New Synthesis of Vinylallenes

By J. GORE* and J. P. DULCERE

(*Département de Chimie Organique, Université Claude Bernard, 43, Boulevard du 11 Novembre 1918, 69-Villeurbanne, France*)

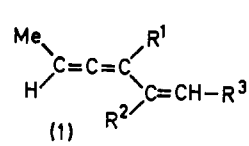
Summary Vinylallenes (1a—f) are obtained in good yield by reaction of MeMgI and 5-chloropent-3-en-1-ynes (2).

IN spite of their synthetic utility[1] vinylallenes (1) are not readily accessible.[1-4] We have, therefore, investigated the reactions of MeMgI with some 5-chloro-3-en-1-ynes (2) easily accessible by ethynylation of $\alpha\beta$-ethylenic ketones followed by reaction of conc. HCl with the enynol,[5] in order to prepare them.

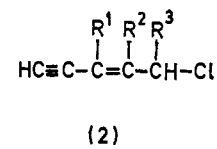
Reduction of 5-chloropent-3-en-1-yne by Zn-Cu couple gave vinylallene.[6] Optimum yields (see Table) of the 1,2,4-trienes (uncontaminated with enynes) were obtained when compounds (2a—f) were heated under reflux in ether for 3—4 h with MeMgI. Yields were calculated on the amount of vinylallenes recovered (chromatography or t.l.c.).

Compounds (1a), (1b), (1e), and (1f) are less stable than (1c) and (1d) and decompose with time or when heated. The last two compounds may be purified by g.l.c.

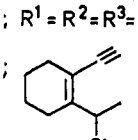
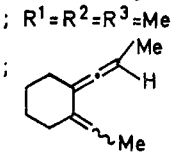
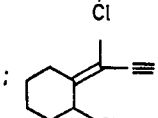
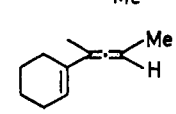
Compound (1a—f) showed a molecular ion (M^+); ν(C=C=C) and ν(C=C) were at 1945 ± 5 and 1635 ± 5 cm^{-1}



(1)



(2)

(2)	(1)	Yield %
a; $R^1=R^2=H$, $R^3=Me$	a; $R^1=R^2=H$, $R^3=Me$	50
b; $R^1=Me$, $R^2=R^3=H$	b; $R^1=Me$, $R^2=R^3=H$	52
c; $R^1=R^2=Me$, $R^3=H$	c; $R^1=R^2=Me$, $R^3=H$	75
d; $R^1=R^2=R^3=Me$	d; $R^1=R^2=R^3=Me$	78
e; 	e; 	48
f; 	f; 	55

respectively. The n.m.r. spectra showed signals at δ 4·8 and 5·5 (vinylic H), 5·15 (allenic H), and 1·6—1·8 p.p.m. (vinylic and allenic Me). The n.m.r. spectra of pure (1a), (1d), and (1e) indicated the presence of a single isomer.

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