

THE REACTION OF ALKYLIDENETRIPHENYLPHOSPHORANES WITH
CHLORODIFLUOROMETHANE. SYNTHESIS OF 1,1-DIFLUORO-1-ALKENES

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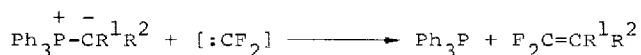
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Although the Wittig reaction has become an important synthetic tool for the organic chemist, the lack of any facile, cheap method to recycle the phosphine oxide has limited its application to small scale laboratory reactions, and it has achieved little significance as an industrial synthetic method. An alternative to the recyclization of the phosphine oxide to phosphine is to avoid its formation in the olefin synthesis, and this report details our initial successful efforts to circumvent this problem in the preparation of 1,1-difluoro-1-alkenes.

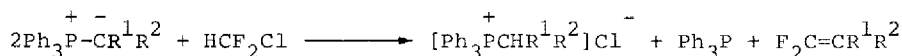
Reimlinger¹ and Oda² have successfully trapped halocarbenes with nitrogen and phosphorous ylides, respectively, to produce halogenated olefins. Although Oda realized only limited success (good conversions, but low yields, of haloolefins) with this method, significantly this method did not produce phosphine oxide. Thus, it appeared that this type of approach might solve the Wittig reaction limitation, if yields of olefins could be improved and facile recovery of phosphine-containing materials could be attained.

Both Reimlinger and Oda employed the haloform/base method for carbene generation. This method, however, produces additional by-products which must be removed in any cyclic process and complicates material recovery. We have explored the possibility of using the ylide as a bi-functional reactant; first as the base to generate the carbene intermediate, and secondly as the trapping

agent for the carbene. Our initial work has focused on the reaction of alkylidene ylides with chlorodifluoromethane and schematically can be outlined as shown below:



overall reaction:



In this scheme, the only by-products are the initial phosphonium salt and phosphine (which can be recycled to salt). No phosphine oxide is obtained, and only the relatively cheap methane is consumed.

We have found that the reaction between non-stabilized alkylidene tri-phenylphosphoranes and chlorodifluoromethane proceeds smoothly at room temperature to give good yields of 1,1-difluoro-1-alkenes. Both primary and secondary alkylidene ylides work equally well in this reaction. The yields of some typical reactions are summarized in Table I.

Table I

R^1	R^2	Solvent	Time	Yield of Olefin ^{3, 4, 5}
H	C_3H_7	Triglyme	4 hrs.	88%
H	$\text{n-C}_6\text{H}_{13}$	"	"	93%
H	$\text{n-C}_{11}\text{H}_{23}$	Et_2O	"	90%
CH_3	CH_3	Triglyme	"	82%
CH_3	C_2H_5	"	"	81%
-- C_5H_{10} --		Et_2O	"	ca. 100%
-- C_4H_8 --		Triglyme	"	90%

The reactions are essentially complete within a few hours at room temperature. The phosphonium salt may conveniently be isolated by filtration

in yields of ca. 90%, the product olefin may be separated either by flash distillation or by steam distillation and isolated by fractional distillation, and the phosphine can easily be recovered in yields of 85% to 90% by dilution of the residue with water, or by recrystallization of the residue after flash distillation of the solvent. The following representative experimental procedure provides operational details for the preparation of 1,1-difluoro-1-alkenes via this procedure.

A solution of methyllithium in ether (50 ml, 0.100 mol) was added dropwise to a well-stirred slurry of cyclohexyltriphenylphosphonium bromide⁶ (42.5 gm, 0.100 mol) in dry ether (150 ml) under dry nitrogen with ice bath cooling. The deep red solution was allowed to warm to room temperature and was stirred for one hour. Chlorodifluoromethane⁷ (4.33 gm, 0.050 mol) was then condensed into the reaction mixture via a Dry Ice cold finger condenser followed by stirring for an additional four hours. The reaction mixture was filtered and the phosphonium salt was washed with ether to give cyclohexyltriphenylphosphonium chloride (17.1 gm, 0.045 mol, 90%). The ether washings and the filtrate were combined and concentrated to ca. 25 ml. This mixture was flash distilled, and the distillate was fractionated through a 15 cm Vigreux column to yield difluoromethylenecyclohexane (5.3 gm, 0.040 mol, 80%), b.p. 104-106° C (lit⁸, b.p. 105-106° C), which was 98% pure by glpc analysis. The residue from the flash distillation was recrystallized from 95% ethanol to yield triphenylphosphine (11.5 gm, 0.044 mol, 88%).

The success of this olefination procedure succinctly demonstrates that the basic alkylidene ylides easily fulfill the role of our bi-functional reactant. Proton abstraction is rapid and carbene trapping efficiency of the relatively unreactive (compared to other halocarbenes) difluorocarbene is excellent. The ease of isolation of olefin and recovery of the phosphonium salt and phosphine is not hampered by additional by-products of carbene formation and permits facile utilization of all phosphine containing materials.

This method of difluoromethylene olefin synthesis compares very

favorably to the Wittig approach, and in some cases offers a useful alternative. For example, whereas enolizable ketones, such as cyclopentanone, gave only trace amounts of difluoromethylenecyclopentane via the Wittig reaction, this method gives a 90% yield of this olefin. Also, significant amounts of aldehydes are consumed in the Wittig approach by reaction with the dihalotriphenylphosphorane (~30% in the case of n-heptaldehyde), whereas in this procedure the alkylidene portion is completely converted to olefin.

Additional work is in progress with other types of alkylidene ylides as well as other types of carbenes. Future reports will elucidate the overall scope of this reaction.

NOTES AND REFERENCES

1. H. Reimlinger, Angew. Chem., 74, 153(1962).
2. R. Oda, Y. Ito, and M. Okano, Tetrahedron Lett., 7(1964); M. Okano, Y. Ito, and R. Oda, Bull. Inst. Chem. Research, Kyoto Univ. Japan, 42, 217(1964), Y. Ito, M. Okano, and R. Oda, Tetrahedron, 22, 2615(1966).
3. All fluoroolefins reported in Table I were unambiguously identified by nmr, ir, and mass spectral analysis.
4. Glpc yields based on thermal conductivity corrections relative to an appropriate internal standard.
5. Yield based on alkylidene ylide.
6. H. J. Bestmann and O. Kratzer, Ber., 96, 1899(1963).
7. Fluorocarbon 22, available from E. I. duPont de Nemours.
8. S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, J. Org. Chem., 30, 2543(1965).