The Protection of Terminal Ethynyl Groups in the Oxidative Couplings of Acetylenes

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THE Glaser and Cadiot–Chodkiewicz oxidative coupling techniques used so successfully in the synthesis of internal polyacetylenes[1] cannot readily be adapted to the preparation of terminal alkynes. In such reactions, direct involvement of acetylene itself, or of bromoacetylene, leads to extensive and uncontrollable polymerisation, whilst easily removed protecting groups [*e.g.*, Cl (ref. 2); CO_2H (ref. 3)] may have a marked destabilising effect on the higher polyacetylene intermediates.

We find that introduction of a trialkylsilyl group[4] provides a simple method for protecting terminal acetylenes in oxidative couplings. Thus the Glaser reaction (Hay modification[5]) of a trialkylsilyl-acetylene or -diacetylene gives the corresponding bistrialkylsilylpolyacetylene (I, II) in good yield.

$$Et_3SiC{\equiv}CH \rightarrow Et_3Si[C{\equiv}C]_2SiEt_3 \qquad (I)$$

$$Me_3Si[C{\equiv}C]_2H \rightarrow Me_3Si[C{\equiv}C]_4SiMe_3 \qquad (II)$$

Treatment of the products with aqueous methanolic alkali[6] affords solutions of the parent acetylenes, $H[C{\equiv}C]_2H$ and $H[C{\equiv}C]_4H$, in quantitative yield (base-catalysed addition of methanol to the triple bond does not occur under the reaction conditions),[7] together with inert hexa-alkyldisiloxane. Cadiot–Chodkiewicz coupling,[1] with an α-bromo-ω-trialkylsilylacetylene(IV)† as one component, forms the basis of a simple two-stage reaction sequence for the stepwise construction of terminal polyacetylenes, $R[C{\equiv}C]_xH$, as illustrated in the following scheme:

$$\underset{(III)}{Ph[C{\equiv}C]_nH} + \underset{(IV)}{Br[C{\equiv}C]_mSiEt_3} \rightarrow$$

$$\underset{(V)}{Ph[C{\equiv}C]_{n+m}SiEt_3} \rightarrow \underset{(VI)}{Ph[C{\equiv}C]_{n+m}H}$$

Thus, starting from phenylacetylene (III; $n = 1$) further acetylene units may be introduced one at a time (IV; $m = 1$) or two at a time (IV; $m = 2$). Treatment of the products (V) with aqueous methanolic alkali gives phenyl-diacetylene or -triacetylene respectively (VI; $n + m = 2,3$) in quantitative yield (characterised by oxidative coupling to the corresponding diphenylpolyines, $Ph[C{\equiv}C]_{4,6}Ph$).[8] Alternatively, the product of the first coupling: solvolysis sequence, phenyldiacetylene (VI; $n + m = 2$), may be extracted from the aqueous methanolic alkali with hexane. Concentration of this solution, achieved without polymerisation, followed by oxidative coupling with a further mole of (IV) ($m = 1$) gives (V) ($n + m = 3$), identical with material obtained from (III) ($n = 1$) + IV ($m = 2$). The technique affords a convenient synthesis of substituted phenyldiacetylenes, $XC_6H_4[C{\equiv}C]_2H$, (X = *p*-F, *m*-Br, *m*-Me) starting from (IV) ($m = 1$) and the readily accessible phenylacetylenes ($X{\cdot}C_6H_4{\cdot}C{\equiv}CH$).[9]

Attractive features of the method are:

(i) The characteristic visible shift of both high and medium intensity u.v. absorption bands of the polyacetylene associated with the introduction of a trialkylsilyl group[10] permits all steps of the synthetic sequence to be followed quantitatively in dilute solution.

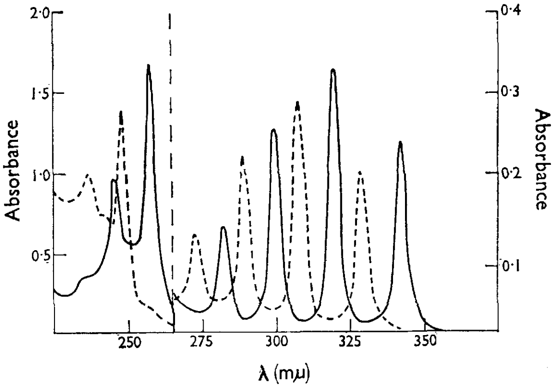

FIGURE. *Ultraviolet spectra of* $Ph[C{\equiv}C]_3SiEt_3$ (——), *and* $Ph[C{\equiv}C]_3H$ (— — —) *in methanol solution.*

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† We are indebted to Dr. U. Krüerke (Union Carbide Research Associates, Brussels) who as far as we are aware carried out the first successful Cadiot–Chodkiewicz coupling involving a silylacetylene ($PhC{\equiv}CH + BrC{\equiv}CSiMe_3$) and who generously supplied us with full experimental details of his unpublished work.

(ii) The trialkylsilyl group(s) apparently exert a stabilising influence on the polyacetylenes reminiscent of the analogous t-butyl group stabilisation.[11]

(iii) The consequent ready isolation of pure samples of the silylpolyacetylenes, their quantitative solvolysis, and the negligible (or accurately known) absorption of the hexa-alkyldisiloxane so formed, permits precise evaluation of the absorption band positions and intensities of terminal polyacetylenes, *e.g.*, $H[C{\equiv}C]_4H$ (methanol) $\lambda_{m\mu}$, ϵ_{max} 225·6 (171,000); 215 (123,000).‡

Attempts to carry out Cadiot–Chodkiewicz coupling reactions as exemplified by:

$$PhC{\equiv}CBr + HC{\equiv}CSiEt_3 \rightarrow Ph[C{\equiv}C]_2SiEt_3$$

$$Et_3Si[C{\equiv}C]_2H + BrC{\equiv}CSiEt_3 \rightarrow Et_3Si[C{\equiv}C]_3SiEt_3$$

have so far been unsuccessful. Use of bulkier alkyl groups on silicon may overcome this limitation.

We thank S.R.C. for a research studentship (to R.E.).

(*Received, November 29th*, 1967; *Com.* 1280.)

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‡ Compare $H[C{\equiv}C]_4H$ (pentane), $\lambda_{m\mu}$ 227, ϵ_{max} 280,000 (C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 2883).

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