

A TRANSITION METAL-CATALYZED DIMERIZATION  
OF NORBORNADIENE

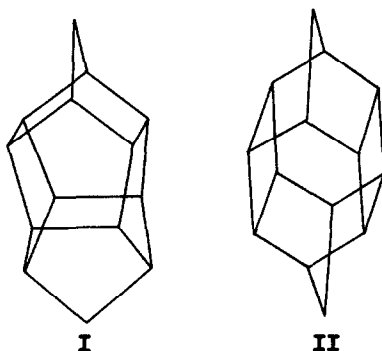
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IRRADIATION with a sunlamp of a mixture of iron pentacarbonyl and norbornadiene leads to a complex mixture of products including the tricarbonyl-iron complex of the diene, a number of ketones, and unsaturated dimers of the diene.<sup>1</sup> In addition to these we have found a saturated dimer to which we have assigned either of the novel structures I or II. It should be



noted that several of the reaction products are formed in the absence of light,<sup>1,2</sup> but we have been unable to obtain the saturated dimer by heating

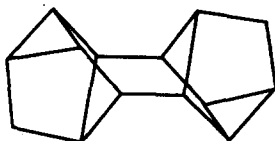
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<sup>1</sup> R. Pettit, J. Amer. Chem. Soc. **81**, 1266 (1959).

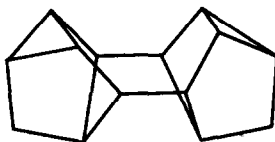
<sup>2</sup> C.W. Bird, R.C. Cookson and J. Hudec, Chem. & Ind. 20 (1960).

the reactants in the dark. Irradiation of norbornadiene alone also fails to yield this compound,<sup>3</sup> indicating that both light and the iron pentacarbonyl are required for the dimerization.<sup>4</sup>

The highly volatile saturated dimer was isolated in 2-3% yield<sup>5</sup> by chromatography on alumina or silica gel, on both of which it was only very weakly adsorbed. After further purification by sublimation the melting point was 165-165.5° (Found: C, 91.03%; H, 9.00%; mol. wt., 175, cryoscopic in t-butanol. Calc. for  $C_{14}H_{16}$ : C, 91.25%; H, 8.75%; mol. wt., 184.)<sup>6</sup> In the mass spectrum, the relative intensities of the peaks at 184, 185 and 186 agree within experimental error with the isotopic distribution



III



IV

<sup>3</sup> Since this dimerization is successful even when performed in a soft glass vessel, it is apparent that the wavelength range of the effective radiation is outside of the region in which norbornadiene absorbs appreciably. See C.F. Wilcox, Jr., S. Winstein and W.G. McMillan, J.Amer.Chem.Soc. **82**, 5450 (1960).

<sup>4</sup> Professor R.C. Cookson has kindly informed us that this dimer is also formed by reaction of the diene with iron enneacarbonyl in the dark, so light is apparently required only for the transformation of the penta- to the enneacarbonyl. For the latter reaction, see R.K. Sheline and K.S. Pitzer, J.Amer.Chem.Soc. **72**, 1107 (1950). It is of interest that irradiation of a mixture of norbornadiene with its iron tricarbonyl complex does not yield the saturated dimer.

<sup>5</sup> This yield is based upon the diene, which has been used as diluent as well as reactant, and hence in large molar excess (2.5:1).

<sup>6</sup> Carbon-hydrogen analyses were performed by the Scandinavian Microchemical Laboratory, Copenhagen, Denmark.

anticipated for the ion  $C_{14}H_{16}^+$ . Consistent with a cage-like structure is the fact that the parent peak at 184 is several times more intense than any other peak in the spectrum.

Evidence for the saturated character of this molecule includes its inertness to bromine and potassium permanganate and its failure to consume hydrogen over Adams' catalyst in acetic acid containing perchloric acid. Moreover, there is no absorption corresponding to carbon-carbon double bond stretching in the infrared spectrum, and the lack of end absorption in the ultraviolet spectrum excludes beyond doubt the presence of unsaturation.

Structures III and IV, derived in a formal sense by the coupling of two norbornadiene nuclei via the termini of their homoconjugated diene systems, can be eliminated through consideration of the infrared and proton magnetic resonance spectra of the 165° dimer. The former taken in carbon tetrachloride has maxima at 3.37, 3.49, 6.90, 7.62, 7.73, 8.10, 8.16, 8.46, 9.30, 10.51, and 11.51 $\mu$ . Incidentally, this and the Nujol mull spectrum are both relatively simple, a fact consistent with a highly symmetrical structure. With regard to III and IV, there is no band in the 12.3-12.5 $\mu$  range (a region in which many tricyclenes and nortricyclenes show prominent absorption), nor is there a band characteristic of cyclopropane derivatives in the 9.8-10 $\mu$  region. More compelling is the absence of a carbon-hydrogen stretching frequency below 3.37 $\mu$ <sup>7</sup> and the lack of absorption in the n.m.r. spectrum at higher field than 8.2 $\tau$ .<sup>8</sup>

The most cogent evidence we can adduce for structures I, heptacyclo-

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<sup>7</sup> L.J. Bellamy, The Infrared Spectra of Complex Molecules pp. 17, 29, 30. John Wiley, New York (1959).

<sup>8</sup> J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance pp. 236, 237. McGraw-Hill, New York (1959); G.V.D. Tiers, Characteristic Nuclear Magnetic Resonance 'Shielding Values' for Hydrogen in Organic Structures. Minnesota Mining and Manufacturing Company, St. Paul, Minnesota (1958).

(5.5.1.1.<sup>4,10</sup>0.2,6<sup>0.3,11</sup>0.5,9<sup>0.8,12</sup>)-tetradecane, or II, heptacyclo-(7.4.10<sup>2,8</sup>0.3,7<sup>0.4,12</sup>0.6,11<sup>0.10,13</sup>)-tetradecane, is provided by the high resolution n.m.r. spectrum. In pyridine at 60 mc the spectrum consists of two sharp, symmetrical peaks at 7.55 $\tau$  and 8.21 $\tau$  corresponding to methine and methylene protons, respectively.<sup>8</sup> As expected, the intensity ratio is 3.1. No fine structure is discernible in either peak under conditions of optimum resolution, whether the solvent be pyridine or carbon tetrachloride.

It is possible to conceive of other saturated structures for C<sub>14</sub>H<sub>16</sub> which are not rigorously excluded by the data outlined above, but to our knowledge all are derivable from norbornadiene only via highly improbable pathways. Since structure II possesses a center of symmetry lacking in I, it was conceivable that a decision between them could be reached by determination of the probable space group through single crystal X-ray examination (i.e. unit cell considerations alone might demand that the molecule possess a center of symmetry.) If this proved not to be the case, X-ray diffraction studies could distinguish I and II only through complete structure elucidation. The determination of the probable space group has not as yet been successful because virtually all of the crystals we have examined have been twinned.<sup>9</sup>

The thermal stability of the cage-like dimer merits comment. Vapor of this substance in a stream of nitrogen has been passed through a Pyrex tube packed with Pyrex helices and heated to temperatures in excess of 500°, and the major portion of the dimer has crystallized unchanged in the cooler part of the pyrolysis tube.

In summary, the low adsorbability, high volatility, relatively high

<sup>9</sup> L. deVries and S. Winstein, J. Amer. Chem. Soc. **82**, 5363 (1960), have encountered similar problems with the birdcage hydrocarbon, crystals of which are "highly disordered."

melting point, chemical inertness, and thermal stability of the 165° dimer are indicative of its cage-like character. Infrared, n.m.r., ultraviolet, and mass spectral data powerfully support structure I or II, but permit no distinction between them.

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