

Influence of a Perfluorobutyl Substituent on the Rearrangement of Prop-2-ynyl Diethylphosphites to Allenic Phosphonates

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The prop-2-ynyl diethylphosphites $n\text{-C}_4\text{F}_9\text{-C}\equiv\text{C-CR}^1\text{R}^2\text{OP(OEt)}_2$ are obtained from the reaction of the corresponding prop-2-ynyl alcohols with diethyl chlorophosphite; the rearrangement of these phosphites into α -perfluorobutylallenic phosphonates is found to depend on the nature of the substituents R^1 and R^2 , and an unexpected HF elimination is found for $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$.

It is well known that allenic phosphonates are readily available from alk-2-yn-1-ols, according to Scheme 1. This reaction is efficient and gives a good yield with a large variety of substituents^{1,2} ($\text{R}^3 = \text{H}$ and $\text{R}^1 = \text{R}^2 = \text{H}$ or Me , $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$; $\text{R}^3 = \text{Me}$, $\text{R}^1 = \text{R}^2 = \text{H}$). We have studied this reaction using the 3-perfluorobutylalk-2-yn-1-ols, $n\text{-C}_4\text{F}_9\text{-C}\equiv\text{C-CR}^1\text{R}^2\text{OH}$, prepared previously.³ Extremely different results were obtained depending on the nature of R^1 and R^2 .

The allene (**3a**) was formed instantly† in 95% yield [i.r. 1965 cm^{-1} ; ^1H n.m.r. δ allenic *gem*-Me 1.82 (s, 3H), 1.93 (s, 3H), OEt 4.32 (m, 4H), 1.33 (t, 6H); ^{19}F n.m.r. $\text{CF}_2\alpha$ (bonded to

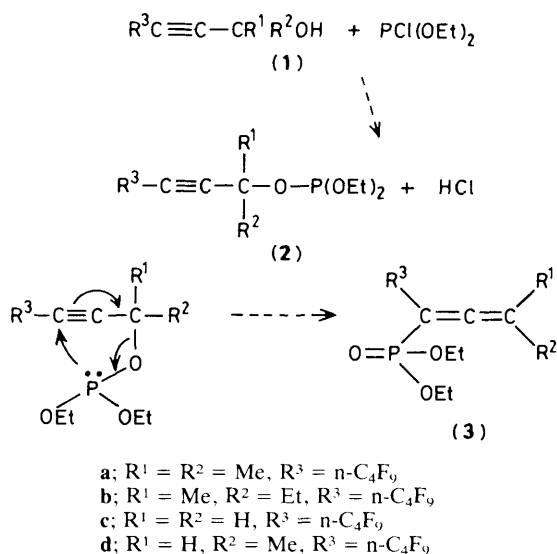
allenic system) 104.8, γ 126.5, β 123.1, CF_3 81.5‡§]. The allenic phosphonate (**3b**) is also formed instantaneously [i.r. 1960 cm^{-1} ; ^{19}F n.m.r. exhibits two kinds of $\text{CF}_2\alpha$ groups: 104.4 and 104.8 (CF_2 bonded to an asymmetric system)].

Starting from (**1c**), the reaction is limited to the formation of the prop-2-ynyl diethylphosphite (**2c**) (i.r. 2105 cm^{-1} [starting

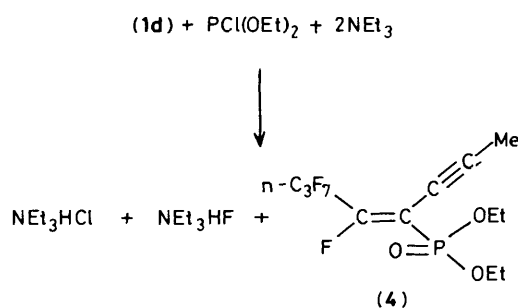
‡ ^1H N.m.r. spectra are referenced to Me_4Si , ^{19}F to CCl_3F and measured with C_6F_6 as internal reference (given in p.p.m.). ^{19}F N.m.r. of starting alcohols (**1**): $\text{CF}_2\alpha$ 98.5, γ 126, β 123, CF_3 81.5 (take as positive with increasing field).

§ The *gem*-dimethyl groups are diastereotopic by virtue of the phosphorus substituent and give rise to two methyl singlets separated by 2.5 Hz. See discussion in ref. 2, p. 3194. The presence of a doublet should not be attributed to P-H coupling which is opposite to what is proposed in ref. 1.

† All the reactions are carried out in CH_2Cl_2 ; the alkynol and diethyl chlorophosphite are mixed in the presence of triethylamine (ref. 1) in order to eliminate liberated HCl. The solvent is evaporated *in vacuo* and the product washed with water.



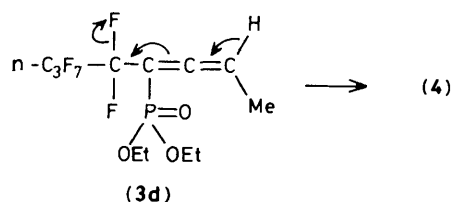
Scheme 1



Scheme 2

alcohol (1c), 2280]; ¹H n.m.r. δ 5.4 (m, 2H), 4.1 (m, 4H), 1.2 (t, 6H); ¹⁹F CF₂α 99.5, γ 126, β 124, CF₃ 81.5).

In the case of (1d), the reaction is instantaneous but leads unexpectedly to compound (4) in 55% yield [unchanged (1d), 30%] (Scheme 2), contrary to the preceding allenic phosphonates. Compound (4) can be distilled b.p. 85–90 °C (0.25 mm Hg) [i.r. 2230, 1630 cm⁻¹; ¹H n.m.r. δ 2.0, 2.07 (d, 3H), (OEt)₂ 1.33 (t, 6H), 4.2 (m, 4H); ¹⁹F n.m.r. vinyl F 103.2, CF₂ β 126.5, α 115.3, CF₃ 79.8]. Triethylamine hydrofluoride has been characterized using ¹⁹F n.m.r. spectroscopy. For this



Scheme 3

reaction, we propose the mechanism shown in Scheme 3 after the intermediate formation of the allenic phosphonate (3d). If NEt₃ is not present in the solvent and liberated HCl is not removed by a flow of nitrogen,² the reaction is limited to the formation of (2d) and addition of further NEt₃ produces no change. Additional work is to be undertaken in order to understand the mechanism of formation of (4). Only one isomer of this compound is observed; we propose the (Z) form for steric reasons.⁴

Starting from the prop-2-ynyl alcohols (1) with R³ = H or Me, the formation of allenic phosphonates is observed¹ with all of the R¹ R² groups used in this work. When R³ = n-C₄F₉, the [2,3] sigmatropic shift involving migration from oxygen to phosphorus is observed only when R¹ and R² are fairly large (Me or Et). Probably by their interaction they decrease the C–C–O angle and favour hybridization at the initially saturated carbon atom. On the contrary when R¹ = R² = H the reaction is limited to the formation of the prop-2-ynyl phosphite (2c). The perfluoroalkyl acetylenic carbon atom probably has a lower electrophilic character than those of MeC≡ or HC≡, which would make attack by the phosphorus atom less likely. For R¹ = H, R² = Me a situation arises which leads to HF elimination. We propose a study of the electrochemical and chemical properties of the allenic phosphonates described in order to evaluate the influence of the perfluoroalkyl group.^{1,5}

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