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(8) See, for example, C. F. Cullis, J. M. Francis, and A. J. Swallow, *Proc. R. Soc. London Ser. A*, **287**, 15 (1965).
(9) See, for example, A. Habersbergerová, Lj. Josimović, and J. Teplý, *Trans. Faraday Soc.*, **66**, 656, 669 (1970).
(10) In addition to the routes proposed here for the formation of photoproducts **11** and **13** there is an alternative, competing pathway involving simple migration of the double bond in the starting olefin. This process is ubiquitous in olefin photochemistry and is the subject of a separate report (ref 5). Its occurrence in competition with the other two routes accounts for the fact that irradiation of **1a** in methanol-*O-d* results in the formation of **11a** with a significantly lower level of deuterium incorporation than for **12a** (ref 4).
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(15) W. Hueckel and S. K. Gupté, *Justus Liebigs Ann. Chem.*, **685**, 105, 118 (1965).
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Transannular Photochemical Ring Closure of 1,2,5,6-Tetramethylenecyclooctane as a Synthetic Route to Small-Ring Propellanes

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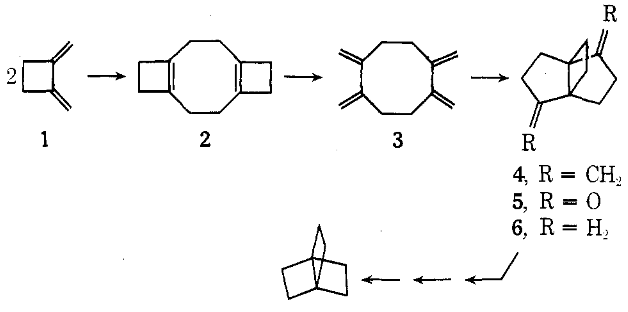
The synthesis of 2,6-dimethylene[3.3.2]propellane (**4**) in three steps and 12% overall yield from allene dimer **1** is reported. The key reaction is the formation of **4** by transannular photochemical ring closure of 1,2,5,6-tetramethylenecyclooctane (**3**). A chemical separation of **4** from isomers that are carried through the synthesis is described, which makes the purification of the intermediates (**1**–**3**) unnecessary. Compound **4** has been converted to the parent [3.3.2]propellane (**6**), which undergoes free-radical addition of bromine across the central bond to give **13**.

The synthesis of small-ring propellanes has been an area of considerable activity in recent years.[2] Theoretical interest in [2.2.2]propellane (**7**)[3] has given special stimulus to the preparation of this molecule. A derivative of **7** has been synthesized by Eaton and his coworkers through two successive ring contractions of [4.2.2]propellane-2-one.[4a] This key intermediate was prepared from the enol acetate of 1,3-cyclohexanedione by photoaddition of ethylene, base-catalyzed elimination of the elements of acetic acid, and photoaddition of a second molecule of ethylene.[4b] Evidence for the intermediacy of the parent compound (**7**) in the electrochemical reduction of 1,4-dibromobicyclo[2.2.2]octane[5] and in the mercury-sensitized photolysis of 1,4-dimethylenecyclohexane[6] has also been reported.

Our route[7] to the [2.2.2]propellane ring system took cognizance of the fact that photochemical ring closure in 1,4-dimethylenecyclohexane provided a formally attractive synthesis of **7**. However, since the ring in this diene prefers a chair conformation,[8] we anticipated that ring closure to **7** might be a rather inefficient process. Moreover, because short-wavelength light or a high-energy sensitizer would be required to excite the isolated double bonds in 1,4-dimethylenecyclohexane, it seemed possible that **7**, if formed, might undergo photoinitiated opening back to the starting material. Finally, were only small amounts of **7** to be formed, for either or both of the above reasons, its separation from unreacted starting material would be problematical. Therefore, we explored the route, outlined in Scheme I, which circumvented these difficulties by effecting photochemical ring closure in 1,2,5,6-tetramethylenecyclooctane (**3**).[9] Cyclooctane rings readily undergo 1,5-transannular reactions;[10] and excitation of **3**, either direct or sensitized, was expected to be easy because of the conjugated diene systems present in the molecule. Moreover, the methylene groups in the anticipated photocyclization product (**4**) could be ozonized to give **5**, a precursor of the parent [3.3.2]propellane (**6**) and, more important, a promising intermediate for the synthesis of **7**.[11] As indicated in Scheme I, a synthesis of **3** can be constructed by noting that **3** is the product of cyclobutene ring opening in **2**, which is in turn a dimer of 1,2 dimethylenecyclobutane (**1**). Thus our synthesis began with attempts to prepare **2** from **1**.

Scheme I



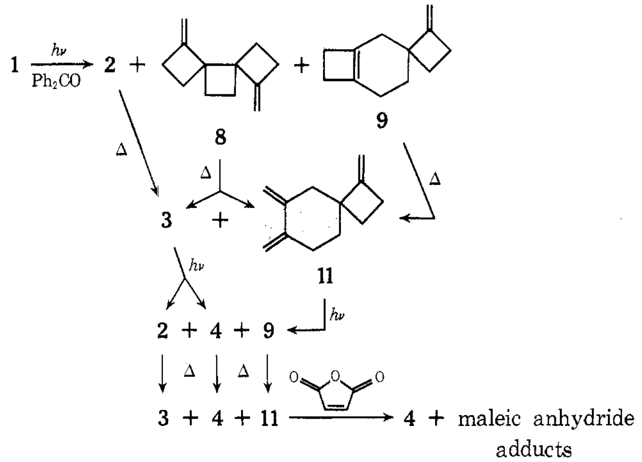
Results and Discussion

The simplest route to **1** is through the thermal dimerization of allene, which also produces about 20% of 1,3-dimethylenecyclobutane.[12] Since we required large amounts of **1**, our first task was to improve the literature method for its preparation. Allene gas was passed through a tube packed with glass balls and heated to 500°. The pyrolysate was collected in a flask cooled with Dry Ice. The flask, containing unreacted allene, allene dimers, and higher oligomers, was then connected to the inlet of the heated tube and allowed to warm to room temperature. Only the allene distilled through the tube, and the pyrolysate was trapped in a second flask. The two flasks were then interchanged and the allene was cycled through the tube again.[13] Allene, recycled thus ten times, gave yields of dimers on the order of 25%. With further recycling even higher yields could be realized.

Although dimerization of butadiene, catalyzed by complexes of Ni^0, gives high yields of 1,5-cyclooctadiene,[14] experiments on the dimerization of 1 to 2 in the presence of $Ni(PPh_3)_4$ were not at all promising. Mixtures of dimers of 1 were obtained, and substantial amounts of starting material remained unreacted. We were discouraged from pursuing further experiments with different ligands on the Ni^0 catalyst by the finding of Heimbach[15] that tris(2-biphenyl phosphite)nickel(0), which gives a 97% yield of 1,5-cyclooctadiene from butadiene,[14] with 2,3-disubstituted butadienes produces the corresponding derivatives of 1,5-cyclooctadiene in only 3–6% yield.

Photosensitized dimerization[16] of 1 proved to be a more promising method for the preparation of synthetically useful quantities of 2. Initial experiments were performed on samples of 1 purified by preparative GLC. However, as expected, the presence of 1,3-dimethylenecyclobutane did not alter the course of the reaction; so the mixture of allene dimers was used for preparative runs. When 1 was irradiated in solution in the presence of benzophenone, three photodimers were isolated by GLC. They were easily identified by NMR as 2, 8, and 9 (Scheme II). Inspection of the NMR spectrum of the crude photolysate showed, however, the two singlets at δ 2.15 and 2.27, belonging to 2, to be absent. Several resonances belonging to neither 8 nor 9 were observed; and on refluxing a benzene solution of the photodimers of 1, these resonances were found to decrease as those belonging to 2 increased in intensity. In analogy with the formation of 1,5-cyclooctadiene by Cope rearrangement of *cis*-1,2-divinylcyclobutane in the sensitized photodimerization of butadiene,[17] the precursor of 2 is almost certainly the syn isomer of 8.

Scheme II



The desired dimer (2) could be separated on a preparative scale from its isomers by spinning band distillation, as well as by GLC. On pyrolysis in a flow system at 330°, it was converted cleanly to 3. At lower temperatures the product (10) of opening just one of the cyclobutene rings in 2 could be isolated. Dimer 9 on pyrolysis at 330° also underwent cyclobutene ring opening to give 11. At temperatures above 200° 8 gave a mixture of 2, 3, 9, 10, and 11. As the pyrolysis temperature was raised, 3 and 11 were isolated in increasing amounts until they became the sole products. At 330° 8 gave 3 and 11 in a ratio of 11:9. Presumably, at temperatures above 200° the most substituted bond in the central cyclobutane ring of 8 is broken, forming a highly stabilized biradical that is partitioned between 2 and 9. At higher pyrolysis temperatures these compounds undergo cyclobutene ring opening, as discussed above, until at 330° only 3 and 11 are detected.

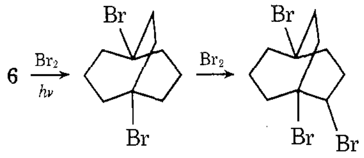
Because 8 constitutes 58% of the original photodimer mixture, while 2 comprises only 29%, the amount of 3 produced from the mixture of photodimers can be maximized by employing the former, as well as the latter, as a source of 3. Although 8 can be separated from 9 by spinning band distillation, 11, the pyrolysis product of 9, is also formed from 8. Therefore, for experiments in which pure samples of 3 were not required the mixture of all three photodimers was pyrolyzed at 330° to give a product consisting of 60% 3 and 40% 11. It was hoped that at higher temperatures 3 and 11 might be equilibrated (via bond cleavage, reclosure, and the intermediacy of 10, or 10, 2, and 9) and that the equilibrium would favor 3. In the event the former expectation was realized, but the latter was not. At 500° 2, 3, 8, 9, and 11 all gave a 50:50 mixture of 3 and 11. Since even at 360° there was some equilibration between 3 and 11, pyrolysis of the crude photolysate was carried out at 330° in order to maximize the amount of 3 present in the pyrolysate.

Samples of pure 3 could be obtained either by pyrolysis of pure 2 or by preparative GLC separation of 3 from 11. On direct photolysis 3 was converted to a 1:1 mixture of 2 and 4. When the photolysis was monitored by GLC, 10 could be identified as the precursor of 2. Sensitized photolysis of 3 was briefly investigated; but while no 2 was formed, the 4 that was obtained was contaminated with several unidentified photoproducts, and GLC analysis indicated a larger loss of volatile material than in the direct photolysis. Since it was found that on direct photolysis 11 only underwent cyclobutene ring closure to 9 and that the presence of 9 and 11 did not affect the photochemistry of 3, for preparative purposes the crude pyrolysate, containing both 3 and 11, was photolyzed. The products then consisted of 2, 4, and 9 with smaller amounts of 10 and 11 present when, in order to minimize polymer formation, the irradiation was not prolonged. From this mixture the desired product of transannular bond formation (4) could be isolated by careful preparative GLC.

The three-step synthesis of 4 described above had the virtue of not requiring purification of any of the intermediates, since the mixture of allene dimers could be photolyzed, the photolysate pyrolyzed, and the pyrolysate photolyzed. However, a tedious GLC separation was required to isolate 4; and we sought a way to circumvent it. Crucial to the solution of this problem was the discovery that 4 proved to be quite stable thermally. When it was pyrolyzed in our flow system at 330°, GLC analysis indicated no new products formed and no appreciable loss of 4. Although the central bond in the [3.3.2]propellane skeleton of 4 is adjacent to two vinyl groups, effective conjugation of them with the bridgehead radicals that would result from cleavage of this bond is geometrically impeded. This fact is probably the origin of the thermal stability of 4, which allowed it to remain intact under conditions which led to cyclobutene ring opening in 2, 9, and 10. Thus, pyrolysis of the crude photolysate, containing 2, 4, 9, 10, and 11, gave a mixture of 3, 4, and 11. Since 3 and 11 are both conjugated dienes, while 4 is not, only the former two compounds underwent Diels–Alder reactions. Consequently, treatment of the crude pyrolysate, containing 3, 4, and 11, with maleic anhydride, followed by chromatography, yielded 4, which was found to be 97% pure by GLC. This chemical separation of 4 from its isomers allowed its preparation by the route shown in Scheme II, without purification of any of the intermediates, in 12% overall yield, based on the weight of allene dimer. Since the crude allene dimer mixture contains only 80% of 1 and since the maximum yield of 4 possible from it by the sequence sensitized photolysis, pyrolysis, direct photolysis is 30%, the maximum theoretical yield of the synthesis shown in Scheme II is 24%, based on the weight of crude dimer. It is somewhat amusing to note that all the steps in this synthesis, starting with the dimerization of allene, require only heat or light; the final purification step alone requires an additional reagent.

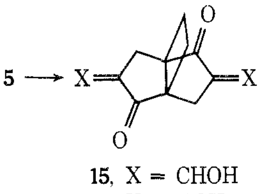
Ozonolysis of 4 in 95% ethanol to the diketone **5** proceeded in 80% yield. When the ozonolysis was done in methanol, in addition to **5**, 20% of another compound (**12**) was also isolated. The mass spectrum and NMR of this second compound were consistent with its formulation as the monodimethyl ketal of **5**, to which **12** was hydrolyzed in dilute aqueous acid. The structure (**5**) for the ozonolysis product of 4 was supported by analytical and spectral data. In particular, the ir showed a sharp absorption at 1740 cm^{-1}, indicating that both carbonyl groups were contained in five-membered rings. The rather complex NMR spectrum could be greatly simplified by stirring a CCl_4 solution of the diketone with D_2O containing K_2CO_3. This resulted in the exchange of four protons and caused the NMR spectrum to collapse to an AA′BB′ pattern for the protons on the two-carbon bridge and a broad singlet for the two nonexchangeable protons on each of the three-carbon bridges. When the exchangeable protons were replaced with bromine by adding Br_2 to a CCl_4 solution of the diketone, not only was the AA′BB′ pattern revealed, but the broad singlet observed in the deuterated ketone was also resolved into an AB quartet.

The structure (**5**) for the diketone was confirmed by its Wolff–Kishner reduction to the parent hydrocarbon (**6**), whose NMR spectrum displayed a sharp singlet for the four equivalent protons on the two-carbon bridge. Subsequently, we learned[18] that [3.3.2]propellane (**6**) had been prepared by a very different route than ours;[19] and comparison of our NMR and ir spectra of **6** with those kindly provided by Professor Cargill showed the compounds prepared by the two different routes to be identical. We briefly investigated the chemistry of **6** and found that, although it was unreactive toward trifluoroacetic acid at 100° for 12 hr and toward bromine at room temperature in the dark, when a solution of **6** in CCl_4 containing Br_2 was exposed to a fluorescent lamp for 3 days, no starting material remained. Two compounds, **13** and **14**, were isolated by fractional crystallization. Following the reaction by NMR showed that **14** was a secondary product, formed from **13**, presumably by the mechanism proposed by Russell and Brown for the reaction of tertiary bromides with molecular bromine.[20] Addition of bromine radicals across the central bond of [*n.m.*2]propellanes has been previously observed in systems where $n \leq 4$ and $m = 2$.[4,21] Although this reaction is much faster when the propellane contains two four-membered rings, our finding that bromine adds to **6** shows that in [*m.n.*2]propellanes, addition of bromine atoms to the central bond occurs for $m + n \leq 6$.



13 14

Whereas Eaton's synthesis of a derivative of [2.2.2]propellane involved two successive contractions of a cyclohexanone ring,[4] our route from **5** required the simultaneous contraction of two cyclopentanone rings. In keeping with the spirit of our synthesis of **5**, we first tried to convert it directly to **7** by gas-phase photodecarbonylation.[22] However, from either direct or mercury-sensitized irradiation of **5**, no material was isolated that could be unequivocally identified as even a decomposition product of **7**. An obvious route from **5** to a derivative of **7** was through a double Wolff rearrangement of the bis(diazo) diketone (**17**).[23] Attempts to prepare the bis(hydroxymethylene) diketone (**15**) for reaction with tosyl azide[23] were not fruitful. Synthesis of the bis(oximino) diketone (**16**) by reaction of **5** with 2 equiv of butyl nitrite[24] was successful, but the conversion of **16** to **17** by reaction with chloroamine, generated in situ,[24] proceeded in yields so low as to be synthetically useless. Further studies of ring contraction in **5** were abandoned when we learned[25] of Eaton's synthesis of [3.2.2]propellan-2-one,[4b] a precursor of a derivative of **7**, one carbonyl less distant than **5**.



15, X = CHOH
16, X = NOH
17, X = N_2

Although our synthesis of **7** or a derivative thereof was abandoned short of the final goal, a number of the compounds prepared are of interest as potential intermediates in the synthesis of other molecules of theoretical import. For instance, **2** undergoes ozonolysis of both double bonds to give cyclododecanetetr-1,4,7,10-one in essentially quantitative yield. This tetraketone has been used in the preparation of a [2.2]pyrrolophane,[26] a nitrogen-bridged [12] annulene,[27] and a derivative of tricyclo[6.4.0.0^{4,9}]dodecane.[28] We are currently exploring the use of **2**, as well as **3** and **13**, in the synthesis of other interesting molecules.

Experimental Section

Dimerization of Allene. Allene gas (61.3 g) from a lecture bottle was passed into a vertical column, 14 in. long and 1 in. in diameter, packed with glass beads and heated to 500 ± 10°. The allene was passed in at a rate of about 1 g/min. The effluent gases were trapped in a 125-ml erlenmeyer flask cooled in Dry Ice–acetone. When all the allene had been passed through the column once, the collection flask was removed and attached to the inlet of the pyrolysis column while a second erlenmeyer flask served as a collector. The allene in the filled erlenmeyer flask was allowed to distil into the heated column at room temperature. Repeated switching of the two flasks[13] allowed the accumulation of allene dimers by recycling the unpyrolyzed allene. After recycling ten times, the unreacted allene was allowed to distil off at room temperature. The residue was transferred to a round-bottomed flask and distilled at room temperature under aspirator vacuum, the distillate being collected in a flask cooled in a Dry Ice–acetone bath. The yield of dimer (pale yellow in color) was 15.0 g (24%). The allene dimers formed a polymer slowly at room temperature and were stored at −20° under nitrogen. The allene dimers could be separated by preparative GLC at 45° on a 0.375 in. × 20 ft column of 20% γ-methyl-γ-nitropimelonitrile on Chromosorb P.

Benzophenone-Sensitized Photolysis of Allene Dimers. The allene dimers (6.1 g) were dissolved in 150 ml of pentane. Benzophenone (0.1 g) was added to the solution and the solution was placed in an immersion well and degassed by bubbling nitrogen through it for 0.5 hr. The solution was photolyzed with a Hanovia high-pressure mercury lamp, using a Pyrex filter. Throughout the photolysis the solution was kept under a positive pressure of nitrogen. After 7 hr the photolysis was stopped and the solvent was removed under reduced pressure. The yield was 4.6 g of a pale yellow liquid. The crude product was chromatographed on 120 g of neutral alumina to remove the benzophenone and polymeric material. Fractions (100 ml) were taken and the column was eluted with pentane. The dienes were eluted in fractions 2–4. The solvent was removed, yielding 4.4 g of product (72%). The diene mixture was stored under nitrogen at −20°. The three compounds in this mixture were easily separable by preparative GLC on a 0.375 in. × 10 ft column of 20% SE-30 on Chromosorb W at 150°. The proportions[29] and retention times (He flow rate 180 ml/min) of the three compounds were as follows: **8**, 58%, 16.6 min; **9**, 13%, 25.4 min; **2**, 29%, 39.9 min. Dimer **1** could also be separated from **8** and **9** by spinning band distillation of the crude dimer mixture with benzophenone added as a chaser solvent. A fraction collected at 75–79° (30 mm) was found to be pure **8**. Fractions collected between 79 and 104° proved to be mixtures of **8**, **9**, and **2**. A fraction collected at 104–108° (30 mm) consisted of 93% **2**, 6% **9**, and 1% **8**. This fraction crystallized, and recrystallization from ethanol afforded pure **2**, mp 41–41.5°. The NMR spectra of these compounds have previously been reported.[9]

Pyrolysis of the Photolysis Mixture (2, 8, 9). The mixture (6.6 g) from benzophenone-sensitized photolysis of the allene dimers was dissolved in 60 ml of hexane and slowly added from a dropping funnel (1 drop every 5 sec) to the top of a pyrolysis column 12 in. long and 0.5 in. in diameter, packed with glass helices, heated to 330°, and with nitrogen passing through it at a rate of 5 ml/sec. The outlet tube from the pyrolysis column reached to the bottom of a volumetric flask that was used as a trap. Several pieces of glass wool were packed into the bottom of the trap and a piece was wrapped around the outside of the outlet from the pyrolysis column so that the glass wool was also in contact with the inner wall of the trap. The glass wool was wetted with hexane before the trap was attached to the column. After all the solution had been added to the pyrolysis column, the column was washed with 20 ml more hexane. The solution collected in the trap was evaporated to yield 5.5 g (83%) of a 60:40 mixture of **3** and **11**, which could be separated by preparative GLC on a 0.375 in. × 10 ft column of 20% Carbowax 20M on Chromosorb W at 130° with a helium flow of 180 ml/min. The retention times under these conditions follow: **11**, 20.1 min; **3**, 23.3 min. The NMR of **11** ($CDCl_3$) showed δ 1.6–1.9 (m, 4 H), 2.1–2.8 (m, 6 H), 4.6–5.0 (m, 6 H); uv λ_{max} (hexane) 230 nm (log ϵ 3.7). The NMR of **3** ($CDCl_3$) showed δ 2.40 (s, 8 H), 4.80 (d, 4 H, J = 2 Hz), 4.90 (d, 4 H, J = 2 Hz); uv λ_{max} 228 nm (log ϵ 4.0); mass spectrum M^+ *m/e* 160.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.14; H, 10.33.

Isolation of 4,5-Dimethylenebicyclo[6.2.0]dec-9-ene (10) from Low-Temperature Pyrolysis of 2. When **2** was pyrolyzed at 220°, GLC analysis on the SE-30 column showed another product of longer retention time than **3**. This product, which itself gave **3** on pyrolysis at 250°, was isolated by preparative GLC and identified as **10** on the basis of NMR, ($CDCl_3$) δ 2.0–2.5 (m, 12 H), 4.73 (d, 2 H, J = 2 Hz), 5.05 (d, 2 H, J = 2 Hz), and uv, λ_{max} 232 nm (log ϵ 3.7).

Unsensitized Photolysis of Pyrolysate (3 and 11). The pyrolysate was photolyzed 2 g at a time in 150 ml of pentane with a Hanovia high-pressure mercury lamp. The solution was degassed thoroughly by bubbling nitrogen through it for 0.5 hr, and the photolysis was done under a positive pressure of nitrogen. The solution was photolyzed for 7 hr and analyzed by GLC on the Carbowax column under the conditions described above. The photolysate consisted of (in order of elution) **4**, 30%; **11**, 10%; **9**, 33%; **10**, 2%; and **2**, 25%. After longer periods of photolysis **11** was converted to **9** and **10** to **2**, so that only three components (**4**, **9**, and **2**) were present in the mixture. However, photolysis for longer times also caused the formation of more polymeric material, which coated the outside of the lamp casing. The NMR ($CDCl_3$) of a sample of **4**, collected from GLC, showed δ 1.4–1.9 (m, 4 H), 1.98 (s, 4 H), 2.3–2.7 (m, 2 H), 2.7–3.2 (m, 2 H), 4.67 (m, 2 H), and 4.82 (m, 2 H).

Chemical Separation of 4. The crude photolysate was dissolved in 60 ml of hexane and pyrolyzed as described before. The hexane was evaporated; the pyrolysate was dissolved in 30 ml of chloroform, which had been filtered through basic alumina; and 7 g of maleic anhydride was added. The mixture was refluxed for 1 hr under nitrogen. The chloroform was removed and pentane was added to the residue. All of the residue, including the solid maleic anhydride adducts, were placed on a column of 100 g of silica gel. The column was eluted with pentane, 100-ml fractions being taken. Fractions 3–7 contained the olefin **4**. These fractions were combined and the solvent was removed. The yield of **4** from 5.5 g of the 60:40 mixture of **3** and **11** was 1.1 g, which was found to be 97% pure by GLC.

Ozonolysis of 2,6-Dimethylene[3.3.2]propellane (4). To 10 ml of 95% ethanol was added 0.4 g of **4**. The solution was cooled to −78° in a Dry Ice–acetone bath, and oxygen rich in ozone was bubbled into the solution at a rate of 0.05 ft^3/min for 12 min until the solution turned blue. The solution was allowed to stand for 4 min and was then purged of ozone by bubbling nitrogen through it for 15 min. To the solution, still at −78°, was added 0.8 ml of dimethyl sulfide. The solution was then kept for 1 hr at −20° in the freezer and for an additional 1 hr at room temperature. GLC analysis showed only one product. The solvent was then removed under reduced pressure and the residue was chromatographed on 15 g of silica gel to remove the dimethyl sulfoxide. The column was eluted with ether, taking 40-ml fractions. The diketone was eluted in fractions 2–5. The chromatographed material was crystallized from ether–pentane, yielding 0.33 g of material (80%), mp 65–73°. Recrystallization yielded pure **5**, mp 75–76°. The mass spectrum showed the parent peak at *m/e* 164; the NMR exhibited a complex pattern between δ 1.8 and 3.0.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.97; H, 7.35.

Deuteration of the Diketone 5. The diketone **5** (20 mg) in 0.2 ml of carbon tetrachloride was stirred with 0.1 ml of D_2O containing 15 mg of potassium carbonate. After 1 hr NMR showed that deuteration was nearly complete. The water layer was removed, and a fresh 0.1 ml of D_2O containing 15 mg of potassium carbonate was added. The mixture was stirred for 1 more hr. The NMR spectrum (CCl_4) was considerably simplified from that of the undeuterated material, showing a broad singlet at δ 2.0 and a symmetrical AA′BB′ pattern of equal intensity centered at δ 2.27. The mass spectrum confirmed that four deuterium atoms had been introduced.

Bromination of the Diketone 5. The diketone **5** (5 mg) was placed in an NMR tube and 0.1 ml of CCl_4 containing 0.004 ml of Br_2 was added. The color of the Br_2 solution began to get lighter immediately and hydrogen bromide was evolved. The NMR showed a symmetrical AA′BB′ multiplet centered at δ 2.73 and an AB quartet centered at δ 3.52 (J = 17 Hz).

Reduction of the Diketone 5 to [3.3.2]Propellane (6). The diketone (0.16 g) was placed in a flask, and 10 ml of ethylene glycol, 0.60 g of potassium hydroxide, and 0.60 ml of 95% hydrazine were added. The solution was refluxed for 24 hr under nitrogen. At the end of this time a thick layer of white solid had collected near the bottom of the condenser. The solid was washed out of the condenser with $CDCl_3$ and an NMR spectrum was recorded. The NMR spectrum showed a sharp singlet at δ 1.64 (4 H) and multiplets centered at δ 1.3 (4 H), 1.6 (4 H), and 2.0 (4 H). GLC analysis of this material showed only one peak. Work-up of the ethylene glycol reaction mixture showed a negligible amount (<2%) of product present in it. To obtain the parent [3.3.2]propellane (**6**) as a solid, it was washed out of the condenser with Freon-114 (bp 3°) in a 0° cold room. The solution was filtered through sodium sulfate into a Pyrex tube. The Freon-114 was allowed to evaporate at room temperature, leaving behind a white solid. A few milligrams of potassium carbonate were added to the tube, which was sealed under pump vacuum. The propellane was allowed to sublime to the tip of the tube by immersing the tube in a water bath at 60°. Because of the ease with which **6** sublimed, it was not possible to determine its melting point accurately.

Bromination of [3.3.2]Propellane (6). To an NMR tube containing 0.2 ml of carbon tetrachloride, 0.05 ml of methylene chloride (as a standard), and 40 mg of [3.3.2]propellane was added 0.05 ml of bromine. The NMR tube was allowed to stand at room temperature under a fluorescent light. After 1.5 hr a new peak could be seen at δ 2.58. After 3 days the NMR spectrum showed that no starting material remained, and the solvent was evaporated. TLC of the residue on silica gel using 5% ether–pentane gave two well-separated spots. The residue was dissolved in pentane and allowed to crystallize in the freezer at −20°; 44 mg of crystals were collected. The NMR of the crystals and the mother liquor showed that the compound with the singlet at δ 2.58 was in the mother liquor and that the crystals were another compound. The crystals were dissolved in pentane and allowed to crystallize again. The compound in the mother liquor was also crystallized from pentane. From each crystallization 15 mg was obtained. NMR and TLC indicated that complete separation of the two compounds had been achieved. The faster moving compound on TLC is the one obtained from the mother liquor, containing the singlet at δ 2.58. The NMR (CCl_4) of the crystals (**13**) from the mother liquor exhibited a sharp singlet at δ 2.58 and multiplets centered at δ 1.8 and 2.6. The ratio of the integration of the low-field to the high-field resonances was 12:4. The mass spectrum of **13** showed no molecular ion; the peaks of highest *m/e* at 215 and 217 corresponded to $M^+ - Br$.

Anal. Calcd for $C_{10}H_{16}Br_2$: C, 40.57; H, 5.45. Found: C, 40.80; H, 5.66.

The NMR ($CDCl_3$) of the less soluble, slower moving compound

(**14**) exhibited δ 2.0 (m, 4 H), 2.7 (m, 10 H) and a poorly resolved quartet at δ 4.86 (1 H, J = 5 and 9 Hz). The mass spectrum of **14** showed no molecular ion; the peaks with highest m/e at 280, 282, and 284 correspond to $M^+ - Br$. Even after three recrystallizations the tribromide melted over a broad range (93–99°), suggesting that it may be a mixture of stereoisomers.

Anal. Calcd for $C_{10}H_{15}Br_3$: C, 32.03; H, 4.03. Found: C, 31.67; H, 4.01.

Preparation of Bis(oximino) Diketone (16). The diketone **5** (0.118 g) was dissolved in 20 ml of dry *tert*-butyl alcohol and the solution was degassed with nitrogen for 15 min. This solution was then added to a flask (under nitrogen) containing 2.02 g of potassium *tert*-butoxide monoalcoholate with stirring. After 10 min 0.4 ml of *n*-butyl nitrite was added through a serum cap and the solution was stirred under nitrogen overnight. The mixture was then diluted with water, extracted four times with ether, acidified with acetic acid, and extracted two times with methylene chloride. The aqueous layer was then saturated with sodium chloride and extracted eight times with ethyl acetate. The ethyl acetate extracts were combined, shaken with saturated sodium chloride solution, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the yellow solid residue was evacuated at 0.2 mm for 2 hr; the yield was 76 mg (48%). The crude **16** did not crystallize readily, and it was purified by washing two times with a 1:4 methanol–ether solution, which removed almost all of the yellow color. The ir of this material showed characteristic absorptions at 1630, 1735, and 3560 cm^{-1}. The NMR (acetone-d_6) showed an AA′BB′ multiplet centered at δ 2.42 (4 H), an AB quartet centered at δ 3.04 (4 H, J = 20 Hz), and a broad peak at δ 3.2 (2 H) which disappeared upon shaking with D_2O.

Preparation of Bis(diazo) Diketone (17). Bis(oximino) diketone (**16**, 48 mg) was added to a flask containing 3 ml of water and cooled in an ice–water bath. Sodium hydroxide solution (0.5 ml, 1 N) was added, and the solution turned bright yellow in color. 0.070 ml of 15 N ammonium hydroxide was then added, followed by 1.7 ml of 5% sodium hypochlorite solution, added dropwise over a period of 15 min. After 1 hr the ice bath was removed. The mixture was allowed to stir at room temperature for 6 hr and then was extracted with five portions of methylene chloride (passed through basic alumina). The methylene chloride extracts were combined and the solvent was evaporated. The residue was a yellow solid, 2.5 mg (5% yield). The ir showed characteristic diazo, 2080 cm^{-1}, and carbonyl, 1660 cm^{-1}, absorptions. The NMR ($CDCl_3$) exhibited (inter alia) an AA′BB′ pattern centered at δ 2.48 and an AB quartet centered at δ 3.20 (J = 14 Hz).

Preparation of Cyclododecanetetr-1,4,7,10-one by Ozonolysis of 2. The ozonolysis was carried out as described above for **4**, except that sufficient CH_2Cl_2 was added to keep **2** in solution. An essentially quantitative yield of the product was obtained. After recrystallization from acetone it had mp 131–132° (lit.[26] mp 129–130), and its NMR and ir matched those described.[26]

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References and Notes

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