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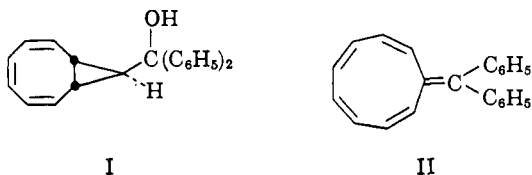
## The Acid-Catalyzed Rearrangement of Diphenylbicyclo[6.1.0]nona-2,4,6-trien-9-ylcarbinol<sup>1</sup>

BY KARL BANGERT AND V. BOEKELHEIDE

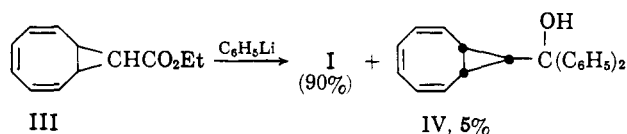
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Diphenylbicyclo[6.1.0]nona-2,4,6-trien-9-ylcarbinol, when treated with fluoroboric acid, is converted to 1,1,4-triphenylbuta-1,3-diene. A possible interpretation of this rearrangement is presented.

The availability of 9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene from another study<sup>2</sup> prompted us to investigate its conversion to diphenylbicyclo[6.1.0]nona-2,4,6-trien-9-ylcarbinol (I) and to study the properties of this derivative. In view of the recent report of Deno and his collaborators on the unusual stability of the tricyclopropylmethyl cation,<sup>3</sup> it seemed possible the carbinol I would yield a similar stable cation. On the other hand, dehydration of I might occur with simultaneous rupture of the three-membered ring to yield II, an example of the still unknown class of fulvenes derived from cyclononatetraene. The present study was undertaken to explore these possibilities.

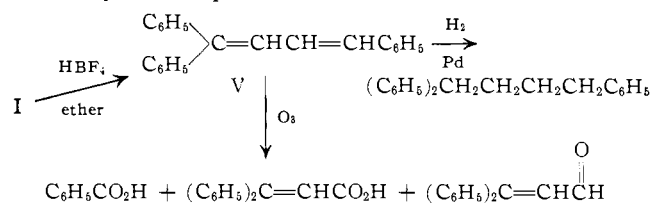


The addition of ethyl diazoacetate to cyclooctatetraene gives 9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (III) as an oil which is largely the *trans* isomer but contains a small amount of the all-*cis* isomer.<sup>2</sup> When this oil was treated with an excess of phenyllithium and the product was isolated by chromatography, the first product to be eluted was the crystalline all-*cis*-carbinol IV, formed in 5% yield. The main eluate containing the *trans* isomer I could not be induced to crystallize but was purified and characterized through its nicely crystalline silver nitrate complex. The assignment of stereochemistry is based on the spin-spin coupling constants of the cyclopropane protons. As Graham and Rogers have shown, *cis*-cyclopropane protons have a larger coupling constant than the *trans*.<sup>2,4</sup> In the case of I, the spin-spin coupling constant of the cyclopropane protons is 5.6 c.p.s., whereas in the case of IV it is 10.8 c.p.s. These conclusions were also supported by experiments using the pure *trans* isomer of III, prepared *via* the silver nitrate complex. In this case the only product isolated was I, formed in 90% yield. Likewise, when the adduct III was hydrolyzed to the acid and re-esterified to give the crystalline methyl ester, reaction of this with phenyllithium gave I as the only product.

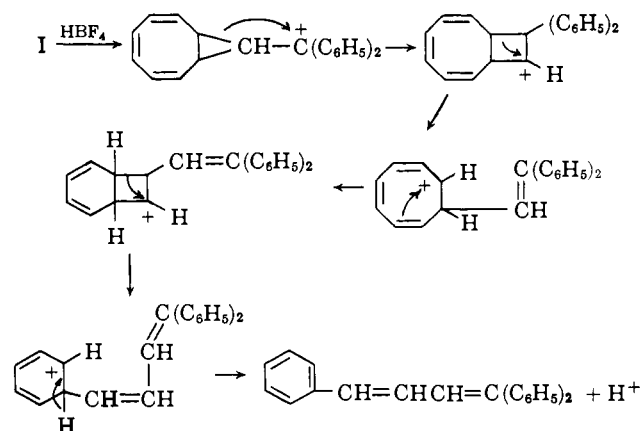


Preliminary experiments revealed that the carbinol I was sensitive to acid, turning red immediately. When compound I was treated with fluoroboric acid in ether for 2 min., followed by purging with water,

chromatography of the reaction mixture over alumina resulted in the isolation of a white crystalline hydrocarbon (V) in 88% yield. The composition of this hydrocarbon, m.p. 102–103°, corresponded to a molecular formula of C<sub>22</sub>H<sub>18</sub>. Surprisingly, its n.m.r. spectrum gave signals for proton resonance only in a narrow region of 2.9 to 3.4  $\tau$ , indicating the complete absence of aliphatic protons. The hope that an aromatic molecule containing the fused eight-four ring system had been formed was short-lived though. Hydrogenation of V over palladium resulted in a rapid absorption of 2 moles of hydrogen. Further, ozonolysis of V led to a mixture of products of which three—benzoic acid,  $\beta$ -phenylcinnamic acid, and  $\beta$ -phenylcinnamaldehyde—were readily identified. From these results it was clear that our hydrocarbon V must be 1,1,4-triphenylbutadiene and this was confirmed by examination of the literature wherein Staudinger had originally reported 1,1,4-triphenylbuta-1,3-diene as white crystals, m.p. 101.5–102°.<sup>5</sup>



It is apparent that the rearrangement of I to give V requires the formation of a new phenyl ring. Although rearrangements of cyclooctatetraene derivatives to benzenoid derivatives have been observed frequently since the early work of Reppe on cyclooctatetraene,<sup>6</sup> the situation in the present instance is complicated by the presence of the cyclopropylcarbinyl system with its propensity for rearrangement. In fact, the rearrangement of 2,2-diphenylcyclopropyl-diphenylcarbinol to 1,1,4,4-tetraphenyl-1,3-butadiene has been observed by Walborsky and Hornyak.<sup>7</sup> However, the reaction sequence shown below



(1) We thank the National Science Foundation for a grant in support of this research.

(2) K. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

(3) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

(4) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

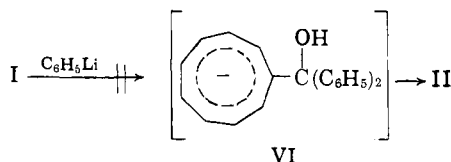
(5) H. Staudinger, *Ber.*, **42**, 4249 (1909).

(6) W. Reppe, O. Schlichting, K. Klages, and T. Toepel, *Ann.*, **560**, 1 (1948).

(7) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6396 (1955).

is the one we favor as a likely interpretation of the present rearrangement.

Further consideration of structure I suggested that a base-catalyzed elimination of water might proceed through the cyclononatetraene anion VI and give the desired fulvene II. When compound I was treated with phenyllithium as base, though, work-up of the reaction mixture led to recovery of the starting carbinol I in 89% yield.



### Experimental<sup>8</sup>

**Diphenylbicyclo[6.1.0]nona-2,4,6-trien-9-ylcarbinol (I).** (a) From *trans*-9-Methoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene.—To a prepared solution of 0.15 mole of phenyllithium in 200 ml. of ether there was added dropwise with stirring a solution of 8.8 g. (0.05 mole) of *trans*-9-methoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene<sup>2</sup> in 30 ml. of ether. After the addition was complete, the mixture was stirred for an additional 1.5 hr. at room temperature. It was then poured onto ice water, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over sodium sulfate and then concentrated under reduced pressure. The residual yellow oil could not be induced to crystallize and so it was chromatographed over alumina (Woelm, neutral, grade 1) using a mixture of petroleum ether (40–60°) containing 5% diethyl ether for elution. The product moved down the column as a single band and from the eluate there was isolated 13.7 g. (92%) of a colorless oil which again could not be induced to crystallize. For analysis and characterization the oil was converted to the corresponding silver nitrate complex by adding it dropwise to a boiling solution of absolute ethanol containing an excess of silver nitrate. During the addition the silver nitrate dissolved and, when the alcoholic solution was cooled, the silver nitrate complex separated in essentially quantitative yield as fine white needles, m.p. 175° dec. (capillary placed in the bath at 165°).

*Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>O·AgNO<sub>3</sub>: C, 56.17; H, 4.29; Ag, 22.90. Found: C, 56.19; H, 4.50; Ag, 22.66.

The carbinol I was regenerated from the silver nitrate complex by dissolving 500 mg. of the crystalline complex in 20 ml. of acetonitrile and adding a solution of 500 mg. of potassium cyanide in 10 ml. of water. The mixture was extracted with ether and the ether extracts were washed with water. After the ether extract had been dried over sodium sulfate, it was concentrated under reduced pressure to give 300 mg. (96%) of a colorless oil. The infrared and n.m.r. spectra of this oil were superimposable with those of the colorless oil obtained after chromatography but before formation of the silver nitrate complex. The n.m.r. spectrum showed the split signal at 4.27 and 4.22  $\tau$ , typical of bicyclo[6.1.0]nona-2,4,6-triene derivatives,<sup>2</sup> and this same split signal was present in the spectrum of the silver nitrate complex but shifted to 3.60 and 3.53  $\tau$ .

(b) From *trans*-9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene.—The pure *trans*-ester was obtained by treating the adduct<sup>2</sup> of cyclooctatetraene and ethyl diazoacetate with silver nitrate in boiling absolute ethanol to form the silver nitrate complex. The resulting solid was recrystallized from absolute alcohol to give in 91% yield the white needles, m.p. 165° dec. (inserted at a bath temperature of 155°), of the pure *trans*-9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene silver nitrate complex.

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>·AgNO<sub>3</sub>: C, 40.02; H, 3.92. Found: C, 40.11; H, 3.92.

Regeneration of the *trans*-9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene was accomplished as before and its conversion to I by treatment with phenyllithium followed as described in (a) and in comparable yield.

**Diphenylbicyclo[6.1.0]nona-2,4,6-trien-9-ylcarbinol (IV).**—When the adduct of cyclooctatetraene and ethyl diazoacetate, estimated to be a 7:93 mixture of *cis* and *trans* isomers, was treated with phenyllithium as described in part (a) above, the work-up by chromatography over alumina (Woelm, neutral, grade 1) using petroleum ether (40–60°) containing 5% diethyl ether led to the separation of two bands. Elution of the first of these bands gave a crystalline solid in 5% yield. After recrystallization from *n*-hexane this was obtained as white crystals, m.p.

168.5–169.5°. Its n.m.r. spectrum showed a split signal at 4.08 and 4.01  $\tau$ , indicating the bicyclo[6.1.0]nona-2,4,6-triene system. The proton signals in the cyclopropane region (7.5–8.3  $\tau$ ) were split showing a coupling constant of 10.8 c.p.s. in accord with the all-*cis* assignment of IV.<sup>4</sup>

*Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>O: C, 87.96; H, 6.71. Found: C, 87.80; H, 6.51.

The second band from the alumina column was a colorless oil (90% yield) whose spectra agreed in all respects with those of I as previously prepared.

**Acid-Catalyzed Rearrangement of I.**—To a solution of 1.5 g. of I (regenerated from its silver nitrate complex) in 50 ml. of anhydrous ether there was added dropwise with stirring 1 ml. of a 50% solution of fluoroboric acid in ether. The mixture immediately became red and, after stirring for 2 min., it was poured into ice water. The ether layer was separated and the aqueous solution was extracted with ether. The combined ether extracts were then washed with water, dried and concentrated under reduced pressure. The residue was taken up in petroleum ether (40–60°) containing 10% ether and chromatographed over alumina (Woelm, neutral, grade 1). From the eluate there was isolated a solid which, after recrystallization from ethanol, gave 1.24 g. (88%) of white, fluorescent needles, m.p. 102–103°. The reported melting point of 1,1,4-triphenylbuta-1,3-diene (V) is 101.5–102°. The n.m.r. spectrum of V showed proton signals centered at 3.0  $\tau$  (15 protons corresponding to the phenyls) and at 3.4  $\tau$  (3 conjugated vinyl protons).

*Anal.* Calcd. for C<sub>22</sub>H<sub>18</sub>: C, 93.47; H, 6.22. Found: C, 93.57; H, 6.43.

**Hydrogenation of V.**—A solution of 5.0 g. of 1,1,4-triphenylbuta-1,3-diene (V) in 100 ml. of ethyl acetate containing 200 mg. of a 10% palladium-on-charcoal catalyst was subjected to hydrogenation at room temperature and atmospheric pressure. The hydrogen uptake corresponded to 2 moles of hydrogen. Removal of the catalyst and solvent followed by distillation of the residue gave 4.8 g. (95%) of a colorless oil, b.p. 173–175° at 0.1 mm.,  $n_D^{20}$  1.5870. These properties are in agreement with those reported for 1,1,4-triphenylbutane by Petrov and Vdovin.<sup>9</sup>

**Ozonolysis of V.**—A stream of oxygen containing about 3% ozone was passed through a solution of 1.4 g. of V dissolved in 70 ml. of methylene chloride and held at –40° until ozone was no longer absorbed. The mixture was then diluted with 120 ml. of methanol and concentrated to about one-half its volume. There was then added 10 ml. of 30% hydrogen peroxide and 60 ml. of a 10% sodium hydroxide solution and the mixture was stirred overnight at room temperature. Water was added and the mixture was extracted with methylene chloride. The aqueous phase was reserved for later examination.

The methylene chloride extract was washed with water, dried, and concentrated under reduced pressure. Addition of ethanol to the residue caused the separation of crystals which were identified as the starting hydrocarbon V. The ethanolic mother liquor was then treated with 2,4-dinitrophenylhydrazine reagent. The solid, which formed, was recrystallized from ethanol to give in low yield brilliant red needles, m.p. 201–202°. Its composition (*Anal.* Calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 64.94; H, 4.15. Found: C, 65.02; H, 4.35) and melting point (lit. gives as m.p. 195–196°<sup>10</sup> 203–204°<sup>11</sup>) are in agreement for the 2,4-dinitrophenylhydrazone of  $\beta$ -phenylcinnamaldehyde.

When the aqueous phase, which had been reserved as indicated above, was acidified, a mixture of crystalline acids separated. This was collected, dried, and subjected to sublimation. The acid which sublimed first was readily identified as benzoic acid by comparison with an authentic sample. The second acid, which sublimed more slowly, gave white crystals, m.p. 161–162°. From its composition (*Anal.* Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>: C, 80.33; H, 5.39. Found: C, 80.68; H, 5.75) and melting point (lit.<sup>12</sup> gives 162°) this acid was identified as  $\beta$ -phenylcinnamic acid.

**Attempted Dehydration of I with Base.**—To a solution of 0.15 mole of phenyllithium in 100 ml. of ether there was added dropwise with stirring a solution of 1.5 g. (0.015 mole) of I (regenerated from its silver nitrate complex) in 10 ml. of ether. When the addition was complete, the mixture was stirred for 1.5 hr. at room temperature. It was then poured into ice water and work-up of the reaction mixture was carried out as described under the preparation of I. After chromatography there was recovered 1.33 g. (89%) of an oil whose infrared and n.m.r. spectra were identical with those of I. No other useful product could be isolated.

(9) A. D. Petrov and V. M. Vdovin, *Zh. Obshch. Khim.*, **27**, 45 (1957).

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(11) S. M. McElvain and L. R. Morris, *J. Am. Chem. Soc.*, **74**, 2657 (1952).

(12) H. Rupe and E. Busolt, *Ber.*, **40**, 4539 (1907).

(8) Analyses by Micro-Tech Laboratories, Skokie, Ill.