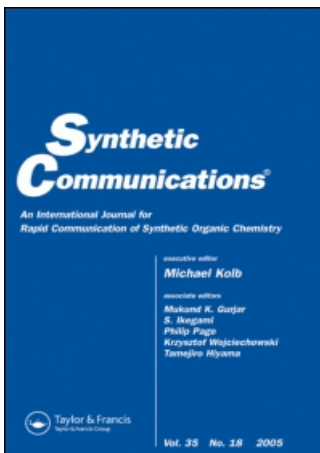


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A NEW METHOD OF FLUOROALKYLATION  
BY A WITTIG REACTION

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SUMMARY

A new method has been developed for the introduction of a perfluorinated chain into an hydrogenated moiety. It is based on the use of a new fluorinated reagent,  $(C_6H_5)_3P^+-CH_2CH_2R_F I^-$  which couple to a non fluorinated aldehyde  $R_H-C \begin{matrix} \equiv O \\ \backslash H \end{matrix}$  in a Wittig reaction.

The lack of mutual solubility of completely hydrogenated ( $R_H$ ) and completely fluorinated ( $R_F$ ) derivatives (oils and surfactants) has been a subject of investigation over the last few years. These studies have shown that the segregation phenomena observed are highly dependent on the molecular structures of the various components (conformations of the various  $R_F$  and  $R_H$  chains) (1).

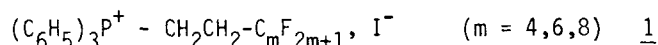
We have been studying these mutual solubility phenomena in relation to the degree of fluorination, using mixtures of partially fluorinated derivatives with completely hydrogenated

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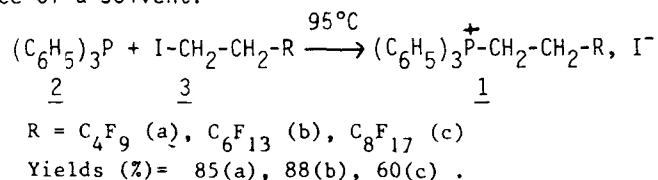
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compounds. We therefore required a method of obtaining partially fluorinated compounds whose degree of fluorination could be varied at will.

We developed a new reagent, a phosphonium salt with an almost completely fluorinated chain of general formula



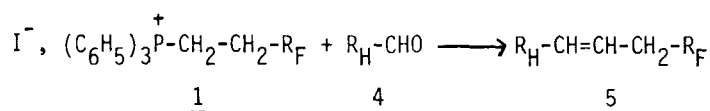
These phosphonium salts 1 were prepared by heating triphenylphosphine 2 and various fluoroalkyl iodides (3) to 95°C in the absence of a solvent.



The phosphonium salts 1 were identified by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR spectroscopy and elemental analysis.

We have previously published details on the surface active properties of these compounds (3).

Reagent 1 can react with aldehydes 4 in a Wittig type reaction to give "mixed" olefins 5 with both hydrogenated and fluorinated portions -



The initial studies were carried out with pentanal, benzaldehyde and terephthalic aldehyde using two types of reaction :

Trials 1,2,3 : N-butyllithium as base/THF/0°, -40°, -70°C

Trial 4 : Lithium diisopropylamide as base/THF/-70°C

The first three trials were unsuccessful, since the ylide formed under such basic conditions decomposed even at low temperatures to liberate fluoride ions (identified by <sup>19</sup>F NMR spectroscopy). Trial four using a weaker base led to low yields of olefins, due to a more stable intermediate ylide.

We were thus able to optimise a more gentle method for production of a more stable intermediate ylide which could condense with an aldehyde before decomposition. We used a method recently developed by Y. Le BIGOT (4) for classical Wittig reactions (hydrocarbon phosphonium salts) carried out in dioxan at 95°C in the presence of hydrated potassium carbonate. The method which is simple to carry out enabled us to produce partially fluorinated hydrocarbons via a Wittig reaction.

It is noteworthy that this procedure is successful when the reactions fail via classical methods. On the other hand, as it has been previously reported by Y. Le BIGOT and coll. (4b) with perhydrogenated phosphonium salts, terephthalic aldehyde is converted into monoolefin 5e with stoichiometric amounts of fluorinated phosphonium salt and aldehyde.

The following table shows the results obtained.

The olefins were obtained as a mixture of Z and E isomers whose configurations and relative proportions were determined by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy. Isomer Z predominated in all cases since the phosphonium salts used formed non stabilised ylides.

These results were encouraging, and are, to our knowledge, the first to use Wittig reactions for fluoroalkylation. We are developing this method for use with bifunctional

Table : Wittig reactions with phosphonium salts  $(\text{C}_6\text{H}_5)_3\text{P}^+\text{-CH}_2\text{-CH}_2\text{-R}_\text{F}, \text{I}^-$

| Compounds   |           | Yields (%) | E/Z (%) |
|---|-----------|------------|---------|
| $\text{C}_4\text{H}_9\text{-CH=CH-CH}_2\text{-C}_6\text{F}_{13}$                          | <u>5a</u> | 45         | 25/75   |
| $\text{C}_6\text{H}_5\text{-CH=CH-CH}_2\text{-C}_4\text{F}_9$                             | <u>5b</u> | 55         | 35/65   |
| $\text{C}_6\text{H}_5\text{-CH=CH-CH}_2\text{-C}_6\text{F}_{13}$                          | <u>5c</u> | 80         | 30/70   |
| $\text{C}_6\text{H}_5\text{-CH=CH-CH}_2\text{-C}_8\text{F}_{17}$                          | <u>5d</u> | 55         | 30/70   |
| p OHC-C <sub>6</sub> H <sub>5</sub> -CH=CH-CH <sub>2</sub> -C <sub>4</sub> F <sub>9</sub> | <u>5e</u> | 60         | 35/65   |

aldehydes other than dialdehydes in order to obtain "mixed" (partially fluorinated) surface active agents.

We will therefore be able to carry out a systematic study of segregation phenomena between hydrogenated and fluorinated compounds (oils and surfactants).

#### Experimental part

0.025 mole of fluorinated phosphonium salt, 0.02 mole aldehyde, 0.03 mole  $K_2CO_3$  (4.15 g), 0.3 ml ( $1.7 \times 10^{-2}$  mole) water and 20 ml anhydrous 1,4-dioxan are put into a 250 ml flask fitted with a condenser and a thermometer. The reaction mixture is maintained at 95°C under constant agitation for 1 to 4 hours. At the end of the reaction, the mixture is filtered at ambient temperature and the solvent is evaporated under vacuum. The residue is taken up in ether to remove most of the triphenylphosphine oxide. After purification on a chromatography column ( $SiO_2$ ,  $C_6H_6$ ) the products are identified by  $^1H$ ,  $^{19}F$  NMR spectroscopy and elemental analysis.

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