

## PHOTOCHEMICAL TRANSFORMATIONS—VIII<sup>1,2</sup>

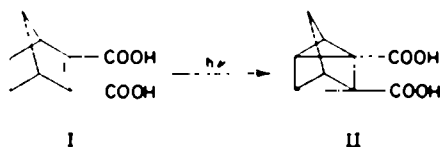
### THE ISOMERIZATION OF $\Delta^{2,5}$ -BICYCLO[2.2.1]HEPTADIENE TO QUADRICYCLO[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]HEPTANE (QUADRICYCLENE)<sup>3</sup>

WILLIAM G. DAUBEN and ROBERT L. CARGILL<sup>4</sup>  
Department of Chemistry, University of California, Berkeley, Calif.

(Received 17 March 1961)

**Abstract**— $\Delta^{2,5}$ -Bicyclo[2.2.1]heptadiene (III) upon ultraviolet irradiation was isomerized in 67 per cent yield to the valence tautomeric quadricyclene (IV) which, in turn, upon being heated, reformed III. The reactions of IV with hydrogen, with acetic acid and with bromine were studied.

In 1954, Cristol and Snell<sup>3</sup> reported the first preparation of the quadricyclo-[2.2.1-0<sup>2,6</sup>.0<sup>3,5</sup>]heptane ring system. Previous workers<sup>5,6</sup> had attempted the synthesis of parent compound of this ring system by purely chemical methods but met with no success. Cristol and Snell<sup>3</sup> found that  $\Delta^{2,5}$ -bicyclo[2.2.1]heptadiene-2,3-dicarboxylic acid (I) upon ultraviolet irradiation was readily transformed to its valence tautomeric structure (II) and they viewed the reaction as proceeding by activation of one of the carbon-carbon double bonds (most likely the unsaturated acid moiety) followed by reaction of this photoactivated bond with the other double bond. The conversion of carvone to carvone camphor is a similar photochemical reaction in which an activated double bond reacts with a near but not activated olefinic linkage.<sup>7</sup> However, on the basis of a



study of the ultraviolet spectra of I and related materials, Jones, Mansfield and Whiting<sup>8</sup> have suggested that one of the excited electronic states in which the non-conjugated double bond interacts with the conjugated diacid system may be involved in this photochemical isomerization. Recently, Wilcox, Winstein and McMillan,<sup>9</sup> using semiempirical wave mechanical calculations, showed that in the lowest excited state (a complex band in the 215 m $\mu$  region) of the parent hydrocarbon,  $\Delta^{2,5}$ -bicyclo-[2.2.1]heptadiene (III), which contains no formally conjugated groups, there is interaction between the two isolated double bonds. If such an excited state is involved

<sup>1</sup> For paper VII, see W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, *J. Amer. Chem. Soc.* **83**, 1768 (1961).

<sup>2</sup> This work was supported in part by Grant No. A-709 (C-6)-Bio, U.S. Public Health Service.

<sup>3</sup> For nomenclature, see S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.* **80**, 1950 (1958).

<sup>4</sup> Postdoctoral Fellow, U.S. Public Health Service, 1960-1961.

<sup>5</sup> M. Lipp, *Ber. Dtsch. Chem. Ges.* **74**, 1 (1941).

<sup>6</sup> T. Hasselstrom and E. M. Falasco, Abstracts of Papers presented at the 125th Meeting of the American Chemical Society, Kansas City, Missouri, March, 1954, p. 39-N.

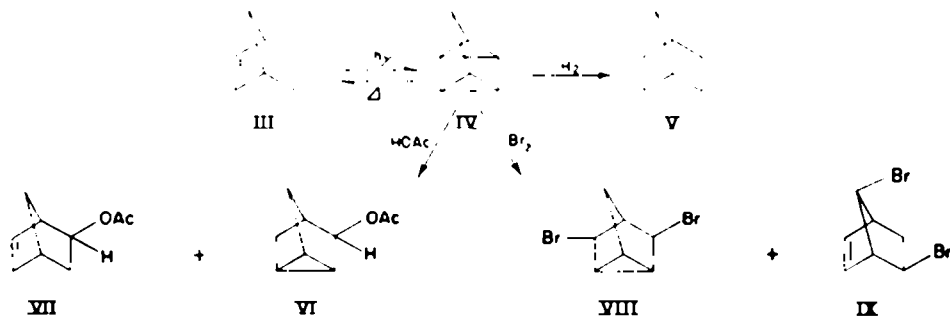
<sup>7</sup> G. Büchi and I. M. Goldman, *J. Amer. Chem. Soc.* **79**, 4741 (1957).

<sup>8</sup> E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.* 4078 (1956).

<sup>9</sup> C. F. Wilcox, S. Winstein and W. G. McMillan, *J. Amer. Chem. Soc.* **82**, 5450 (1960).

in the valence tautomeric reaction then it should be possible to convert III to the valence tautomeric IV, quadricyclene.<sup>10</sup>

When an ethereal solution of  $\Delta^{2,5}$ -bicyclo[2.2.1]heptadiene (III) was irradiated with a G.E. AH-6 high pressure mercury lamp, all the characteristic ultraviolet bands of III disappeared and the end absorption at 205  $m\mu$  dropped to about 25 per cent of the original value. Upon short path distillation, there was obtained in 67% yield a monomeric photoisomer (IV) which was saturated ( $\epsilon_{205}$  400). The irradiation product upon normal distillation slowly reverted to the starting diene and upon being heated in a sealed tube at 200–220° for 5 min the photoisomer was readily converted to III.



Such a heat induced reversal is characteristic of a valence tautomeric structure such as IV, quadricyclene. In line with the conclusion that no skeletal rearrangement had occurred was the finding that IV upon tetrahydrogenation yielded bicycloheptane (V).

The infrared spectrum of IV differed in the expected manner from that of the starting diene III. The latter compound possessed a band at 3040  $cm^{-1}$  (olefinic hydrogen stretching)<sup>11</sup> the intensity of which was about one-third that of the 2990  $cm^{-1}$  band of the saturated carbon-hydrogen absorption and also showed a very intense band at 725  $cm^{-1}$ , characteristic of a *cisoid* disubstituted olefin<sup>11</sup>. The photoisomer possessed a band at 3050  $cm^{-1}$ , characteristic of either olefinic or cyclopropyl hydrogens,<sup>11</sup> but the intensity of the band was equal to the 2990  $cm^{-1}$  band. The *cisoid* disubstituted olefin band at 725  $cm^{-1}$  was missing.

The nuclear magnetic resonance spectrum (Fig. 1) offered the best evidence for the quadricyclene structure. The spectrum showed only two bands<sup>12</sup> centered at 8.01 $\tau$  and 8.59 $\tau$ , clearly showing the absence of any vinyl protons. This feature, together with the ultraviolet end absorption, established the saturated character of the photoisomer. The 8.01 $\tau$  band was a triplet ( $J = 1$  cps) and represented the absorption of two protons. A triplet structure would be expected for the methylene hydrogens on C<sub>7</sub> when coupled with the hydrogen atoms on C<sub>1</sub> and C<sub>4</sub>. The 8.59 $\tau$  band was at least a quintuplet and represented the absorption for six protons. The structure of the band was typical of that found for an  $ab_2X_2$  system in which the chemical shift between *a* and *b* is small.<sup>13</sup> Such would be the case for the hydrogens on the two

<sup>10</sup> The finding of Cookson and Crundwell [*Chem. & Ind.* 1004 (1958)] that Isodrin with two nonadjacent but interacting chromophores ( $\lambda_{max}$  198  $m\mu$  ( $\epsilon$  9000)) was cyclized to Photodrin with ultraviolet light represents another example of this type of excited state.

<sup>11</sup> I. J. Bellamy, *The Infrared Spectra of Complex Molecules*. John Wiley, New York (1956).

<sup>12</sup> We are indebted to Dr. Robert E. Lundin, Western Regional Research Laboratory, U.S. Department of Agriculture, for these measurements.

<sup>13</sup> J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* p. 126. McGraw-Hill, New York (1959).

cyclopropyl rings, the protons on  $C_1$  and  $C_4$  being slightly different from those on  $C_2$ ,  $C_3$ ,  $C_5$  and  $C_6$ . Of particular interest was the position of these cyclopropyl hydrogen absorptions. In a simple substituted cyclopropane, such as norcarane (bicyclo[4.1.0]heptane), the methylene protons absorb at  $9.98\tau$  and the methine cyclopropyl protons at  $9.29\tau$ .<sup>14</sup> A similar methine cyclopropyl proton in nortricylene absorbs still lower at  $8.99\tau$ . Thus, the lowering of the cyclopropyl proton absorption

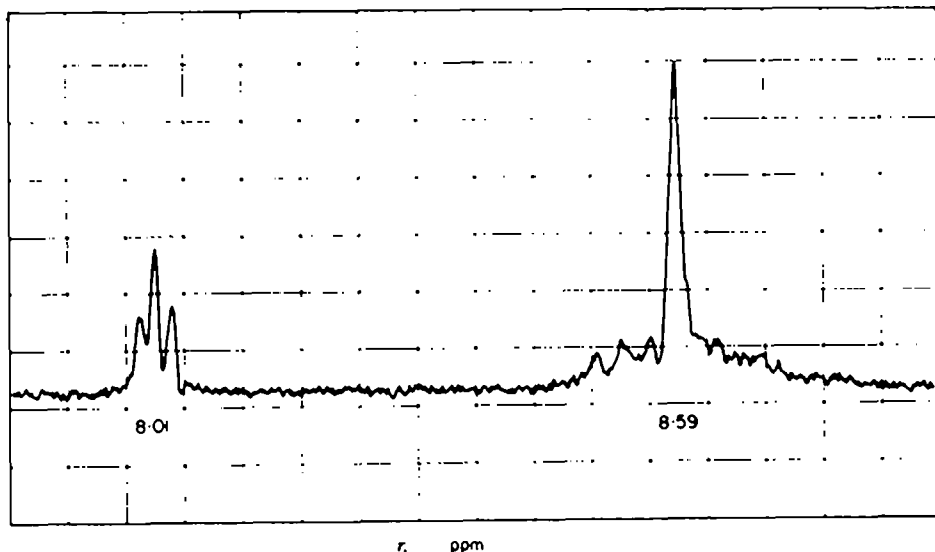


FIG. 1. NMR spectrum of quadricyclene (IV) in carbon tetrachloride.

to  $8.59\tau$  in quadricyclene is not surprising since the placement of the two connected cyclopropyl rings in adjacent planes could be expected to deshield the cyclopropyl hydrogens even more. A similar effect was found in the related diacid II of Cristol and Snell<sup>3</sup> in which the cyclopropyl protons absorb between  $7.48$ – $7.82\tau$ . This extra lowering is due to a deshielding by the carboxylate group which in cyclopropanecarboxylic acid is known to lower absorptions by about  $1\tau$  unit (methylene protons in cyclopropanecarboxylic acid,  $8.98$ – $9.12$ ).<sup>14</sup>

Quadricyclene was quite stable when stored, but, as would be expected for such a highly strained structure, the compound was quite reactive. When IV was allowed to stand for 26 hr at room temperature with glacial acetic acid, it was transformed into nortricyclyl acetate (VI) and *exo*-norbornenyl acetate (VII). Under the same conditions  $\Delta^{2,5}$ -bicyclo[2.2.1]heptadiene and nortricyclyl acetate were stable. Also, as was found by Cristol and LaLonde<sup>15</sup> with diacid II, bromine in carbon tetrachloride reacted rapidly with quadricyclene to yield a mixture of 2,6-dibromonortricyclene (VIII) and *exo*-5-anti-7-dibromonorbornene (IX).

This conversion of  $\Delta^{2,5}$ -bicyclo[2.2.1]heptadiene to quadricyclene by means of ultraviolet irradiation and the previous finding of Cookson and Crundwell<sup>10</sup> using Isodrin, point to the possibility of preparing highly strained systems by ring closure

<sup>14</sup> K. B. Wiberg, private communication.

<sup>15</sup> S. J. Cristol and R. T. LaLonde, *J. Amer. Chem. Soc.* **80**, 4355 (1958).

between any two isolated, but nearby, olefinic double bonds if the latter groups as measured by the ultraviolet absorption, show interaction in an electronic excited state.

### EXPERIMENTAL<sup>16,17</sup>

#### *Quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (quadricyclene) (IV)*

A solution of 10 ml (9.0 g, 0.098 mole) of bicyclo[2.2.1]heptadiene<sup>18</sup> in 2 l. of dry ether was irradiated for 110 hr with a G.E. A-H 6 mercury lamp.<sup>19</sup> The ether was removed by distillation from a water-bath at 50° until the volume of the residue was about 50 ml. The concentrated solution was extracted with a saturated solution of silver nitrate, washed with water, dried, and concentrated by distillation to a volume of about 20 ml. The ethereal solution upon VPC, after the ether peak, showed one peak (DEGS,<sup>20</sup>  $\frac{1}{4}$ " column, 48°, retention time, 8 min). The product was distilled through a short path still and arbitrarily three fractions of colorless distillate were collected, block temperature, 50-60°, 60-75°, and 75-77°. VPC analysis showed that each fraction contained a small amount of ether, approximately 95% of photo product and a few per cent of other substances (cycloheptatriene and toluene were absent), the yield was 6.0 g (67%) of a colorless liquid and there was 2 g of a yellow viscous residue. When the product was distilled in a normal Claisen flask, it slowly reverted to bicycloheptadiene but the b.p. was about 98°.

All physical measurements and subsequent reactions were carried out with pure samples of "quadricyclene" collected from VPC. The  $n_D^{20}$  was 1.4804 and the molecular weight as determined by mass spectrometry<sup>21</sup> was 92. In the ultraviolet there was no maximum only end absorption,  $\epsilon_{290}^{10H} 400$ . (Found: C, 91.41; H, 8.91. Calc. for C<sub>7</sub>H<sub>8</sub>(92.13): C, 91.25; H, 8.75%)<sup>22</sup>

#### *Pyrolysis of quadricyclene (IV) to bicyclo[2.2.1]heptadiene (III)*

A sample of 109 mg (1.19 mmoles) of IV in a nitrogen atmosphere was sealed in a Pyrex tube and the tube was heated in a salt bath at 200-220° for 5 min. After cooling, the product was analyzed by VPC, using a DEGS column (10 ft by  $\frac{1}{4}$ ") at 35° and there were only two components, the ratio of the faster to the slower moving material was 2:1. The materials were separated using a  $\frac{1}{4}$ " DEGS column at 50°. The material which appeared at 4 min was identified as bicyclo[2.2.1]heptadiene by infrared spectra and by VPC retention times. The minor, slower moving material (8 min) was unreacted quadricyclene.

#### *Hydrogenation of quadricyclene (IV) to bicyclo[2.2.1]heptane (V)*

A solution of 103 mg (1.12 mmoles) of IV in 15 ml of dry ether was hydrogenated over 26 mg of pre-reduced platinum oxide at atmospheric pressure and 23°. At the end of 25 min, 55 ml (2 mmoles) of hydrogen had been absorbed with no apparent change in rate during the hydrogenation. The catalyst was removed, most of the ether distilled (bath-temp. 50°) and the product collected from VPC (DEGS,  $\frac{1}{4}$ ", 35°). The infrared spectrum and the VPC retention time of the product were identical with those of an authentic sample of bicyclo[2.2.1]heptane, prepared by hydrogenation of bicyclo[2.2.1]heptadiene.

#### *Reactions of quadricyclene (IV) with acetic acid*

A solution of 62 mg (0.675 mmole) of IV in 1.0 ml of glacial acetic acid was allowed to stand under a nitrogen atmosphere for 26 hr. Ether (2 ml) and water (4 ml) were added and the excess acetic acid was neutralized with solid sodium bicarbonate. The two layers were separated and the water layer extracted again. From the combined ether layer two esters were isolated in approximately

<sup>16</sup> Analyses by the Microanalytical Laboratory, University of California, Berkeley.

<sup>17</sup> Identification by VPC means upon vapor phase chromatography that the unknown compound in question and the authentic material possessed identical retention times and when the two components were mixed, only a single peak was observed.

<sup>18</sup> Kindly supplied by the Shell Development Company, Emeryville, California.

<sup>19</sup> For details of the irradiation apparatus, see W. G. Dauben and R. L. Cargill, *Tetrahedron* 12, 186 (1961).

<sup>20</sup> Diethylene glycol succinate, supplied by Wilkens Instrument Co.

<sup>21</sup> We are indebted to Dr. D. P. Stevenson, Shell Development Company, for this determination.

<sup>22</sup> The sample was dried over sodium.

equal amounts by the use of VPC (DEGS, 104°, 20 and 28 min). The faster moving fraction was shown to be nortricycyl acetate by comparison in the usual manner with authentic material.<sup>23</sup> The slower moving fraction was identified as *exo*-norbornenyl acetate by the means of infrared spectra and VPC. An authentic sample of both the *endo* and the *exo* isomer was obtained from a mixture of the two acetates<sup>24</sup> by preparative VPC (¼" Glycerol column).

*Reaction of quadricyclene (IV) with bromine*

A solution of 213 mg (1.33 mmoles) of bromine in 1.2 ml of carbon tetrachloride was added, dropwise, to a solution of 111 mg (1.20 mmoles) of II in 1 ml of carbon tetrachloride at 0° in the dark. The bromine color was discharged immediately and heat was evolved. The resulting solution was colorless and the infrared spectrum of the reaction mixture was identical with that of an authentic mixture of 2,6-dibromonortricyclene and *exo*-5-*anti*-7-dibromonorbornene prepared by the addition of bromine to bicyclo[2.2.1]heptadiene.<sup>25</sup>

<sup>23</sup> We are indebted to Mr. G. H. Berezin for a sample of nortricyclenol.

<sup>24</sup> Kindly supplied by Professor J. D. Roberts and Dr. Marjorie C. Casserio.

<sup>25</sup> L. Schmerling, J. P. Lewis and R. W. Welch, *J. Amer. Chem. Soc.* **78**, 2819 (1956).

<sup>26</sup> S. Winstein, *J. Amer. Chem. Soc.* **83** 1516 (1961).