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THERMAL REARRANGEMENTS OF CIS-BICYCLO[6·2·0]DECA-9-ENES AND A NEW COPE REARRANGEMENT

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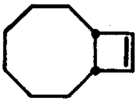
We wish to report the thermal behavior of the *cis*-bicyclo[6·2·0]decenes, I-III.[1] The known[2] thermal rearrangement of bicyclo[3·2·0]hepta-2,6-diene to cycloheptatriene is here shown to be extended to the bicyclic systems above which also possess the condensed cyclobutene moiety. It is also shown that the observed stereospecific reactions are in each case in direct support of the theoretical predictions of Woodward and Hoffmann[3] for electrocyclic reactions of the type $2\pi,2\sigma \rightarrow 4\pi$ and $6\pi \rightarrow 4\pi,2\sigma$.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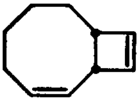
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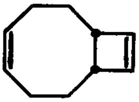
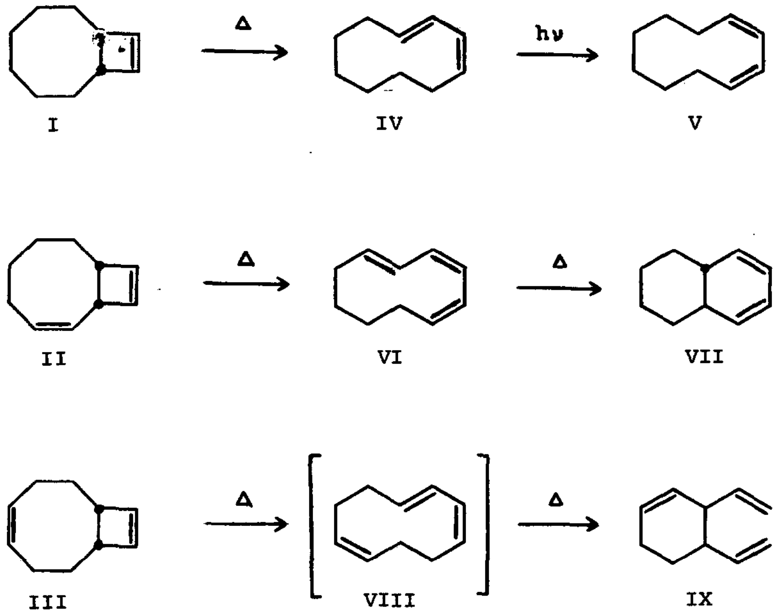

III

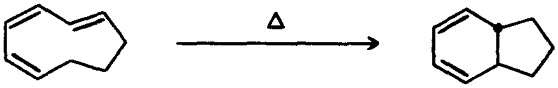
When *cis*-bicyclo[6·2·0] deca-9-ene, I, was heated to 200° for one hour in the vapor phase, a 95% conversion to the known[4] *cis,trans*-1,3-cyclodecadiene, IV, occurred. This stereoisomer can only result via the predicted[3] conrotatory process. The structure of IV was confirmed by its infra-red spectrum, identical in every respect to that previously published,[4] by its catalytic hydrogenation with platinum in ether to cyclodecane and by its nmr spectrum;[5] (3.82τ multiplet (2H), 4.62τ multiplet (2H), 7.91τ multiplet (4H) and 8.68τ multiplet (8H)). IV was also found to be quantitatively converted to the *cis,cis* isomer, V, by acetone sensitized irradiation in pyrex for 72 hours. Similar sensitized photochemical *cis-trans* isomerizations have been studied in detail by Hammond.[6]

The infra-red spectrum of V was found identical with that previously reported.[4] The nmr of V[5] was, as expected, very similar to that of IV. (4.08τ multiplet (2H), 4.54τ multiplet (2H), 7.84τ multiplet (4H), 8.65τ multiplet (8H)). These and other transformations are outlined in Figure I.



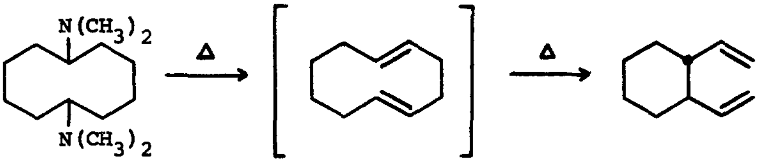
When *cis*-bicyclo[6·2·0]deca-2,9-diene, II, was heated to 140° for one hour, again in the vapor phase, a 30% conversion to VI, *cis,cis,trans*-1,3,5-cyclodecatriene, resulted. The sterochemistry of this product, namely the generated *trans* double bond, was again in complete agreement with the predicted[3] conrotatory ring opening. VI showed a maximum in the ultra-violet region at 271 mμ (ε=4880), its infra-red spectrum exhibited the expected absorptions including 969, 979 and 989 cm^{-1} for the *trans* double bond.[7] Its nmr spectrum consisted of a multiplet at 4.94τ (6H), a multiplet at 7.71τ (4H) and a multiplet at 8.46τ (4H). Hydrogenation of VI with platinum in ether led to cyclodecane as the only product by vpc analysis.[8] When II was heated strongly to 220° for 1 hour in the vapor phase, no starting material could be detected, instead *trans*-bicyclo[4·4·0]deca-2,4-diene,[9] VII, and VI were found to be the major products (90%). With 1 hour heating the ratio of VII and VI was 65/35;[8] while 2 hours at the same temperature increased the ratio to 75/25. The structure of VII was confirmed by its facile conversion to trans-decalin by hydrogenation over platinum in ether, by its maximum in the ultra-violet at 261 mμ, in complete accord with the published value,[9] and by its nmr spectrum; 4.39$^{\tau}$ multiplet (4H), 7.85$^{\tau}$ to 9.10τ multiplet (10H).

It is clear that II is easily converted to VI via a conrotatory process and that VI closes thermally at higher temperatures to VII, the process being disrotatory as expected. Analogy is found for this process in the thermal ring closure of cis,cis, trans-1,3,5-cyclononatriene to trans-bicyclo[4·3·0] nona-2,4-diene reported recently by Vogel.[7]



When cis-bicyclo[6·2·0]deca-4,9-diene, III, was heated in the vapor phase to 200° for 1 hour a 95% conversion to 3,4-divinyl cyclohexene, IX, occurred. IX showed only end absorption in the ultra violet region. Its nmr spectrum consisted of a multiplet centered at 4.22τ (4H), a multiplet at 5.00$^{\tau}$ (4H) and multiple bands from 7.00 to 8.50$^{\tau}$ (6H). In general the nmr spectrum showed analogy to that previously reported[10] for 4-vinyl cyclohexene. The infra-red spectrum of IX showed strong absorptions at 3080 cm^{-1} (terminal vinyl C-H stretch), 1633 cm^{-1} (double bond stretch) and at 910 and 990 cm^{-1} (symmetrical and unsymmetrical bending of the terminal vinyl type hydrogens). Hydrogenation of the above thermolysis mixture led to only two products by vpc analysis.[8] The mixture consisted of 95% 1,2-diethylcyclohexane which was identical to an authentic sample prepared via an alternative route[11] and 5% cyclodecane, identified by comparison of its vpc retention time to that of a known sample and by its nmr spectrum; singlet 8.49τ.

On the basis of the cyclodecane formation and by analogy to the thermal behavior of I and II, it is reasonable to expect the primary thermal process to be the formation of VIII, cis,trans,cis-1,3,7-cyclodecatriene, which containing a 1,5 diene system, can undergo a facile Cope rearrangement to the observed product. Grob and Schiess[12] have observed a similar rearrangement in their generation of 1,5-cyclodecadiene from 1,5-bisdimethylamino cyclodecane. Their



only observable product was not the cyclodecadiene but trans -1,2-divinyl cyclohexane. This same rearrangement has also been noted in the naturally occurring sesquiterpenes germacrone[13] and dihydrocostunolide.[14] On the basis of the cis, trans nature of the reacting 1,5 diene system of VII, and the known 4-center pathway of the Cope rearrangement,[15] it is most probable that the vinyl groups in IX are cis but to this date no stereochemical evidence has been obtained.

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