New Synthetic Routes to Conjugated Diallenes from Bromoallenes and Prop-2-ynyl Acetates. Novel C–C Coupling with Copper(I) Chloride

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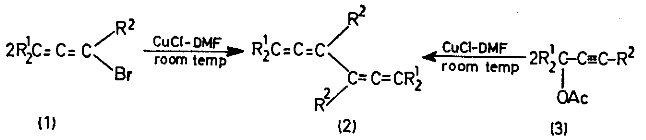
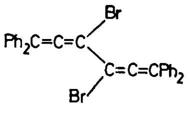
Summary The reactions of the bromoallenes (**1**) and the prop-2-ynyl acetates (**3**) with CuCl in dimethylformamide (DMF) at room temperature both afford the conjugated diallenes (**2**) in good yield.

We have shown that the 1,2,4,5-tetraene (**4**) can be prepared easily by the reaction of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with conc. HBr in AcOH.[1] However, no general route to 3,4-dialkyl and 3,4-diaryl-hexa-1,2,4,5-tetraenes has been established. We report here two synthetic routes to the conjugated diallenes (**2**) from the bromoallenes (**1**) and the prop-2-ynyl acetates (**3**), *via* novel C–C couplings with CuCl.

A solution of (**1a**) (10 mmol) and CuCl (20 mmol) in DMF (10 ml) was kept at room temperature for 1 h. The crude crystals resulting from the addition of dil. HCl were filtered off and recrystallized to afford (**2a**), m.p. 235 °C (decomp.), in 72% yield; ν_{max} 1950 cm^{-1} (C=C=C), λ_{max} 247 (ϵ 38,000) and 256 nm (38,200); τ 2·1—3·0 (m, Ph); *m/e* 534 (M^+) and 267 ($M^+/2$).† Similar treatment of (**1b**), (**1c**), and also (**3a**—**c**) afforded the diallenes (**2a**—**c**). Compounds (**2b**), m.p. 201 °C (decomp.), and (**2c**), m.p. 173·5—174 °C, gave comparable spectral data, and the data for (**2a**—**c**) were analogous to those for (**4**).[1]

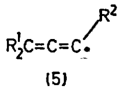


(1) (2) (3)



(4)

a; $R^1 = R^2 = Ph$
b; R^1_2 = biphenyl-2,2′-diyl, $R^2 = Me$
c; R^1_2 = biphenyl-2,2′-diyl, $R^2 = Ph$



(5)

The reactions of both (**1**) and (**3**) can be interpreted by assuming the allene radical (**5**) as an intermediate.

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† The i.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$ and $CDCl_3$ respectively. The mass spectra were measured with an ionization energy of 75 eV. All new compounds gave satisfactory elemental analyses.

[1] M. Higashi, F. Toda, and K. Akagi, *Chem. and Ind.*, 1969, 491.