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THE IN SITU GENERATION OF $Ph_3P=C(CF_3)_2$. A FACILE ONE POT CONVERSION OF ALDEHYDES TO BIS-TRIFLUOROMETHYL OLEFINS.[1]

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Summary. The in situ reaction of triphenylphosphine with tetrakis(trifluoromethyl)-1,3-dithietane in the presence of aliphatic or aromatic aldehydes gives good to excellent yields of bis-trifluoromethyl olefins.

Although much recent work has produced useful synthetic routes to various types of fluoromethylene ylides[2], little work has been reported on halogenated ylides other than methylene derivatives. Undoubtedly, the notable lack of success with these homologous ylides is a consequence of the instability of these intermediates due to the facile beta elimination of halide ion that is possible.

$$R_3\overset{+}{P}\text{-}\overset{-}{C}H\text{-}CH_2X \longrightarrow [R_3\overset{+}{P}\text{-}CH=CH_2]X^-$$

X = halogen

Halogenated ylides, which contain only beta fluorines[3], are the only examples of a stable (non-methylene) ylide that have been reported. Middleton has prepared a stable phosphorane from hexafluorothioacetone and trialkyl phosphites.[4] Workers in this laboratory have prepared stable phosphorus and nitrogen ylides from hexafluorocyclobutene and triarylphosphines and tertiary amines and have elucidated their structures.[5]

$$CF_3\overset{\overset{S}{\|}}{C}CF_3 \quad + \quad 2\ (RO)_3P \longrightarrow (RO)_3P=C(CF_3)_2 \quad + \quad (RO)_3PS$$

M = P, N

Unfortunately, both Middleton's phosphorane[6] and the cyclobutane ylides[7] failed to react with aldehydes in a Wittig type of reaction.

However, we have now discovered that the phosphonium analog of Middleton's phosphorane can be generated in situ from tetrakis(trifluoromethyl)-1,3-dithietane and triphenylphosphine.[8] Subsequent in situ Wittig reaction with the appropriate aldehyde gives the resultant bis-trifluoromethyl olefins in good to excellent yields.[9] Both aliphatic and aromatic aldehydes work equally well, and the position of substitution or the type of substituent on the aromatic ring has little effect on the reaction. Ketones failed to give olefin under these conditions, since decomposition of the ylide occured faster than olefination of the ketone. Table I summarized the results with illustrative types of aldehydes.

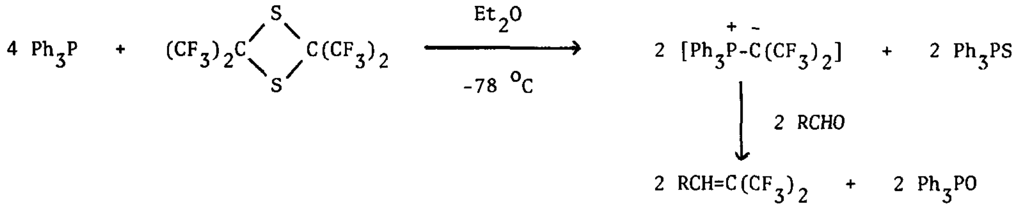

Table I

R	% Yield[a,b]	bp (mm Hg)
C_6H_5	99 (50)	52 (10)
p-$CH_3C_6H_4$	65 (42)	71 (11)
p-OMeC_6H_4	52 (40)	67 (1.3)
m-$CF_3C_6H_4$	89 (64)	48 (4)
$NO_2C_6H_4$	70 (48)	64 (0.4)[c]
C_6F_5	100 (62)	70 (30)
$CH_3CH(Ph)$	61 (26)	90 (3)
$CH_3(CH_2)_5$	100 (38)	70 (32)
PhCH=CH	60 (56)	77 (2.5)
2-Furfuryl	69 (31)	38 (9)
2-Pyridyl	55 (42)	61 (11)

[a] Yields were determined by ^{19}F NMR vs. $C_6H_5CF_3$; isolated yields are given in parentheses.
[b] All products exhibited spectral data in accord with the assigned structure and gave satisfactory elemental analyses. [c] mp 37.5 - 38 °C.

Operational details of the experimental procedure are outlined below for the preparation of β,β-bis(trifluoromethyl)styrene. Triphenylphosphine (25 g, 95 mmole) and benzaldehyde (4.7 ml, 46.4 mmole) were dissolved in 250 ml of anhydrous diethyl ether. The mixture was cooled to - 78 °C and 5 ml (23.2 mmole) of tetrakis(trifluoromethyl)-1,3-dithietane was injected in one portion. The mixture was slowly warmed to room temperature, and the resultant yellow solution was stirred at room temperature overnight. Most of the Ph_3PO and Ph_3PS were removed by filtration on a Hirsch junnel and the filtrate concentrated by rotary evaporation. The concentrated filtrate was extracted thoroughly with pentane, washed with 40% $NaHSO_3$, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. Simple distillation gave 5.1 g (50%) β,β-(bis(trifluoromethyl)styrene, bp 52 ° (10 mm). ^{19}F NMR showed a quartet at 57.2 ppm, J_{CF_3,CF_3} = 7.8 Hz, for the CF_3 group trans to the vinyl hydrogen and a quartet of doublets at 63.3 ppm, J_{H,CF_3} = 1.4 Hz, for the CF_3 group cis to the vinyl hydrogen.[11] The mass spectrum showed a parent ion at m/e 240 (calcd. 240); IR showed the C=C at 1663 cm^{-1}.

The tetrakis(trifluoromethyl)-1,3-dithietane is easily obtained from the commercially available hexafluoropropene by the method of Knunyants.[12] Consequently, the availability of suitable aldehyde procursors, ease of preparation of the dithietane, simplicity of the reaction method, and good overall yields in a on-pot procedure make this method attractive as a useful synthetic route to bis-trifluoromethyl olefins and the hexafluoroisopropylidene ylide. The alternative route to these olefins via the reaction of hexafluoroacetone[13] and phosphonium ylides requires the prior preparation of the appropriate ylide and hence the appropriate halide precursor for phosphonium salt formation. Except for simple cases these halide precursors are not easily obtained. Hence, the synthetic route described herein from the dithietane has significant advantate over this alternate route and is the current method of choice.

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References and Notes

1) Presented in part at the 4th Winter ACS Symposium on Fluorine Chemistry, Daytona Beach, Florida, January 1979.

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3) When alpha fluorines are present in the ylide, such as in $Ph_3\overset{+}{P}-\overset{-}{C}FCF_2CF_3$, no stability is found. Immediate collapse occurs to produce the vinyl phosphorane, $Ph_3P(F)CF=CFCF_3$; D. J. Burton, S. Shinya and R. D. Howells, J. Am. Chem. Soc., in press.

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6) $(MeO)_3P=C(CF_3)_2$ gave no reaction with benzaldehyde or trifluoroacetophenone. In situ generation of $(MeO)_3P=C(CF_3)_2$ from $(MeO)_3P$ and tetrakis(trifluoromethyl)-1,3-dithietane in the presence of benzaldehyde also failed to produce olefin; unpublished work of Y. Inouye.

7) Numerous attempts to carry out a Wittig reaction with either the phosphorus or nitrogen ylides have met with a total lack of success; unpublished work of R. D. Howells, P. D. VanderValk and S. Shinya.

8) Other phosphine, such as $\underline{n}$-Bu_3P and $(Me_2N)_3P$, give diminished yields of olefins. The ylide shows little stability under these conditions; consequently in situ generation and capture of the ylide gives best results.

9) Previous attempts to prepare $Ph_3P=C(CF_3)_2$ from $[Ph_3\overset{+}{P}CH(CF_3)_2]X^-$ failed[10], since the alkylation of the appropriate $(CF_3)_2CHX$ derivative failed to produce the required phosphonium salt.

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11) The spectral properties of this olefin were identical in all respects to an authentic sample prepared from hexafluoroacetone and $Ph_3P=CHPh$.

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13) Hexafluoroacetone is currently not available in the U.S.A.

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