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SUBSTITUENT EFFECTS ON RATES OF ELECTROCYCLIZATIONS: VALENCE ISOMERIZATION OF 1,8-DIPHENYL-*TRANS*-1, *CIS*-3, *CIS*-5, *TRANS*-7-OCTATETRAENE[6]

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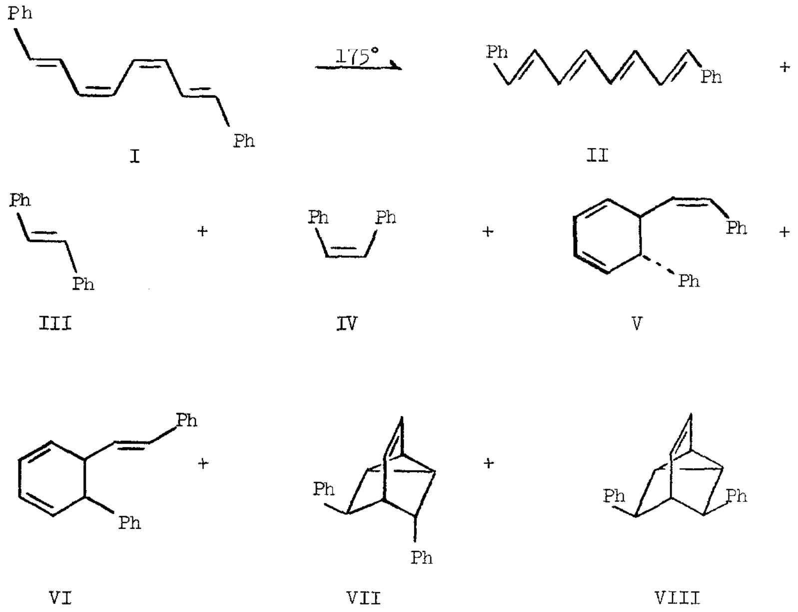
The stereospecific conrotatory cyclization of *trans*-2, *cis*-4, *cis*-6, *trans*-8-decatetraene was recently shown to procede rapidly at or below room temperature both by us (1) and by Huisgen, et al. (2). Crystalline 1,8-diphenyl-*trans*-1, *cis*-3, *cis*-5, *trans*-7-octatetraene (I), m.p. 191-193°, was reported (3) to isomerize to the all trans form when heated above its melting point. In view of its expected rate of electrocyclization, we have reinvestigated the thermal behavior of I.

In solution I is stable for several hours at 120°, but when heated at 175° for 7 hrs. it is converted to a mixture of seven products. Separation by preparative TLC (silica gel/hexane) gave 11% II, 24% III, ca. 0.5% IV, 15% of a mixture of V + VI, 26% VII and 20% VIII. Compounds II, III and IV were identified by comparison with authentic samples. VIII, m.p. 84.5-85°, M.W. 258* takes up one mole of hydrogen to give *cis*-6,8-diphenyltricyclo$[3.2.1.0^{2,7}]$ octane, IX, m.p. 94.5-95°, M.W. 260. The nmr spectrum of VIII shows ten phenyl protons at 7.1 ppm, two olefinic protons at 6.03 (q) and 4.83 (t), two benzylic protons at 3.4 (d?), the bridgehead methinyl proton at 3.15 (t) and three

* All molecular weights reported were determined by mass spectral means.



cyclopropyl protons between 1.65 - 2.1 (m).* All spectral and analytical data for VIII and IX are in agreement with the proposed structural assignments. Similarly VII, m.p. 53-54°, M.W. 258, is reduced to trans-6,8-diphenyltricyclo[3.2.1.$0^{2,7}$]octane, X, m.p. 67-68°, M.W. 260. The nmr spectrum of VII* clearly shows the non-equivalent positioning of the two phenyl groups. Again spectral and analytical data for VII and X are compatible with the proposed structures. The mixture of V and VI shows λ_{max} 256 ($\epsilon \approx 20{,}000$). At 175° one component (presumably V) is converted to VII, while the other (VI) is stable. Hydrogenation of the mixture gave two isomeric hydrocarbons, M.W. 264, with essentially identical mass spectra.

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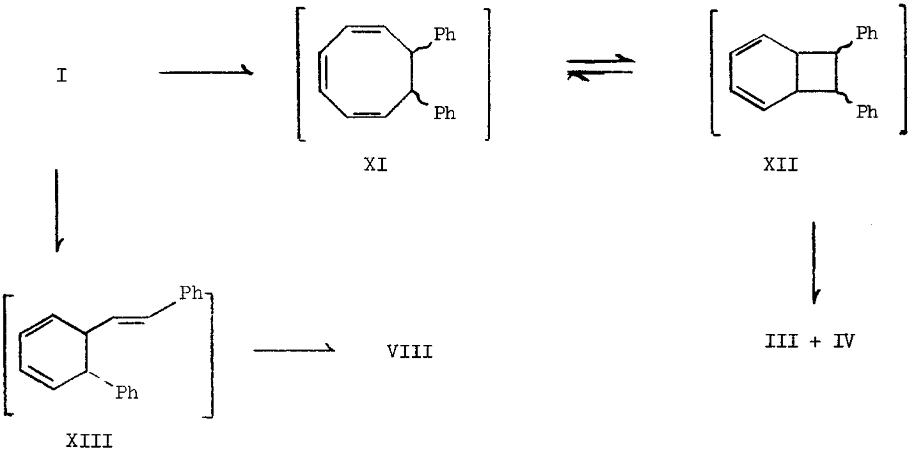
* A complete analysis of all coupling constants and chemical shift assignments will be made in the full paper.

The paths to these products can be separated into two sets, one involving no prior cis-trans isomerization of I, the second dependent upon that isomerization. A sample of 3,4,5,6-tetradeuterio I was rearranged and the positions of the labels in all products were in accord with the suggested mechanisms. The rates of formation of III + IV and of VIII were determined at 178°, k_{3+4} = 7 x 10^{-5} sec.$^{-1}$ and k_8 = 6 x 10^{-5} sec.$^{-1}$. Since no trace of XI, XII or XIII was found, the rate determining steps are assumed to be I → XI and I → XIII respectively. A ring closure rate for <u>trans</u>-2,

Set 1



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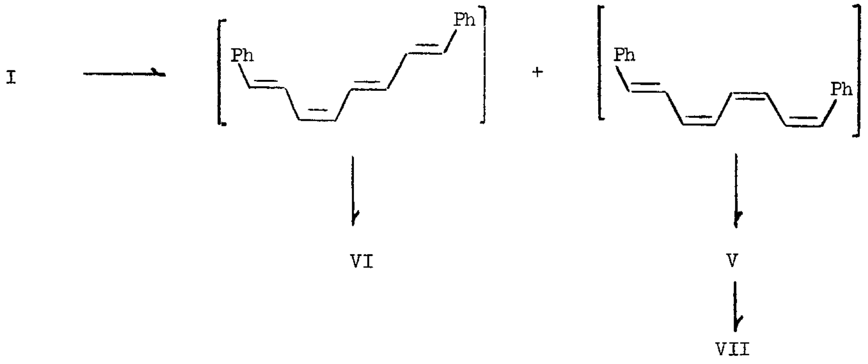

cis-4, cis-6-octatriene of 2.2×10^{-5} sec.$^{-1}$ at 178° has been reported (4). Thus a phenyl and a styryl group cause little alteration of the rate of a $3\pi \rightarrow 2\pi + \sigma$ electrocyclic reaction, whereas two phenyl groups retard the rate of a $4\pi \rightarrow 3\pi + \sigma$ process by a factor of ca. 10^8. Each phenyl group causes a change in $\Delta G^{\ddagger}$ of ca. 5 kcal./mole. A change of similar magnitude was noted for the influence of phenyl groups on the cyclobutene ring opening (5). At present the reasons for these interesting rate influences are not entirely clear and further studies are in progress.

References

1. E. N. Marvell and J. Seubert, J. Amer. Chem. Soc., 89, 3377 (1967)
2. R. Huisgen, A. Dahmen and H. Huber, ibid., 89, 7130 (1967).
3. M. Akhtar, T. A. Richards and B. C. L. Weedon, J. Chem. Soc., 933 (1959).
4. E. N. Marvell, G. Caple and B. Schatz, Tetrahedron Letters, 385 (1965).
5. M. Pomerantz and P. H. Hartman, ibid., 991 (1968).

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