Selenophens from Diacetylenes

By R. F. CURTIS,* S. N. HASNAIN, and J. A. TAYLOR

(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea*)

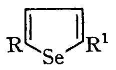
THE synthesis of thiophens by the addition of hydrogen sulphide to substituted diacetylenes is well established.[1]

Various 2,5-disubstituted selenophens were required for other investigations and since selenophen is not readily accessible[2] a parallel approach to the selenophen system was attempted. Our early experiments[3] were unsuccessful until it was realised that the addition of hydrogen selenide to the diyne system is strongly catalysed by Ag^+ and Cu^+ ions. This catalytic effect is also observed, in the addition of hydrogen sulphide to produce thiophens; rigorous purification to remove metal ions produces very slow reaction.

In a typical experiment, ethanol (40 ml.) containing sodium ethoxide (0·02 mol.) and silver acetate (5 mg.) was saturated with a rapid stream of hydrogen selenide (from aluminium selenide) at room temperature. 5-Phenylpenta-2,4-diyn-1-ol (I) (0·01 mol.) was added and the mixture was warmed on the water bath at 60° under a slow stream of hydrogen selenide until the di-yne absorption in the i.r. spectrum had disappeared, to give 2-hydroxymethyl-5-phenylselenophen (II), (Table).

TABLE

$R{-}C{\equiv}C{-}C{\equiv}C{-}R^1 \rightarrow$



(I)	$R = Ph, R^1 = CH_2OH$	(II)	m.p. 117—8°	(97%)
(III)	$R = R^1 = Me_2C(OH)$	(IV)	m.p. 107°	(52%)
(V)	$R = R^1 = Ph$	(VI)	m.p. 171°	(65%)
(VII)	$R = MeC{\equiv}C; R^1 = CH_2OH$	(VIII)*	—	(46%)
(IX)	$R = R^1 = CH_2OH$	(X)	b.p. 180°/0·2 mm.	(62%)
(XI)	$R = Me{\cdot}CHOH; R^1 = CH_2OH$	(XII)	b.p. 117°/0·05 mm.	(57%)

* Characterised after oxidation to the corresponding aldehyde, m.p. 77°. This aldehyde is the selenium analogue of Junipal.[4]

In the same way the diynes (III), (V), (VII), (IX), and (XI) were converted to the corresponding selenophens as indicated in the Table. The use of this reaction for synthesis of selenophen either directly or *via* the derivatives (X) or (XII), is being investigated.

(*Received, February* 12*th*, 1968; *Com.* 169.)

---

[1] K. E. Schulte, J. Reisch, W. Herrmann, and G. Bohn, *Arch. Pharm.*, 1963, **296**, 456.
[2] H. D. Hartough, "Thiophene and its Derivatives," Interscience, New York, 1952, p. 480.
[3] G. T. Phillips, and R. F. Curtis, unpublished results.
[4] J. H. Birkinshaw and P. Chaplen, *Biochem. J.*, 1955, **60**, 255.