Tetrahedron Letters No. 13, pp 1019 - 1020, 1973. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF TWO NATURALLY OCCURING ALLENEDIYNES, (±) OCTA-2, 3-DIENE-5,7-DIYN-1-ol AND (±) UNDECA-5,6-DIENE-8,10-DIYN-1-ol BY AN ALLENIC BROMIDE/BUTADIYNYL(TRIMETHYL)SILANE COUPLING REACTION.

By Phyllis D. Landor, S.R. Landor* and J.P. Leighton
(Department of Chemistry, Makerere University, Kampala, Uganda
and Woolwich Polytechnic, London S.E. 18)

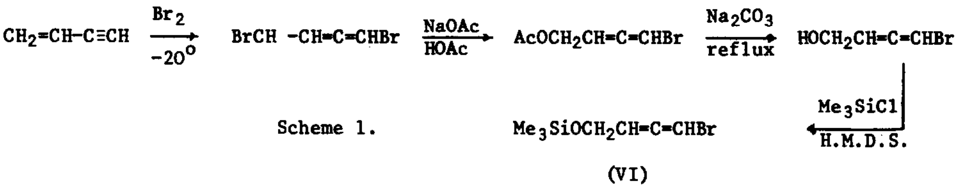
(Received in UK 5 February 1973; accepted for publication 8 February 1973)

The natural allenes produced by micro-organisms[1] reported so far all contain the allenediyne system C=C=CH-C≡C-C≡C-, but no satisfactory method for their synthesis has hitherto been available[2]. We now report a new general procedure whereby an allenic bromide (I) is reacted with butadiynyl-(trimethyl)silane (II)[3] in which the termial acetylene of the allenediyne is protected by a stablising trimethylsilyl group.

$$\underset{(I)}{R_1R_2C{=}C{=}CHBr} + \underset{(II)}{H(C{\equiv}C)_2SiMe_3} \xrightarrow[D.M.F.]{CuBr/Bu_3N} \underset{(III)}{R_1R_2C{=}C{=}CH\text{-}(C{\equiv}C)_2SiMe_3} \xrightarrow[NaOH/MeOH]{10\ sec} \underset{(IV)}{R_1R_2C{=}C{=}CH\text{-}(C{\equiv}C)_2H}$$

The trimethylsilyl protected allenediynes (III; R_1=Me,R_2=Me,Et, or Pr) were obtained in ca 70% crude yield, purified by dry column chromatography on deactivated, acid washed alumina, and desilylated with methanolic sodium hydroxide.[5]

Application of this method to the synthesis of (±) octa-2,3-diene-5,7-diyn-1-ol (IV; R_1= $HOCH_2$, R_2= H)[4] involved coupling the allenic bromide (VI)[6], obtained from vinylacetylene according to Scheme 1, with butadiynyl(trimethyl)silane (II).

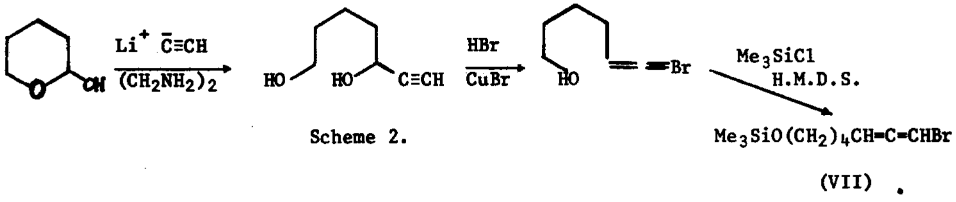


$$CH_2{=}CH\text{-}C{\equiv}CH \xrightarrow[-20^o]{Br_2} BrCH\ \text{-}CH{=}C{=}CHBr \xrightarrow[HOAc]{NaOAc} AcOCH_2CH{=}C{=}CHBr \xrightarrow[reflux]{Na_2CO_3} HOCH_2CH{=}C{=}CHBr \xrightarrow[H.M.D.S.]{Me_3SiCl} \underset{(VI)}{Me_3SiOCH_2CH{=}C{=}CHBr}$$

Scheme 1.

Dry column chromatography gave (±) 8-trimethylsilylocta-2,3-diene-5,7-diyn-1-ol (III; R_1=$HOCH_2$,R_2=H) (18%) which had ν_{max} 3,300 (OH), 2,200 (C≡C), 2,100 (C=CSi), and 1945 (C=C=C) cm^{-1}, λ_{max} 291, 274, 259, 246, 233 (sh), 220 and 214 nm (ε 10,800, 12,800, 6,800, 3,600, 3,000, 40,000, 34,000). Desilylation with aqueous methanolic sodium hydroxide gave (±) octa-2,3-diene-5,7-diyn-1-ol (61%), with i.r. and u.v. spectra in close agreement, with data published for the natural material.[4]

Similarly, (±) undeca-2,3-diene-5,7-diyn-1-ol[4] was synthesised from 1-bromo-7-trimethylsilyloxyhepta-2,3-diene (VII), which was prepared by the method outlined in Scheme 2, and butadiynyl(trimethyl)silane (II).



Scheme 2.

Column chromatography on deactivated Woelm acid alumina gave (±) 11-trimethylsilylundeca-5,6-diene-8,10-diyn-1-ol (III; $R_1=HO(CH_2)_4$, $R_2=H$) (22%), which had ν_{max} 3,300 (OH), 2,200 (C≡C), 2,100 (C≡C-$SiMe_3$), 1945 (C=C=C), λ_{max} 291, 274, 259, 246, 232.5 (sh), 220 and 214 nm (ε 11,300, 14,200, 10,800, 7,200, 5,800, 40,800, 41,500). Desilylation gave (±) undeca-5,6-diene-8,10-diyn-1-ol with spectroscopic data in close agreement with that of the natural product.[4]

[1] Sir Ewart Jones, Chem. Brit., 1966, 6.

[2] cf previous work by S.R. Landor, B.J. Miller, J.P. Regan and A.R. Tatchell, Chem. Comm. 1966, 585. C.S.L. Baker, P.D. Landor and S.R. Landor, J. Chem. Soc., 1965, 4659.

[3] R. Eastmond and D.R.M. Walton, Chem. Comm., 1968, 204, D.R.M. Walton and F. Waugh, J. Organometal. Chem., 1972, 37, 45.

[4] R.E. Bew, J.R. Chapman, E.R.H. Jones, B.E. Lowe and G. Lowe., J. Chem. Soc., 1966, 129.

[5] All new compounds gave correct elemental analyses and spectroscopic data.

[6] cf slightly different procedure by M.V. Mavrov, E.S. Voskanyan, and V.P. Kucherov, Invest. Akad. Nauk. S.S.S.R., Ser. Khim, 1967, 2774.