

**Spiro[5.5]undecane Sesquiterpene Analogues. Bridging Vinyl Ether
and Vinyl Acetal Formation *via* Intramolecular Attack by
an Enol During Bromination**

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Summary Bromination of 7,11-diphenylspiro[5.5]undecane-1,9-dione (**2**) in dichloromethane indicated the

involvement of an unexpected proximity effect when the bridged acetal (**4**) and the bridged ether (**5**) were isolated.

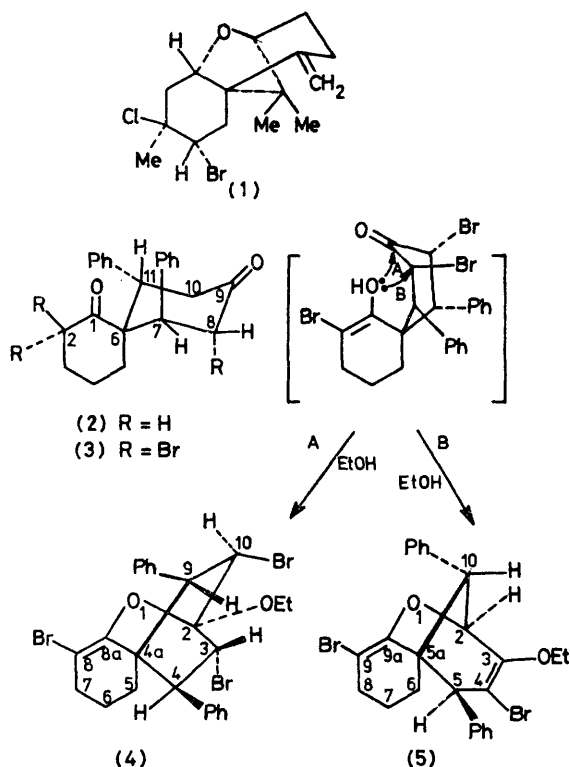
THE halogenated spiro-sesquiterpenoids from various species of red algae of the genus *Laurencia* have recently attracted attention.^{1,2} The isolation of oxygen-bridged chamigrene sesquiterpenes such as nidifocene (1)² prompted this report of possible future biogenetic interest.

The readily available, racemic 7,11-diphenylspiro[5.5]-undecane-1,9-dione (2)³ was brominated in dichloromethane or chloroform with 3 mol. equiv. of bromine in the same solvent, followed by treatment with ethanol or triethyl orthoformate to give two compounds: the vinyl acetal⁴ (4) (58%), m.p. 184–186 °C; i.r. (CHCl₃): 1680 (vinyl bromoether) cm⁻¹; n.m.r. (CDCl₃): δ 1.37 (3H, t, *J* 7.0 Hz, CH₂Me), 3.63 (2H, d, *J* 7.0 Hz, benzylic 4- and 9-H), 4.05 (2H, q, *J* 7.0 Hz, CH₂Me), 4.73 (1H, d, *J* 7.0 Hz, >CHBr), and 5.09 (1H, d, *J* 7.0 Hz, >CHBr), both the 1H doublets collapsing to singlets on irradiation at δ 3.63; and the vinyl ether⁴ (5) (17%), m.p. 177–179 °C; i.r. (KBr): 1695 and 1653 (vinyl-bromoether) cm⁻¹; n.m.r. (CDCl₃): δ 1.40 (3H, t, *J* 7.0 Hz, CH₂Me), 3.93 (1H, s, benzylic 10-H), 4.14 (2H, ABq, *J* 7.0 Hz, CH₂Me), 4.17 (1H, s, benzylic 5-H), and 5.00 (1H, s, 2-H).

The remarkable ease with which the above bridged compounds were formed suggested that both rings could attain conformations such that the C-1 carbonyl group (as the enol) was within bonding distance of the C-9 carbonyl group and the C-8 carbon bearing the bromine. Treatment of the spirodiketone (2) with 3 mol. equiv. of bromine in glacial acetic acid containing acetic anhydride and HBr resulted in the tribromide⁴ (3) (69%), m.p. 149.5–154 °C (decomp.); i.r. (CHCl₃): 1712 (C=O) cm⁻¹; n.m.r. (CDCl₃): δ 3.03 (2H, apparent q, *J*_{vic} 3.0 Hz, *J*_{gem} 6.0 Hz, collapses to d, *J* 6.0 Hz, on irradiation at δ 4.27, 10-CH₂), 3.40 (1H, d, *J* 12.0 Hz, coupled to signal at δ 6.07, benzylic 7-H), 4.28 (1H, q, *J* 3.0 and 6.0 Hz, collapses to a doublet, *J* 3.0 Hz, on irradiation at δ 3.03, benzylic 11-H), 6.07 (1H, d, *J* 12.0 Hz, collapses to a singlet on irradiation at δ 3.40, 8-CHBr). Addition of smaller amounts of bromine gave (3) as well as more polar intermediates (t.l.c.) which could all be converted into (3) with further additions of bromine. The X-ray crystal structure of (3)⁴ clearly indicated that the C-1 carbonyl oxygen was in fact within an average distance of 3.0 Å to C-9 as well as to the two flanking carbons C-8 and C-10.

A possible pathway to these bridged products (4) and (5), in a non-polar medium, involves monobromination at C-2. Since the bromine is consumed nearly instantaneously in the reactions in both CH₂Cl₂ and AcOH–HBr, nucleophilic attack in CH₂Cl₂ on the other ring by the C-1 OH group of the bromine stabilised enol must be extremely rapid, faster than a second bromination at C-2 of the enol which would lead to a geminal 2,2-dibromide and prevent the bridging

process. In the polar acetic acid–hydrobromic acid solvent, acid-catalysed opening and further bromination of an initially formed acetal of type (4) would result in a geminal dibromide at C-2. Initial experiments aimed at isolating the possible intermediates indicate that the ease of bromination of the three methylene groups of (2) follows the order



$2\text{-CH}_2 > 2\text{-CHBr} > 8\text{-CH}_2 > 10\text{-CH}_2$, which explains the results obtained in the different solvents. These experiments will be reported elsewhere.

The structural similarity between nidifocene (1) and the bridged ether (5)[†] is evident and the occurrence of spirocyclic sesquiterpenoids having suitably disposed carbonyl groups in both rings suggests that such intramolecular carbonyl–enol reactions as reported here may be possible in Nature.

(Received, 9th February 1978; Com. 137.)

[†] All compounds in this communication except (1) are racemates and only one isomer is shown. Compounds (3), (4), and (5) gave unsatisfactory combustion data although the number of bromine atoms could be deduced from the analysis. For this reason the structures were determined by X-ray crystal structure analysis.

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