Tetrahedron Letters No.23, pp. 1461-1463, 1964. Pergamon Press Ltd.
Printed in Great Britain.

A ONE-STEP SYNTHESIS OF 1,1-DIFLUOROOLEFINS FROM ALDEHYDES BY A MODIFIED WITTIG SYNTHESIS

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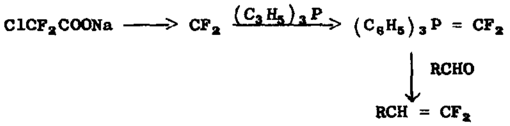
(Received 3 April 1964; in revised form 20 April 1964)

We report a one-step transformation of aldehydes to 1,1-difluoroolefins by heating a solution of an aldehyde, triphenylphosphine and sodium chlorodifluoroacetate.

Presumably the reaction proceeds with the *in situ* formation of difluorocarbene which reacts with triphenylphosphine to form the ylid which undergoes a Wittig reaction with the aldehyde to form the 1,1-difluoroolefin:



$$\begin{tikzcd} ClCF_2COONa \arrow[r] & CF_2 \arrow[r, "(C_3H_5)_3P"] & (C_6H_5)_3P = CF_2 \arrow[d, "RCHO"] \\ & & RCH = CF_2 \end{tikzcd}$$

Formation of difluorocarbene by decomposition of sodium chlorodifluoroacetate in solution has been reported.[1] Seyferth demonstrated that

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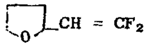
*Deceased.

1a. J. M. Birchall, G. W. Cross, and R. N. Haszeldine, Proc. Chem. Soc., 1960, 81.

1b. L. H. Knox, Preprints, Second International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1962, page 277. L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, P. W. Landis, and A. D. Cross, J. Am. Chem. Soc., 85, 1851 (1963).

chlorocarbene, generated from methylene chloride and butyl lithium, reacted with triphenylphosphine to form the ylid.[2] Similar trapping with triphenylphosphine of dichlorocarbene,[3] of chlorocarbene,[4] and of methylene,[5] and the use, in a Wittig reaction, of the ylids formed have been reported. Speziale[3b] was unsuccessful in attempts to trap difluorocarbene, generated from chlorodifluoromethane, with triphenylphosphine, nor could he substantiate Franzen's[5b] claims that difluorocarbene, generated from dibromodifluoromethane, could be trapped with triphenylphosphine.

The general procedure used at the present time is as follows. A solution of 0.1 mole of the aldehyde, 0.11 mole of triphenylphosphine and 0.11 mole of sodium chlorodifluoroacetate in 50 ml of either anhydrous 1,2-dimethoxyethane (monoglyme) or anhydrous 2,2'-dimethoxydiethyl ether (diglyme) is heated in a nitrogen atmosphere until 0.11 mole of gas has been evolved. This requires about 72 hours for refluxing monoglyme and about 18 hours for diglyme at a bath temperature of 90°. The solution is filtered hot to remove sodium chloride (quantitative yield), and the product is distilled through a spinning band column. The pot residue consists of a quantitative yield of triphenylphosphine oxide.

The reaction appears to be general for aromatic, heteroaromatic, and aliphatic aldehydes. The following compounds have been prepared to date (b.p., yield, λ_{max}^{film} $CH = CF_2$): $CH_3(CH_2)_5CH = CF_2$ (120°, lit.[6] 119; 16%, 5.72μ);  (49°/1.5 mm, 60%, 5.75μ); 

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2. D. Seyferth, S. O. Grim and T. O. Read, J. Am. Chem. Soc., 82, 1510 (1960). Ibid., 83, 1617 (1961).
3a. A. J. Speziale, G. J. Marco, and K. W. Ratts, ibid., 82, 1260 (1960).
3b. A. J. Speziale and K. W. Ratts, ibid., 84, 854 (1962).
4. G. Wittig and M. Schlosser, Angew. Chem., 72, 324 (1960).
5a. V. Franzen and G. Wittig, ibid., 72, 417 (1960).
5b. V. Franzen, ibid., 72, 566 (1960).
6. J. L. Anderson, U.S. Pat., 2,733,278 (Jan. 31, 1956). C. A. 50, 15,575c.

(approximately 80-85°,[7] 75%, 5.74µ); -CH = CF_3 (53°/38 mm, lit.[8] 58°/49 mm, 22.5%, 5.82µ); F--CH = CF_2 (47°/30 mm, 65%, 5.76µ). Elemental analysis, infrared, mass, and n.m.r. spectra obtained on samples separated by gas chromatography are consonant with the assigned structures.

Polymerization during the workup appears to be a problem with some of the 1,1-difluoroolefins; addition of 0.1% (based on olefin) of hydroquinone to the distillation pot and avoidance of high temperatures are advisable.

Work in progress is directed at establishing optimum conditions, determining the mechanism,[9] extending the range of useful halogenated acetates, and investigating similar transformations of ketones.

Acknowledgment: This work was supported by an internal grant from Stanford Research Institute.

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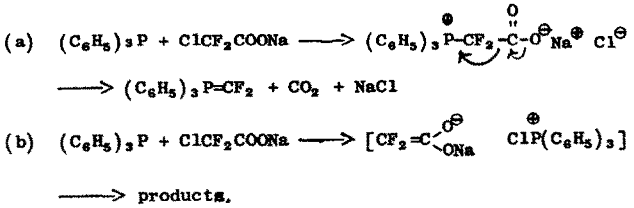
[7] The product codistilled with monoglyme. Flashed in vacuo from diglyme in subsequent experiment, and purified by GLC. Polymerizes readily at room temperature.

[8] J. Drysdale, J. Am. Chem. Soc. 79, 319 (1957).

[9] Two other plausible mechanisms were suggested by the referee:



$$\text{(a)}\quad (C_6H_5)_3P + ClCF_2COONa \longrightarrow (C_6H_5)_3\overset{\oplus}{P}-CF_2-\overset{\overset{O}{\|}}{C}-O^{\ominus}Na^{\oplus}\ Cl^{\ominus}$$

$$\longrightarrow (C_6H_5)_3P{=}CF_2 + CO_2 + NaCl$$

$$\text{(b)}\quad (C_6H_5)_3P + ClCF_2COONa \longrightarrow [CF_2{=}C{\scriptstyle\begin{matrix}\nearrow O^{\ominus}\\ \searrow ONa\end{matrix}}\quad Cl\overset{\oplus}{P}(C_6H_5)_3]$$

$$\longrightarrow \text{products.}$$