

# Bicyclo[6.2.0]decatetraene Dianions and Related Cyclooctatetraene Derivatives

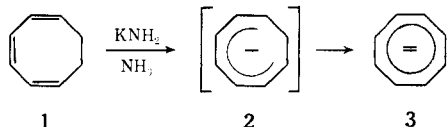
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**Abstract:** The bicyclo[6.2.0]deca-1,3,5,7-tetraene dianion (**5**) was produced by the addition of three different substances, **4**, **6**, and the tautomeric system **8**  $\rightleftharpoons$  **9**, to potassium amide in liquid ammonia. Similarly, the cyclooctatetraene dianion (**3**) and dianion **11** were produced by the addition of cyclooctatetraene (COT) and the 53° dimer of COT (**10**), respectively, to potassium amide in liquid ammonia. <sup>1</sup>H nmr data are given for dianions **5** and **11**, and <sup>13</sup>C nmr data are given for dianions **3** and **5**. The former two dianions were oxidatively quenched with iodine to afford the labile cyclooctatetraene derivatives, **6** and **12**, respectively. Thus the alkylation of cyclooctatetraene *via* its dianion, followed by base-promoted deprotonation of the cyclooctatriene product and oxidative quenching of the resulting dianion, represents a convenient and useful procedure for the synthesis of substituted cyclooctatetraenes.

Cyclooctatetraene dianions have most commonly been prepared by a two-electron reduction of the corresponding cyclooctatetraenes. This has been effected by alkali metals in ether solvents or in liquid ammonia,<sup>2</sup> by electrolytic reduction<sup>3</sup> and by various organometallic compounds.<sup>4,5</sup>

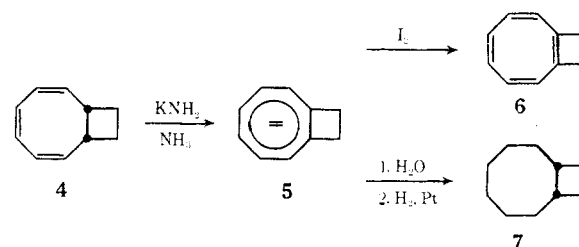
In contrast, there are only a very few reports in the literature of the formation of cyclooctatetraene dianions by a second method, *viz.*, by removal of two protons from cyclooctatetraenes. The possibility of this occurrence was alluded to a number of years ago with regard to the facile base-promoted isomerization of 1,3,6-cyclooctatriene to 1,3,5-cyclooctatriene.<sup>6</sup> Cyclooctatetraene dianions have also been postulated as intermediates in the catalysis of H-D exchange in cyclooctatetraene by base and cyclooctatrienes.<sup>7</sup> More recently **3** has been directly observed by nmr spectroscopy during an attempt to prepare the cyclooctatrienyl anion (**2**).<sup>8</sup> The latter apparently is unstable and undergoes disproportionation to **1** and **3**.



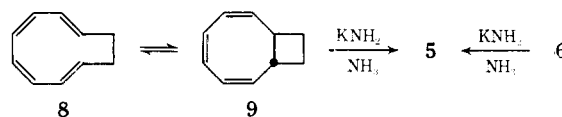
For several years now we have been studying the preparation of novel cyclooctatetraene dianions by the base-promoted removal of two protons from cyclooctatriene derivatives. In this paper, we report the results of the initial phase of our research which deals with the preparation of bicyclo[6.2.0]decatetraene dianions<sup>9</sup> and with the oxidation of these species to the corresponding cyclooctatetraene derivatives.<sup>10</sup>

## Results

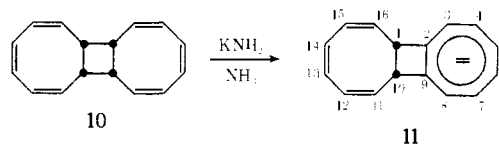
Treatment of *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**4**)<sup>11</sup> with a twofold excess of potassium amide in liquid ammonia produces a deep-red solution, the nmr spectrum of which (at 37°) displays two sharp singlets at  $\delta$  3.33 (cyclobutyl) and 5.60 (aromatic) with an area ratio of 1:1.5. Upon oxidative quenching of this solution into a suspension of iodine in pentane, compound **6**, identified by comparison of its nmr and ir spectra with published data,<sup>12</sup> was obtained cleanly. When this same solution was quenched with water and the resulting complex mixture of isomers was catalytically hydrogenated, **7**<sup>12,13</sup> (identified by comparison of its nmr spectrum with that of the major product of hydrogenation of **4**) was obtained as 92% of the product mixture.



The above data conclusively show that the bicyclic skeleton is retained in the anion, the assigned structure of which (**5**) is also consistent with the nmr data. The same anion is also cleanly produced by the addition of the tautomeric system **8**  $\rightleftharpoons$  **9** (consisting of *ca.* 40% **8** and 60% **9** at  $-76^\circ$ )<sup>11</sup> or of tetraene **6** to potassium amide in liquid ammonia. <sup>13</sup>C nmr data for **5** are given in the Discussion section.

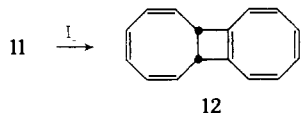


Treatment of **10**<sup>14</sup> with an eightfold molar excess of potassium amide in liquid ammonia at *ca.*  $-78^\circ$  in a sealed nmr tube immediately afforded a deep purple solution whose nmr spectrum (at  $-65^\circ$ ) is consistent with dianion **11**. The six protons of the dianion ring absorb as a broad-

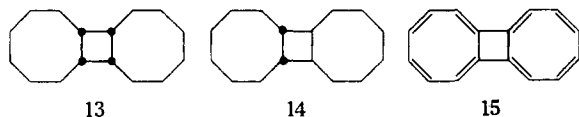


ened singlet at  $\delta$  5.62 (compared with  $\delta$  5.60 for the corresponding protons in **5** (at 34°)); the bridgehead protons are shifted downfield (singlet at  $\delta$  4.46) owing to deshielding by the adjacent diatropic ring; H<sub>12</sub> and H<sub>15</sub> appear as a two proton doublet ( $J = 11.5$  Hz) at  $\delta$  6.56, and H<sub>11</sub> and H<sub>16</sub> give rise to a similar doublet at  $\delta$  5.89 with the downfield peak overlapping a singlet for H<sub>13</sub> and H<sub>14</sub> at  $\delta$  5.94. The lack of an observable coupling between H<sub>10</sub> and H<sub>11</sub> (H<sub>1</sub> and H<sub>16</sub>) is indicative of a dihedral angle of *ca.* 105° between these protons as suggested by molecular models; *i.e.*, the cyclooctatriene ring in **11** is folded into a tub-like conformation. Dianion **11** suffers decomposition between successive scans when the nmr probe temperature is raised to about  $-30^\circ$  and considerable solid material is formed in the sample tube at this temperature. In contrast, solutions of dianion **5** are stable for at least 2 years at room temperature.

Quenching of dianion **11** into a suspension of iodine in pentane at  $-78^\circ$  in an inert atmosphere afforded heptaene **12**. The latter compound is extremely labile since samples were seen (by nmr) to degenerate in purity after storage in solution under argon for several days at  $-20^\circ$  or after rotary evaporation of solvent in air. We were nevertheless able to obtain **12** in at least 80% purity after careful work-up.



There is no doubt as to the structure of this compound since its nmr spectrum bears a striking resemblance to the appropriate portions of the spectra of **4** and **6**. The six-proton multiplet of the tetraene ring ( $\delta$  5.2–5.6) is virtually identical with that of **6** ( $\delta$  5.3–5.6). The olefinic signals of the triene ring appear as broadened singlets at  $\delta$  5.74 (2 H) and 5.92 (4 H) (compared with  $\delta$  5.73 (2 H) and 5.92 (4 H) for **4**), and the two bridgehead protons appear as a singlet at  $\delta$  3.37. In order to confirm that the skeletal structure of the original cyclooctatetraene dimer remained in **12**, the latter was catalytically hydrogenated to afford two major products, a (43%) and b (54%), and three detectable minor products (by glpc analysis). Separation of the major components by preparative glpc gave pure b as a crystalline solid whose melting point and infrared and nmr spectra were identical with those of **13** (obtained by catalytic hydrogenation of **10**).<sup>14</sup> Compound a was obtained slightly impure as a viscous oil which could not be induced to crystallize. Its infrared spectrum is significantly different from that of **14**,<sup>15</sup> and its structure is uncertain at this time.



Finally, treatment of **12** with an excess of potassium amide in liquid ammonia in a sealed nmr tube at *ca.*  $-78^\circ$  instantly gave a deep purple solution. Over a short period of time, this solution coated the inner walls of the nmr tube with solid, thereby making it difficult to obtain good spectra. However, the spectra obtained in two trials showed as the major feature a broadened singlet centered at  $\delta$  4.0 with a weak signal barely distinguishable from baseline noise at  $\delta$  6.55. We were unable to obtain any evidence for **15**<sup>16</sup> by quenching a similar solution into a suspension of iodine in pentane.

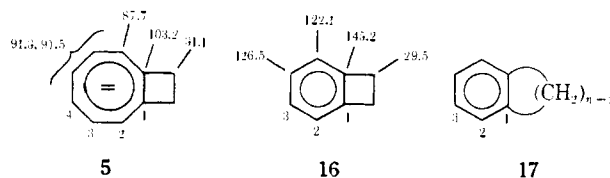
## Discussion

**The Bicyclo[6.2.0]deca-1,3,5,7-tetraene Dianion.** The facile preparation of dianions **5** and **11** demonstrates that the base-promoted removal of two protons from cyclooctatrienes in strongly basic media represents an excellent route to substituted cyclooctatetraene dianions and is clearly to be preferred to an alternate route involving two-electron reduction of the corresponding cyclooctatetraenes (*i.e.*, **6** and **12**). In fact, the reaction sequence exemplified by the alkylation of cyclooctatetraene to afford **4**, followed by treatment with base and quenching with iodine to produce **6**, represents a convenient and useful route to substituted cyclooctatetraenes.

Dianion **5** has now been prepared by the treatment of four different precursors, **4**, **8**  $\rightleftharpoons$  **9**, **6**, and 7-chlorospiro[2.7]deca-4,9-diene,<sup>10b</sup> with potassium amide in liquid ammonia. The formation of **5** from **4**, which involves an oxidation–reduction reaction promoted in some manner by potassium amide (not potassium), is somewhat unusual. Further

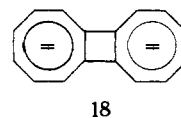
details of this reaction are discussed in a report of an analogous reaction of cyclooctatetraene.<sup>17</sup>

The <sup>13</sup>C chemical shifts for dianion **5** in liquid ammonia are given below,<sup>18</sup> along with those for benzocyclobutene.<sup>19a</sup> The assignment of the signal at  $\delta$  103.2 in the spectrum of **5** to the carbons adjacent to the ring fusion was made by analogy to the relative positions of the corresponding carbons in benzocyclobutene and is therefore tentative.



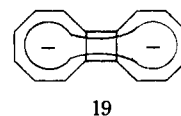
Günther and coworkers have recently noted that the signal for C<sub>2</sub> and C<sub>5</sub> in benzocycloalkenes (**17**,  $n = 3-6$ ) moves upfield, and that for C<sub>3</sub> and C<sub>4</sub> moves downfield as the strain in the cycloalkene ring increases.<sup>19a</sup> In this regard, it is interesting to note that the downfield shift of C<sub>2</sub> and C<sub>7</sub> and of C<sub>3</sub>–C<sub>6</sub> in **5** (4.0 and *ca.* 0.3 ppm, respectively) relative to **3** ( $\delta$  91.7, also in liquid ammonia) is substantially less than the corresponding downfield shift of C<sub>2</sub> and C<sub>5</sub> and of C<sub>3</sub> and C<sub>4</sub> in benzocyclobutene (**16**) (6.6 and 2.2 ppm, respectively) relative to benzene ( $\delta$  128.7 ppm).<sup>20</sup> This may indicate that the strain introduced by the four-membered ring in **5** is less than that in **16**, a result which is expected on the basis of the larger C–C–C bond angle in **3** ( $135^\circ$ ) relative to benzene ( $120^\circ$ ). However, additional work on this problem is required since the response of the chemical shift in **3** to substitution by unstrained alkyl groups is presently unknown.<sup>21</sup>

**Anions Derived from the 53° Dimer of Cyclooctatetraene.** The intermediacy of dianion **11** has been inferred by Schröder<sup>7</sup> but this species has never been directly observed. Its clean formation in the presence of excess potassium amide in liquid ammonia indicates that tetraanion **18** is not stable



enough to be formed under these strongly basic conditions. This is not particularly surprising since the electrostatic repulsion between two dianionic rings as well as any destabilization associated with the formation of a peripheral 20  $\pi$  electron system should render the generation of the second dianionic ring much more difficult than that of the first. This is supported by the results of self-consistent Hückel ( $\omega$  technique) molecular orbital calculations which indicate a loss of delocalization energy on going from dianion **11** to tetraanion **18**.

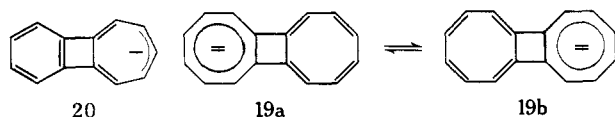
Heptaene **12** contains both a cyclooctatetraene ring, as in **6**, and a cyclooctatriene ring, as in **4**. It was therefore of interest to determine whether this compound would suffer reduction of the former subunit or deprotonation of the latter on treatment with potassium amide in liquid ammonia. If the second course were to be followed, a potentially interesting 18  $\pi$ -electron dianion (**19**) would result.



It is clear from the nmr spectrum produced by the treatment of **12** with potassium amide in liquid ammonia at low temperature that reduction to afford dianion **11** does not occur. However, since a broadened singlet at  $\delta$  4.0 was the only signal observed, there are no coupling constants or rel-

ative integration values available to aid structure determination. Not surprisingly, in view of the lability of **12**, we were unable to obtain quench products from the above solution. Since the  $\delta$  4.0 signal is not as strong as might be expected in view of the quantity of **12** employed, we cannot completely exclude the possibility that it originated from the *ca.* 20% impurities which apparently contaminated the samples of **12**. Nevertheless, this peak does appear at a relatively high-field position and probably results from some negatively charged species.

While an extensive discussion of the possible origin of this peak is unwarranted at this time, we might briefly point out that our recent finding<sup>22</sup> of a significant peripheral diamagnetic ring current in anion **20** (a 14  $\pi$ -electron system) suggests that a similar ring current might exist in planar **19** (an 18  $\pi$ -electron system), and that this compound would not be expected to absorb as high as  $\delta$  4.0. On the other hand, the situation might be different if **19** were rapidly interconverting between two equivalent nonplanar conformations (**19a**  $\rightleftharpoons$  **19b**). In contrast to the case of planar ( $D_{2h}$ ) **19**, the contribution of a potential paramagnetic component of the ring current would be "symmetry allowed"<sup>23</sup> in the nonplanar conformation. A further investigation of this problem is planned.



In summary, the present study demonstrates that the deprotonation of cyclooctatrienes in a strongly basic medium provides a good route to novel cyclooctatetraene dianions, including labile ones such as **11**. In addition, this reaction, when preceded by alkylation of the cyclooctatetraene dianion and followed by oxidative quenching of the substituted dianions, is a key step in a potentially useful and convenient synthesis of cyclooctatetraene derivatives.

## Experimental Section

Infrared (ir) spectra were obtained on carbon tetrachloride solutions in a 0.1-mm sodium chloride cell on a Perkin-Elmer 337 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained on carbon tetrachloride solutions with tetramethylsilane (TMS) as internal standard or on liquid ammonia solutions with trimethylamine ( $\delta_{\text{TMS}}(\text{NH}_3)$  2.135) as internal standard on a Varian A-60D spectrometer. Carbon-13 spectra were obtained at 25.2 MHz with a Varian XL-100 spectrometer by using acetone- $d_6$  contained in a concentric tube as a lock signal. Chemical shifts were determined relative to dioxane contained in a tube of equivalent geometry and are reported relative to TMS ( $\delta_{\text{TMS}} = \delta_{\text{dioxane}} + 67.4$ ).<sup>18,24</sup> Gas-liquid partition chromatography (glpc) analyses were obtained on a Varian-Aerograph 1200 flame ionization instrument, whereas a Varian-Aerograph A-90P3 thermal conductivity instrument was used for preparative work. Peak areas are uncorrected for response factors.

**General Technique for Obtaining Nmr Spectra in Liquid Ammonia.** The following procedure was used for preparing nmr samples of all anions described in this work. A minute crystal of ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was placed in a medium-walled nmr tube, and the tube was flame-dried under a stream of ammonia introduced *via* a long syringe needle. The bottom of the tube was then placed in a Dry Ice-acetone bath without removing the needle, and *ca.* 0.5 ml of ammonia was condensed. Trimethylamine (an internal standard) was added in a similar fashion from a lecture bottle. To the frozen ammonia was added a clean piece of potassium wire (42 to 63 mg, 1.08 to 1.62 mg-atoms) or a similar molar amount of another alkali metal, and the tube was sealed and set aside in a shielded place to warm to room temperature. (*Caution: such tubes have been known to explode owing to the hydrogen pressure which builds up during amide formation.*) Potassium amide formation was usually complete in 5–10 min at room temperature. (Cesium

reacts even more rapidly, while sodium and lithium require longer periods of time.) Complete amide formation is signaled by the change of the blue metal ammonia solution to a pale yellow metal amide solution with a gray precipitate. The tube was then refrozen in the Dry Ice-acetone bath and cautiously opened by breaking off the top. The amide was cleaned from the tube walls with a pipe cleaner, and 30 to 50  $\mu\text{l}$  (or an equivalent amount of solid) of the appropriate hydrocarbon was introduced from a syringe. A glass wool plug was tamped tightly into place about halfway down the tube, and the tube was resealed. The amide solution was allowed to thaw, and the tube was then shaken while taking care to keep the sample cold. The sample was then filtered through the glass wool plug by inverting it momentarily in the Dry Ice bath. The end of the tube containing the freshly filtered solution was inserted into the nmr probe.

**Nmr Spectra of Dianions 3, 5, and 11.** (a)  $^1\text{H}$  nmr samples of **5** were prepared by adding **4**, **8**  $\rightleftharpoons$  **9**, or one-tenth of the pentane extracts from the preparation of **6** (*vide infra*) to potassium amide in liquid ammonia as described above in the general method. A sample of **11** was prepared from 52 mg (0.025 mmol) of **6** and potassium amide (from 78 mg (2.0 mg-atoms) of potassium) in ammonia. The  $^1\text{H}$  nmr spectrum of the deep purple solution was recorded at  $-65^\circ$ . The spectrum indicated decomposition between successive scans when the probe temperature was raised to *ca.*  $-30^\circ$ , and considerable solid material was formed in the tube at this temperature. No temperature dependence of the chemical shifts was observed.

(b)  $^{13}\text{C}$  nmr samples of **3** and **5** were prepared by the addition of *ca.* 0.3 ml of a mixture of 1,3,6- and 1,3,5-cyclooctatriene or of **4**, respectively, to excess potassium amide in *ca.* 3.5 ml of liquid ammonia in a 12-mm o.d. medium-walled tube. A sealed 5-mm tube containing acetone- $d_6$  was added to this tube, the larger tube was sealed, and the sample was filtered through a glass wool plug as described above in the general method.  $^{13}\text{C}$  spectra were recorded at *ca.*  $-30^\circ$  and reported as ppm downfield from TMS (see above).

**Oxidative Quenching of Dianion 5 to Bicyclo[6.2.0]deca-1,3,5,7-tetraene (6).** *cis*-Bicyclo[6.2.0]deca-2,4,6-triene<sup>11</sup> (0.5 g, 3.8 mmol) was added to a solution of potassium amide (from 1.0 g (0.026 g-atom) of potassium) in 35 ml of liquid ammonia at *ca.*  $-30^\circ$ . The reddish-brown solution was stirred for 20 min after which time the contents of the flask was *cautiously* added to a vigorously stirred suspension of 20 g (0.079 mol) of iodine in 100 ml of pentane. Water (150 ml) was then carefully added to the brown-black solution, followed by 2.0 g of sodium thiosulfate. The organic layer was separated, the aqueous layer was extracted twice with pentane, the combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was concentrated under reduced pressure. The nmr spectrum of the resulting solution was identical with that previously reported for **6**<sup>11a,b</sup> and showed essentially no other peaks except for those of the solvent. Partial replacement of the pentane with carbon tetrachloride, addition of a known amount of benzene, and analysis by nmr indicated the yield to be at least 50%. Extensive polymerization occurred at room temperature when most of the solvent was removed. *Caution is strongly recommended since it is possible that an explosive substance, nitrogen triiodide, may be formed in this procedure.* However, we have never experienced any problems.<sup>25</sup>

**Conversion of Dianion 5 to *cis*-Bicyclo[6.2.0]decane (7) via Aqueous Quenching and Hydrogenation.** *cis*-Bicyclo[6.2.0]deca-2,4,6-triene (**4**) (0.5 g, 3.8 mmol) was added to a solution of potassium amide (from 1.00 g (0.026 g-atom) of potassium) in 35 ml of liquid ammonia at *ca.*  $-30^\circ$ . After the contents of the flask had been stirred for 20 min, it was added to a vigorously stirred mixture of 100 ml of water and 50 ml of pentane. The organic layer was separated, the aqueous layer was washed twice with pentane, and the combined organic layers were dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. One-fifth of this material was added to a suspension of prereduced platinum oxide (10 mg) in 4 ml of glacial acetic acid. The mixture was stirred under hydrogen at atmospheric pressure and room temperature until hydrogen uptake had ceased, then added to 30 ml of water, and extracted with 5 ml of pentane. Analysis of the pentane extracts by glpc (8% Carbowax 20M on 100/120 Chromosorb P at  $70^\circ$ ) showed at least four components in the ratio of 0.6:7:92:0.4 with relative retention times of 1.00, 1.5, 2.0, and 2.3, respectively. The major component was separated by glpc

and shown to be **7** by comparison of its nmr spectrum with authentic material (*vide infra*).

**Hydrogenation of *cis*-Bicyclo[6.2.0]deca-2,4,6-triene (**4**) to **7**.** *cis*-Bicyclo[6.2.0]deca-2,4,6-triene (46 mg, 0.35 mmol) in 3 ml of absolute ethanol was added to a suspension of prerduced platinum oxide (20 mg) in 5 ml of absolute ethanol. The mixture was stirred under hydrogen at atmospheric pressure and room temperature until hydrogen uptake (2.7 mol equiv) had ceased. The solution was then added to 75 ml of water, extracted twice with 5 ml of pentane, and analyzed by glpc (8% Carbowax 20M on 100/120 Chromosorb P at 70°). The sole component (**7**) was collected and gave an nmr spectrum (CCl<sub>4</sub>) which showed a broad multiplet between  $\delta$  1.7 and 2.6 (cyclobutyl) and a relatively sharp multiplet between  $\delta$  1.1 and 1.7 and centered at  $\delta$  1.42.<sup>7b</sup> The relative areas of the two multiplets were *ca.* 1:2, respectively.

**Oxidative Quenching of Dianion **11** to **12**.** Of many procedures tried, the following gave the best results. A 0.5-l. three-necked flask fitted with a Dry Ice condenser, a mechanical stirrer, a gas inlet tube, and a stopcock at the bottom connected to a second 0.5-l. flask (which was fitted with a Dry Ice condenser, a gas inlet tube, and a magnetic stirring bar) was dried under argon, and 250 ml of ammonia was condensed into it. Potassium amide (from (0.42 g (0.011 g-atom) of potassium) was generated in the upper flask. This flask was then cooled with Dry Ice placed in a jacket fashioned from a polystyrene bucket, and dimer **10** (0.8 g, 3.85 mmol) dissolved in 10 ml of dry ether was added (over 5 min) to afford a deep purple solution. The addition funnel was rinsed with 10 ml of dry ether which was then added to the upper reaction flask, and the mixture was stirred vigorously under argon for 70 min. Runs at *ca.* -30° gave considerable side product and poor product recovery, whereas runs near -78° gave very little conversion of the starting dimer. The best results were obtained when the Dry Ice jacket was left undisturbed except for adding more Dry Ice as needed. Thus a small insulating space was allowed to form between the mass of Dry Ice and the flask so that the temperature of the reaction mixture was not maintained as low as -78°.

The anion solution was added slowly over about 5 min to a vigorously stirred suspension of 25 g (0.098 mol) of iodine in 50 ml of pentane under argon and cooled with Dry Ice. (See *cautionary note in the description of the preparation of 6*.) Saturated aqueous ammonium chloride (30 ml) was then added slowly to the deep green emulsion, followed by 30 ml of water. Excess ammonia was allowed to distil out under argon flow for about 5 min, after which sodium thiosulfate was added slowly. The mixture was transferred under argon to a separatory funnel cooled in a beaker of ice. By working quickly, the pentane layer was separated and the aqueous phase extracted three times with about 70 ml of pentane. The combined deep green pentane solutions were stored immediately on Dry Ice under argon. After storage overnight, some fine brown crystalline material had formed and was removed with a spatula under argon for nmr analysis (see Results section).

The best nmr samples of **12** gave integrations approximately 45% too high for the olefinic protons of the triene ring, and it was evident that this was due to an impurity. Indeed, compounds with strong nmr signals coinciding with those for the triene ring of **12** were detected in fractions eluting from a column both before and after compound **12**. If, as suggested by the nmr of these fractions, the impurity is a double bond isomer of **12** with 10 or 11 olefinic protons, then the best samples of **12** were approximately 80% pure.

Filtration of crystalline **12** at room temperature in air gave considerable solid material which was insoluble in carbon tetrachloride; **12**, in contrast, is quite soluble. Solutions of impure **12** are deep green, and the compound crystallizes from pentane (after long standing at -78°) as fine crystals varying in color from yellow to reddish brown.

Attempted purification of **12** on a chromatographic column (silica gel-pentane) under nitrogen and maintained at -10 to -20° by cooled methanol circulated through a jacketed column was unsuccessful. Compound **12** was obtained in approximately 55% purity with the major impurities absorbing at  $\delta$  5.62-5.95. Other fractions with their major absorptions coinciding with those of **12** in this region and with additional signals about one-third as intense in the  $\delta$  2.2-3.7 region were obtained in fractions with approximately one-half and twice the elution volume of **12**.

**Hydrogenation of **12**.** Ethanol (5 ml) was added to a pentane solution of **12** (60 ml) from a fresh reaction mixture, and the result-

ing solution was concentrated on a rotary evaporator to about 3 ml. This suspension in ethanol, estimated to contain at least 100 mg of *ca.* 80% pure **12**, was added to a suspension of prerduced platinum oxide (80 mg) in ethanol (3 ml) on an atmospheric pressure hydrogenation line. The mixture was stirred under hydrogen at 0-5° for 80 min, after which time the mixture was allowed to warm to room temperature. Hydrogen uptake ceased after an additional 60 min. Analysis of the product mixture after work-up by glpc (10% Carbowax 20M on 70/80 Anachrome ABS at 115°) showed two major products: a (43%) followed by b (54%). The latter had a retention time identical with that of the major hydrogenation product of dimer **10**. Under the above glpc conditions, a was closely preceded and followed by small shoulders (less than 3% of the reaction mixture). Pure b was collected after two passes as a crystalline solid (**13**, mp 117-118° (lit.<sup>7b</sup> 117-118°), ir and nmr spectra identical with those of hydrogenated **10**). Compound a (containing some of the shoulder impurities) was collected as a colorless oil which could not be induced to crystallize.

**Treatment of **12** with Potassium Amide-Ammonia. Nmr Spectrum.** A sealed nmr tube was prepared as previously described by using ammonia (0.5 ml), potassium wire (53 mg, 1.3 mmol), and a trace of trimethylamine as internal standard to which was added solid **12** obtained in the following way. About 30 ml of the crystalline material suspended in pentane was syringed into a centrifuge tube packed in Dry Ice. The tube was stoppered and centrifuged for several minutes at -78°. The supernatant solution was then removed by syringe and the solid **12** removed by spatula under a stream of nitrogen (which evaporated most of the remaining solvent) and pushed into the nmr tube with an applicator stick. The amount of solid added was estimated to be about 50 mg. A glass wool plug was then inserted, and the tube was sealed. A deep purple solution resulted upon mixing, and the spectrum (see Results section) was obtained at -65°. Two tubes prepared in this way gave identical nmr spectra.

**Treatment of **12** with Potassium Amide-Ammonia. Iodine Quench.** Powered dimer **10** (0.25 g, 1.20 mmol) was added directly to potassium amide (12 mmol) in ammonia (40 ml) and stirred for 12 min at -33° prior to iodine quench and work-up as described above. The entire extract containing impure (estimated 60-70% pure) **12** was then added to potassium amide (10.7 mmol) in ammonia (25 ml), stirred for 5 min at -33°, and quenched into iodine under hexane at -78°. After the usual work-up, the entire hexane extract was concentrated to about 1 ml for nmr analysis which gave a very weak spectrum of the starting material (dimer **10**) as the only detectable species.

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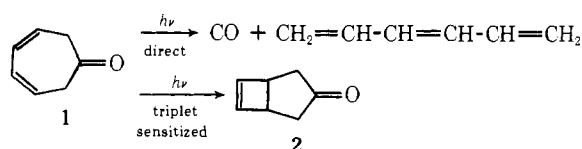
## Photochemistry of Bicyclo[4.2.1]nona-2,4-dien-9-one, a Bridged 3,5-Cycloheptadienone<sup>1</sup>

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**Abstract:** The direct and triplet-sensitized photochemistry of the title compound **7** has been studied and is compared with similar investigations of simple 3,5-cycloheptadienones and other 2,7-bridged derivatives to assess the control of molecular geometry on singlet and triplet photochemistry in these systems. Direct photolysis of **7** gives cyclooctatriene **10** by decarbonylation ( $\Phi = 0.66$ ), the *endo*-cyclobutene derivative **11** ( $\Phi = 0.14$ ), and a third labile unidentified product. Photolysis of **7** sensitized by acetone, benzophenone, Michler's ketone, or triphenylene gives a new ketone, dihydrobarbaralone **18**, by an oxa-di- $\pi$ -methane rearrangement. Products **10** and **11** are seen only in the case of acetone sensitization, suggesting either some singlet transfer to **7** or competitive light absorption by **7**. Products were identified on the basis of spectral data and chemical transformations. Fluorescence emission from **7** can be observed at room temperature and 77°K, and similar emission is seen from all of the other 3,5-cycloheptadienones studied. It is concluded that the singlet-derived photodecarbonylation, which occurs from systems in which the diene moiety is either twisted or constrained to be planar, is probably a concerted chelotropic reaction. Deactivation to the ground state of **7** from S<sub>1</sub> is relatively inefficient and unimportant, as is intersystem crossing to T<sub>1</sub>. Electrocyclic closure of the excited singlet to the cyclobutene **11**, which is not observed with twisted 3,5-cycloheptadienones, suggests that such singlet reactivity is seen only when the diene moiety is planar and is probably a simple concerted disrotatory cyclization. When the diene moiety is twisted, cyclobutene formation can be observed but only on sensitized photolysis *via* T<sub>1</sub>, supporting the earlier hypothesis that the reaction in such cases involves further twisting toward a *cis-trans* geometry, followed by thermal conrotatory ring closure. These reactions support Dauben's concept of ground state conformational control of photochemical reactions. The 1,2-acyl shift (oxa-di- $\pi$ -methane rearrangement) is seen only on triplet sensitization and is shown for the first time to be highly efficient ( $\Phi = 0.89$  using Michler's ketone in benzene). The mechanism of the transformation is discussed and comparison is made with some anomalous results reported previously.

The photochemistry of 3,5-cycloheptadienone (**1**) and related compounds has been a subject of continuing interest for well over a decade. In the original study of Chapman and his coworkers,<sup>4</sup> it was found that **1** underwent efficient photofragmentation to carbon monoxide and a mixture of acyclic hexatrienes, a reaction which could not be quenched by either piperylene or naphthalene. Schuster and coworkers later found that triplet-sensitized photolysis of **1** followed an entirely different course, leading to the valence tautomer bicyclo[3.2.0]hept-6-en-3-one (**2**).<sup>5</sup> Since none of



**2** was formed on direct photolysis of **1**,<sup>4,5</sup> it was unambiguous in this case that the photodecarbonylation occurred exclusively *via* a singlet excited state to the exclusion of in-

tersystem crossing to the triplet manifold, from which in turn only valence tautomerization occurs. *Cis,cis*-diene triplets with favorable geometries (such as 1,3-cyclooctadiene **3**)<sup>6</sup> had been shown to undergo photoisomerization to a *cis-trans* diene followed by an orbital symmetry-allowed thermal electrocyclic ring closure to a *cis*-fused cyclobutene derivative. However, attempts to trap the analogous intermediate *cis,trans*-3,5-cycloheptadienone (**4**) derived from **1**

