

A Novel Transylation between Ylides from Different Elements. A One-pot Synthesis of *trans*-Fluorovinyl Epoxides

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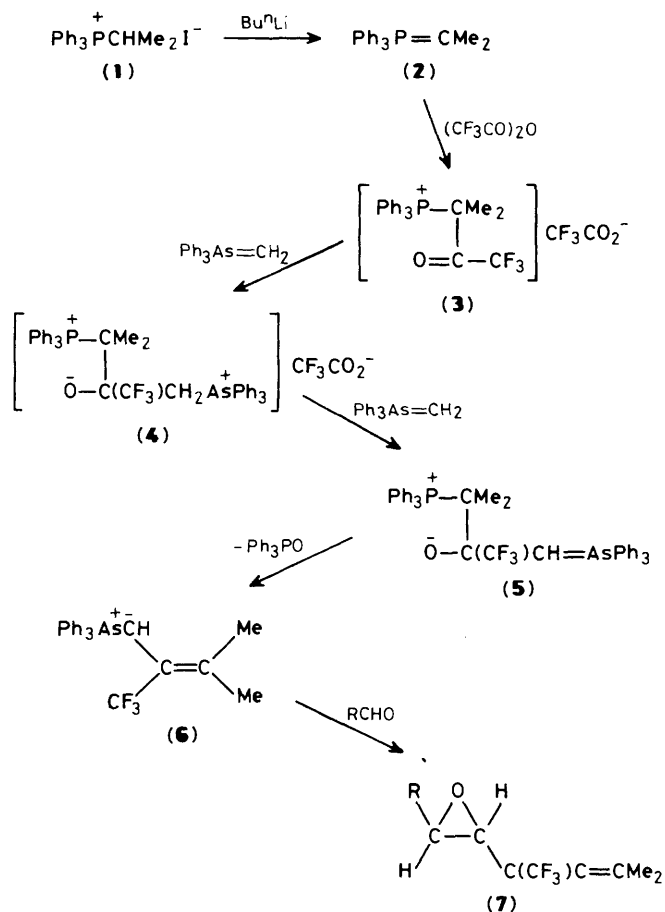
A novel transylation reaction between ylides from different elements and one-pot synthesis of *trans*-fluorovinyl epoxides are described.

Transylation was first proposed by Bestmann between phosphonium ylides and salts to afford another ylide as a result of basicity differences between the ylides.¹ To our knowledge, transylation between ylides from different elements has not been reported. We now report such a reaction and its application to the one-pot synthesis of *trans*-fluorovinyl epoxides.

Epoxides are useful intermediates in the synthesis of biologically active compounds.² Vinyl epoxides have been prepared *via* arsonium ylides,³ but as a mixture of *trans*- and *cis*-isomers ranging from 6:4 to 4:6. Still *et al.* reported a highly stereoselective synthesis of *trans*-epoxides *via* arsonium ylides, but a mixture of solvents [tetrahydrofuran (THF)–10% hexamethylphosphoramide (HMPA)], potassium bis-(trimethylsilyl) amide, and arsonium fluoroborates were necessary to give high stereoselectivity.⁴ Our reaction gave exclusively *trans*-fluorovinyl epoxides.

The reaction sequence is shown in Scheme 1. A novel transylation occurs in which the simple phosphonium ylide (**2**) is converted to a complex arsonium ylide in four steps. It is noteworthy that after nucleophilic addition of methylenetriphenylarsorane to (**3**), deprotonation of (**4**) to give (**5**) and elimination of triphenylphosphine oxide occur spontaneously to afford the new ylide (**6**).

In a general procedure *n*-butyl-lithium (3 mmol) was added dropwise with stirring to a suspension of isopropyltriphenylphosphonium iodide (**1**) (3 mmol) in dry THF (30 ml) at -70°C under nitrogen. The reaction mixture was stirred for 15 min at 0°C , cooled to -70°C , and trifluoroacetic anhydride (2.6 mmol) was slowly added until the characteristic ylidic colour disappeared. After stirring at -70°C for 2 min, a solution of methylenetriphenylarsorane [generated from methyltriphenylarsonium iodide (6 mmol) and *n*-butyl-lithium (6 mmol) in THF (10 ml)] was slowly added over 0.5 h, and



Scheme 1

Table 1. Synthesis of *trans*-fluorovinyl epoxides.

Compound	R	M.p./°C	Yield ^a (%)
(7a)	C ₆ H ₅	100—102/0.2 ^b	45
(7b)	4-ClC ₆ H ₄	55	63
(7c)	2-ClC ₆ H ₄	41	40
(7d)	4-FC ₆ H ₄	48—49	40
(7e)	4-BrC ₆ H ₄	52—53	35
(7f)	4-CH ₃ OC ₆ H ₄	52—53	55
(7g)	2-CH ₃ OC ₆ H ₄	50—51	42
(7h)	4-NO ₂ C ₆ H ₄	97	55

^a Isolated yields. All products exhibited n.m.r., i.r., and mass spectral data consistent with the assigned structures. ^b B.p. (°C/mmHg).

then the aldehyde (5 mmol) was added. After stirring for 5 min and standing overnight, the product was isolated by column chromatography [silica gel, light petroleum (b.p. 60—90 °C) eluent]. The results are shown in Table 1.

This one-pot synthesis of fluorovinyl epoxides is stereospecific, giving the *trans*-isomer, as judged on the basis of their ¹H n.m.r. spectra, should be useful in the synthesis of biologically active compounds.

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