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trans-9,10-Dihydronaphthalene, Precursor of [10]Annulene

By E. E. VAN TAMELEN* and R. H. GREELEY

(Department of Chemistry, Stanford University, Stanford, California 94305)

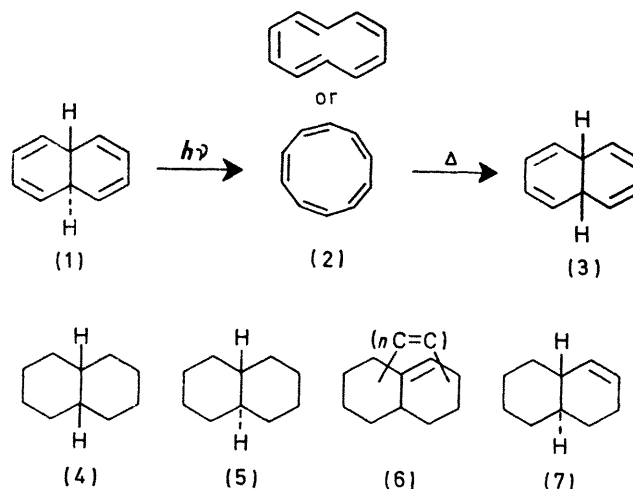
Summary In confirmation of the original findings of van Tamelen and Burkoth, and in confutation of the later report of Masamune and Seidner, *trans*-9,10-dihydronaphthalene is converted on u.v. irradiation at -190° into [10]annulene.

In 1967, van Tamelen and Burkoth¹ described the first synthesis and characterization of a key member in the $[\text{CH}]_{10}$ series, *trans*-9,10-dihydronaphthalene (**1**). U.v. photolysis of (**1**) carried out under carefully controlled conditions at -190° , gave rise to cyclodeca-1,3,5,7,9-pentaene ([10]annulene), the first monocyclic member in the [10]annulene series.² Generated and behaving according to the Woodward-Hoffmann rules,³ the unstable (**2**) was converted thermally into *cis*-9,10-dihydronaphthalene (**3**).⁴ In further confirmation of structure (**2**), hydrogenation afforded cyclodecane⁵ in good yield.

Two years later, Masamune and Seidner⁶ reported that (**1**) was completely recovered after irradiation at -190° ; while at distinctly higher temperatures, 1–2% of (**2**) is generated, together with (**3**) and isomers derived therefrom.† These authors did not point out that the amounts of (**3**) and (**3**)-derived hydrocarbons, observed as products in their own experiments, reflect (*vide supra*) initial quantitative conversion of (**1**) into (**2**), in indirect but strong support of our original findings.

In re-examining the van Tamelen and Burkoth system, we have confirmed, despite many variables and the inaccessibility of some of the original equipment, the photochemical transformation at -190° of (**1**) to [10]annulene. In our experiments, the product (**2**) was converted by di-imide-catalytic reduction into cyclodecane (identified by g.l.c. and n.m.r.), and concurrently, by thermal reorganization into (**3**) followed by hydrogenation, into *cis*-

decalin (**4**). Furthermore, we have uncovered a major reason for the photolysis discrepancies: at -190° , the consumption of (**1**) is inversely related to its concentration. For example, at *ca.* $2.5 \times 10^{-2}\text{M}$, less than 3% of starting material was consumed, while at *ca.* $6 \times 10^{-4}\text{M}$ 22% underwent reaction in an equivalent irradiation time of 5 min. The van Tamelen and Burkoth runs appear to have involved lower starting concentrations than these while 0.35–0.45 M concentrations of (**1**) were used in the



Masamune and Seidner attempts. Thus, in addition to known differences in irradiation media^{1,6} and possible u.v. lamp variations, a poor quantum yield of reaction (**1**) \rightarrow (**2**) would account for the disparity in results: at extremely low concentrations, a reasonable conversion is possible; while

† G.l.c., n.m.r., and u.v. comparison showed that (**1**) prepared by the original route¹ was identical in all respects with corresponding material obtained by the methods of Masamune and Seidner⁶ and M. Jones, jun., and L. T. Scott, *J. Amer. Chem. Soc.*, 1967, **89**, 150. The u.v. maxima observed for samples obtained by the three methods were in agreement with the values reported by Masamune *et al.*⁷ (λ_{max} 276 nm), and in conflict with the value (λ_{max} 231 nm) reported earlier by van Tamelen and Burkoth.¹

at much higher molarity levels, only a trace of starting material would be consumed. At appropriately low concentrations, change of (1) to (2) can be accomplished at a sufficiently low temperature to permit preservation of (2) and its controlled reduction to cyclodecane; while at the higher concentrations used by Masamune and Seidner, photochemical conversion of (1) into (2) can only be accomplished at temperatures so high that (2) cannot be retained, but is transformed *in situ* to (3) and (3)-derived isomers, observed as products in their experiments. In these laboratories yields (based on starting material consumed) of cyclodecane, produced as described, ranged from 12–40%. Therefore, the original work of van Tamelen and Burkoth, as confirmed here, constitutes the first detection and proof of structure of the parent [10]annulene (2), shown by its chemical properties not to possess the aromatic stabilization that might have been expected on purely electronic grounds.

Reduction of (1) has given a variety of results,⁵ Jones,

Reich, and Scott reported⁸ that hydrogenation in methanol with PtO₂ gave *cis*-decalin (4) and *trans*-decalin (5) in a 15:85 ratio; Burkoth and van Tamelen claimed exclusive formation of (4) over Pt;⁵ and Masamune *et al.*,⁷ using N₂H₂/H₂, Pd-C, found only (5) as product. We found that PtO₂ promoted hydrogenation gave (4) and (5) in a 6:94 ratio. The generation of (4):(5) mixtures can be explained by assuming varying degrees of Pt-promoted isomerization to Δ¹⁽⁹⁾ intermediates (6), followed by hydrogenation. Di-imide (generated from azodicarboxylate) reduction of (1) furnished in good yield a product which had g.l.c. behaviour characteristic of (4) and which was not further affected by di-imide. At first thought to be (4), the di-imide reduction product was identified as *trans*-Δ¹⁽²⁾-octalin (7), by (i) Pd-C catalysed hydrogenation to (4), (ii) its n.m.r. spectrum: τ 1.0–2.2 (14 CH/CH₂), 5.2–5.6 (2C=CH), and (iii) comparison with an authentic sample.‡

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‡ Base-induced decomposition of 1-decalone toluene-*p*-sulphonylhydrazone generated a mixture of Δ¹⁽²⁾- and Δ¹⁽⁹⁾-octalins, from which the desired isomer was obtained by g.l.p.c., first with Carbowax 20 on Chromosorb P followed by DC550 on Chromosorb G.

¹ E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, 1967, **89**, 151.

² Stable, bridged [10]annulenes have been made by E. Vogel and his co-workers, (*e.g.* E. Vogel and H. D. Roth, *Angew. Chem. Internat. Edn.*, 1964, **3**, 228) and by F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, 1964, **86**, 3168.

³ R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

⁴ E. E. van Tamelen and B. C. T. Pappas, *J. Amer. Chem. Soc.*, 1963, **85**, 3296.

⁵ For a review see T. L. Burkoth and E. E. van Tamelen, in 'Non Benzenoid Aromatics,' Academic Press, New York, 1969, vol. 1, pp. 63–116.

⁶ S. Masamune and R. T. Seidner, *Chem. Comm.*, 1969, 542.

⁷ S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, 1968, **90**, 5286.

⁸ M. Jones, jun., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, 1970, **92**, 3118; and personal communication from Prof. Jones, 1967.