

Abnormal Cope Rearrangement of *cis,trans*-Cyclodeca-1,5-diene Derivatives with a Furan Ring

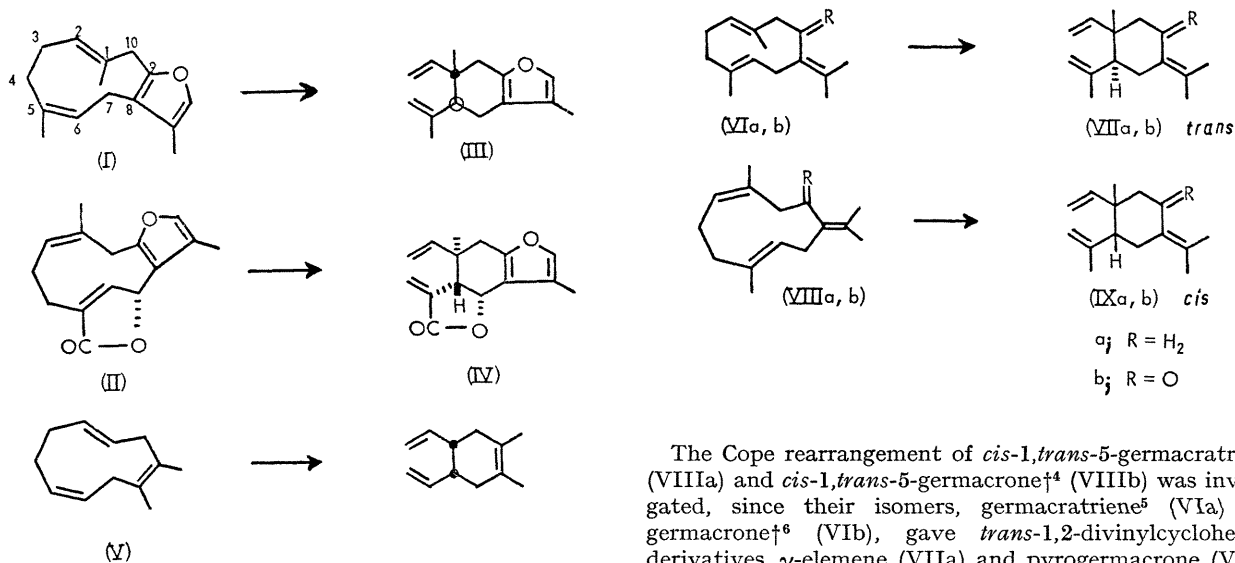
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Summary The abnormal Cope rearrangement of *cis,trans*-furanodiene (I) and neolinderalactone (II) is caused not by the methyl groups on the double bonds at C-1 and C-5, but by the furan ring.

cis,trans-FURANODIENE (I) and neolinderalactone (II) undergo abnormal Cope rearrangement to the *trans*-1,2-divinylcyclohexene derivatives isofuranogermacrene (III)

8,9-dimethylcyclodeca-*trans*-1,*cis*-5,*cis*-8-triene^{2,3} (V), give *cis*-1,2-divinylcyclohexane derivatives. It was suggested that this discrepancy for compounds (I) and (II) was due to the effect of either the methyl groups on the C-1 and C-5 double bonds, or that of the furan ring. We now examine the effect of the methyl groups at the double bonds on the stereoselectivity of this rearrangement.



and isolinderalactone (IV), respectively,¹ although certain *cis,trans*-cyclodeca-1,5-diene compounds,² in particular

The Cope rearrangement of *cis*-1,*trans*-5-germacratene⁴ (VIIIa) and *cis*-1,*trans*-5-germacrone⁴ (VIIIb) was investigated, since their isomers, germacratene⁵ (VIa) and germacrone⁶ (VIb), gave *trans*-1,2-divinylcyclohexane derivatives, γ -elemene (VIIa) and pyrogermacrone (VIIb), respectively.

The rearrangement products were two oils (IXa), ν_{\max} (CCl₄) 1637, 1001, 911, and 891 cm⁻¹, τ 8.98 (Me, s), 8.32

* As *cis,trans*-furanodiene (I) and compound (V) have a furan ring and a double bond, respectively, at positions 8 and 9, germacrone isomers (VIb and VIIIb), which have *sp*² carbons at positions 8 and 9, were subjected to Cope rearrangement.

(3Me), and 5.32—3.60 (5-vinyl protons), and (IXb), ν_{\max} 1687, 1640, 1607, 1303, 1282, 1209, 919, and 897 cm^{-1} , λ_{\max} (EtOH) 256.5 nm (ϵ 6600), τ 8.93 (Me, s), 8.22 (2Me, s), 7.95 (Me), and 5.22—4.02 (5-vinyl protons). These physical data (and g.l.c. and t.l.c. data) for (IXa) and (IXb) were analogous to those for γ -elemene (VIIa) and pyrogermacrone (VIIb), respectively, thus establishing that (IXa) and (IXb) are both *cis*-1,2-divinylcyclohexane derivatives. Thus, methyl groups at C-1 and C-5 have no effect on the stereoselectivity of this rearrangement.

The 1,5-dimethylcyclodeca-*cis*-1,*trans*-5,*cis*-8-triene (XVIII) was derived from (VIIIb), because (XVIII) has the same double-bond system as (I), except that the furan ring is replaced by the *cis*-double bond.

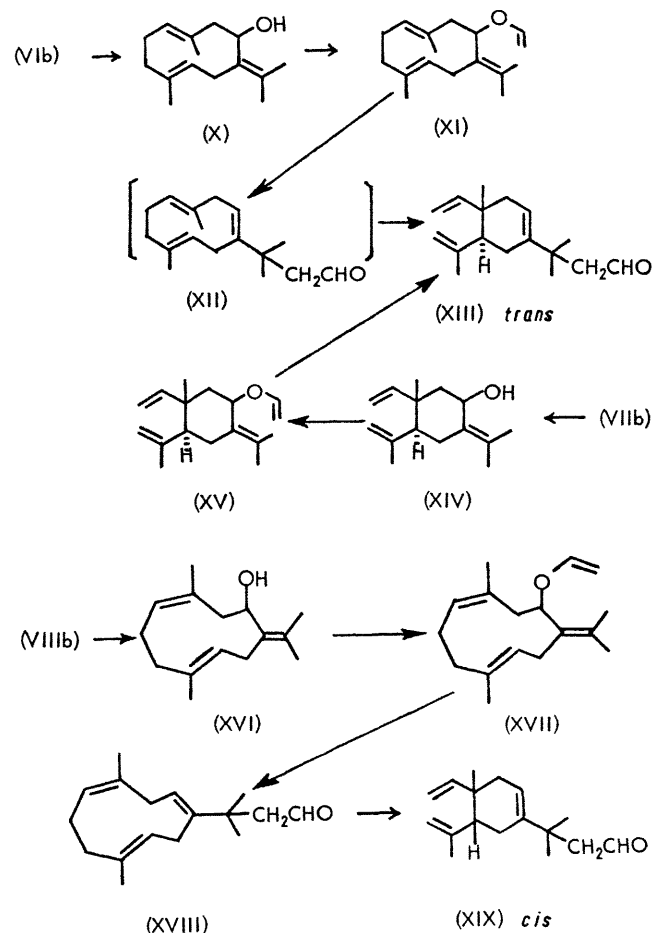
An alcohol^{5,6} (X) derived from germacrone (VIb) was heated under reflux in ethyl vinyl ether with mercury(II) acetate for 20 h under nitrogen to give a vinyl ether (XI), an oil, ν_{\max} (CCl_4) 1635, 1614, 1193, 1180, 1063, and 1041. Although by Claisen rearrangement (XI) should have given the cyclodeca-*trans*-1,*trans*-5,*cis*-8-triene derivative (XII), it was in fact converted on heating at 110°, into an oil (XIII), ν_{\max} (CCl_4) 2711, 1727, 1638, 912, and 893 cm^{-1} , by a simultaneously-occurring Cope rearrangement. Pyrogermacrone (VIIb), a *trans*-1,2-divinylcyclohexane derivative, was reduced with lithium aluminium hydride in ether to give an alcohol (XIV), ν_{\max} (CCl_4) 3570, 3451, 1636, 1043, 908, and 892 cm^{-1} , which was converted into a vinyl ether (XV), ν_{\max} (CCl_4) 1635, 1610, 1191, 1180, 911, and 893 cm^{-1} under the same conditions as those used for (X). Claisen rearrangement of (XV) occurred (100°, 15 h) to give compound (XIII). Thus, (XIII) is a *trans*-1,2-divinylcyclohexene derivative.

cis-1,*trans*-5-Germacrone (VIIIb) gave an alcohol (XVI), m.p. 124—125°, ν_{\max} (CCl_4) 3585, 3466, 1653, 995, 978, and 830 cm^{-1} , by the same reduction. Its vinyl ether (XVII) was obtained under the same conditions as those used for the *trans,trans*-isomer (X) and showed i.r. bands at 1635, 1609, 1188, 1177, 1027, and 827 cm^{-1} . Claisen rearrangement of (XVII) occurred at a lower temperature, 80°, to give the aldehyde (XVIII) as an oil, ν_{\max} (CCl_4) 2706, 1727, and 824 cm^{-1} . When (XVIII) was heated at 110° for 17 h in a sealed tube, it smoothly underwent Cope rearrangement to give an oil (XIX) in good yield; ν_{\max} (CCl_4) 2710, 1728, 1638, 912, and 892 cm^{-1} . These physical data correspond, but are not identical, with those for (XIII), thus establishing (XIX) as a *cis*-1,2-divinylcyclohexene derivative.

(XVIII) underwent a normal Cope rearrangement in the same way as (V), giving a *cis*-1,2-divinylcyclohexene derivative (XIX). Therefore, it was concluded that the abnormality of (I) and (II) on Cope rearrangement is not caused by the methyl groups on the double bonds at C-1 and C-5, but by the furan ring.

(I) and (II) did not undergo the rearrangement¹ unless

heated at 200° and 300°, respectively, and the yield was poor in both cases. It is possible that a ten-membered ring having *cis*- and *trans*-double bonds at C-1 and C-5, respectively, loses a considerable degree of flexibility on the



introduction of a furan ring at positions 8 and 9. It is less difficult for a derivative having a *cis*-double bond in the same position, (C-8 and -9), to meet the stereochemical requirement for transformation into the preferred transition state for this rearrangement.

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⁴ Preceding communication.

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