1	CF_3	n-C_6H_{13}	n-C_5H_{11}	H	THF	67	88[c]
2			n-C_5H_{11}	H	hexane	70	70[c]
3			Ph	H	THF	rt	42[c]
4			Cl	Cl	hexane	rt	40[d]
5	CF_3	Ph	n-C_5H_{11}	H	THF	rt	64[c]
6			n-C_5H_{11}	H	hexane	rt	66[c]
7			Ph	H	THF	rt	40[c]
8			Cl	Cl	hexane	rt	62[d]
9	n-C_7F_{15}	n-C_3H_7	n-C_5H_{11}	H	THF	67	90[c]
10			Ph	H	THF	rt	46[c]
11			Cl	Cl	hexane	rt	47[d]

[a] The yields are of pure isolated compounds.

[b] All the products **3** were fully characterized on the basis of their spectroscopic (IR, MS, ^1H and ^{19}F NMR spectra) and analytical data.

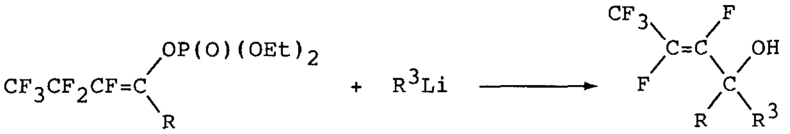
[c] Obtained as a mixture of (E,E)- and (E,Z)-stereoisomer.

[d] (E)-Stereoisomer only.

11). Triphenylphosphonium methoxycarbonylmethylide and the anion of triethyl phosphonoacetate did not participate in the reaction of **1**, probably due to their lower nucleophilicity.

The reaction of **1** with other carbon nucleophiles, such as butyllithium, phenyllithium and lithium acetylide, occurred readily at -78 or 0 °C to give polyfluorinated (E)-allylic alcohols in good yields, as shown in Scheme 3.

These reactions can simply be explained as follows. The attack of a nucleophile on the phosphorus atom in **1** followed by the elimination of fluoride ion results in the formation of (E)-F-1-alkenyl ketone, which reacts with another nucleophile to produce the final product.



R = c-C_6H_{11}, R^3 = n-C_4H_9 (91%)
R = n-C_6H_{13}, R^3 = Ph (66%); PhC≡C (75%); n-C_6H_{13}C≡C (71%)

Scheme 3

To be noted is that the enol phosphates **1** may efficiently act as synthetic equivalents to (E)-F-1-alkenyl ketones **5** in the above-cited reactions, because the latter compounds are not easily accessible [7].

Further studies on the synthetic applications of **1** and related compounds are in progress.

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