

EFFECTIVE DEPHOSPHORYLATION CATALYZED BY FLUORIDE ION:
A NOVEL SYNTHESIS OF TERMINAL F-ALKYLACETYLENES FROM F-ALKANOYL CHLORIDES

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Abstract: 1H-F-1-Alkene-1-phosphonates, easily accessible from F-alkanoyl chlorides, underwent dephosphorylation on treatment with a catalytic amount of fluoride ion at 0°C to room temperature to give terminal F-alkylacetylenes in good yields.

Terminal acetylenes are one of the most valuable intermediates in organic synthesis and a variety of synthetic methods for such compounds, especially for fluorine-free acetylenes, have been developed so far.¹ In contrast, only a few, extremely restricted methods² are known for synthesizing F-alkyl-substituted terminal acetylenes.

In this communication, we report the first example of an efficient dephosphorylation at the sp²-hybridized carbon atom catalyzed by fluoride ion, which provides a novel method for the synthesis of mono(F-alkyl)acetylenes from F-alkanoyl chlorides.

F-Alkanoyl chlorides (1) were converted to (Z)-1H-F-1-alkene-1-phosphonates (2) by the reaction with triethyl phosphite followed by the reduction with butyllithium-cuprous iodide reagent.³ When phosphonates 2 thus prepared were treated with a catalytic amount (10 mol%) of tetrabutylammonium fluoride (TBAF) at 0°C to room temperature for 2 h, the corresponding F-alkylacetylenes (3)⁴ were produced in good yields, together with a quantitative amount of diethyl fluorophosphate.

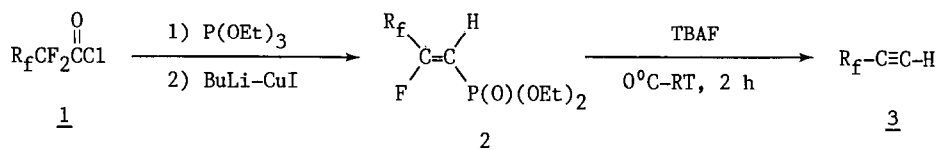


Table I shows the results of the reaction with some spectroscopic data of 3. Ethereal solvents such as tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and triglyme (TG) could be used except for diethyl ether. The use of cesium fluoride, instead of TBAF, as a source of fluoride ion gave satisfactory results⁵ though an excess amount (1.0-1.5 equiv) of it was needed for completion of the reaction. Potassium fluoride did not cause the present reaction at all, the starting phosphonates 2 being recovered unchanged.

To be noted is that the dephosphorylation at the sp²-hybridized carbon atom⁶ occurs efficiently by the action of fluoride ion under very mild conditions. Probably, the formation of a strong phosphorus-fluorine bond (117 Kcal/mol)⁷ during the reaction plays an important role in allowing this unique type of elimination to proceed.

Table I. Preparation of Terminal F-Alkylacetylenes (3)

R _f in <u>2</u>	Source of F ⁻	Solvent	Yield of <u>3</u> %	¹⁹ F NMR δ ^a	IR ν _{C≡C} ^b
CF ₃ CF ₂	TBAF	THF	89 ^c	-25.0	2140
		DME	85 ^c		
		TG	73		
	CsF	MeCN	74 ^{c,d}		
		TG	82 ^{c,d}		
CF ₃ (CF ₂) ₅	TBAF	TG	85	-21.7	2150
CF ₃ (CF ₂) ₇	TBAF	TG	74	-21.0	2155
CHF ₂ (CF ₂) ₈	TBAF	THF	75	-21.9	2150
		TG	78		

a) For the difluoromethylene adjacent to an acetylene bond, expressed in ppm down-field from external trifluoroacetic acid. b) In cm⁻¹. c) Determined by ¹⁹F NMR. d) More than one equivalent of CsF was used.

The general procedure for the present reaction is as follows: To a solution of (Z)-1H-F-1-alkene-1-phosphonate 2 (3 mmol) in anhydrous THF (8 ml) was gradually added a solution of TBAF (1M in THF, 0.3 ml) under a nitrogen atmosphere at 0°C. After being stirred at room temperature for 2 h, the reaction mixture was poured onto ice-water followed by extraction (diethyl ether), drying (Na₂SO₄), and evaporation. Silica gel chromatography or distillation of the crude product gave pure F-alkylacetylene 3. In the case of R_f=C₂F₅, F-ethylacetylene was collected at -70°C from the reaction mixture (TG used as a solvent) under reduced pressure.

Further studies on the synthetic application of this reaction as well as its mechanism are now underway.

References and Notes

- See, for example: L. Brandsma and H.D. Verkruijsse, "Synthesis of Acetylenes, Allenes, and Cumulenes," Elsevier, 1981.
- M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Halsted Press, 1976; R. D. Chambers, "Fluorine in Organic Chemistry," Wiley, 1973; P. Calas, P. Moreau, and A. Commeyras, J. Chem. Soc., Chem. Commun., 433 (1982); K. Baum, C. D. Bedford, and R. J. Hunadi, J. Org. Chem., 47, 2251 (1982).
- T. Ishihara, T. Maekawa, and T. Ando, Tetrahedron Lett., 24, 4229 (1983).
- The spectroscopic properties (IR, NMR, and mass spectrum) of all compounds were entirely consistent with the assigned structure.
- In this case, acetonitrile or TG was used as a solvent.
- For an intramolecular Wittig reaction under pyrolytic conditions, see: Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kuroda, and I. Kumadaki, Tetrahedron Lett., 23, 343 (1982); S. T. D. Gough and S. Trippett, J. Chem. Soc., 1962, 2333.
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