

INTERCONVERSION OF 9, 10-DIHYDRONAPHTHALENE AND
BICYCLO[4.2.2]DECA-2, 4, 7, 9-TETRAENE*

W. von E. Doering and J. W. Rosenthal[#]

Sterling and Kline Chemistry Laboratories

Yale University, New Haven, Connecticut 06520

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PHOTOISOMERIZATION of 9, 10-dihydronaphthalene (II) to bullvalene (III)¹ gave two unknown substances one of which is now recognized as a potential intermediate in the formation of bullvalene and as another occupant of the thermal energy surface interrelating bullvalene, Nenitzescu's hydrocarbon, 9, 10- 1, 2- and 1, 4-dihydronaphthalene. Shortly after its characterization by NMR spectrum [a complex multiplet centered at $\delta = 3.20$ ppm (rel. area 2.0) and another multiplet spread between 6.45 and 5.40 ppm (rel. area 8.0)], UV spectrum [$\lambda_{\text{max}} = 260$ m μ ($\epsilon = 4400$); 270 m μ ($\epsilon = 4390$); 280 m μ ($\epsilon = 2800$)] and IR spectrum [3040 cm⁻¹ (strong), 3015(s), 2960 (w), 2920(w), 1660 (broad and very weak), 1390(m), 980(m), 940(m) and 835(m)], I was shown to be identical with the major product of decomposition of the p-tosylhydrazone of 9-aldehydebicyclo[6.1.0]nona-2, 4, 6-triene.^{2, 3, 4} Jones and Scott

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1. W. von E. Doering and J. W. Rosenthal, J. Amer. Chem. Soc. **88**, 2078 (1966).
2. We thank Dr. M. Jones, Jr., Princeton Univ., for comparison of IR spectra.
3. M. Jones, Jr. and L. T. Scott, J. Amer. Chem. Soc. **88**, 0000 (1966).
4. P. Radlick and W. Fenical, J. Amer. Chem. Soc. **88**, 0000 (1966).

agreed to establish its structure and have adduced sufficient evidence to warrant identification of the substance (I) with bicyclo[4.2.2]deca-2, 4, 7, 9-tetraene (Ia).

Both sets of workers found that I could be converted by ultraviolet irradiation in Pyrex to bullvalene in high yield, an observation which we have confirmed. Irradiation with a 275-w G.E. RS sunlamp in Pyrex in pentane solution affords 20% of the theoretical amount of bullvalene after 2.5 hr and 80% after 15 hr; irradiation in quartz with a 10-w low-pressure mercury lamp afforded bullvalene in 66% of th. along with recovered I (33%) and a trace (1%) of unidentified material.

When the irradiation of 9, 10-dihydronaphthalene (II) is carried out in Pyrex and interrupted after an appropriate time, I can be isolated in 26% of theory along with recovered II (24%) and III (10%). This method is convenient for the synthesis of small quantities of I, since II is itself available from the thermal rearrangement of bullvalene or Nenitzescu's hydrocarbon. In quartz, the rapid further photoisomerization of I to bullvalene makes it difficult to interrupt the reaction at the optimum time.

Heating I at 245° for 4 hr in the presence or absence of diphenylamine causes clean rearrangement to 9, 10-dihydronaphthalene (20%) and naphthalene (80% of theory). I must therefore be added to the previous set of thermally interrelated isomeric C₁₀H₁₀ hydrocarbons.¹ The search for other isomers is being continued, but so far the potentially attractive intermediates, tetracyclo[4.4.0.0.^{2, 10}0^{5, 7}]-



deca-3, 8-diene¹ and the cyclodeca-1, 3, 5, 7, 9-pentaenes [(cis)⁵, (cis)⁴(trans)¹ and (cis)³(trans)²_{1, 5}], have not been detected.