Proximity Effects. XLIX.[1] Reactions of Medium–Sized Cycloalkyl Radicals

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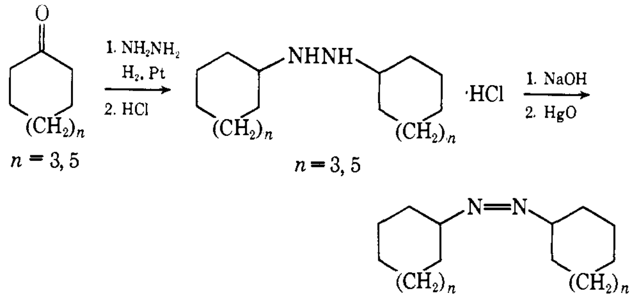
Abstract: Azocyclooctane, azocyclodecane, dicyclooctylmercury, and dicyclodecylmercury have been synthesized and subjected to photolysis and pyrolysis. The reaction products are generally consistent with the intermediacy of cyclooctyl and cyclodecyl radicals. Varying amounts of *cis*-bicyclo[3.3.0]octane and bicyclodecanes were found in addition to the normal disproportionation and coupling products in the case of the two azo compounds. The two mercury compounds gave essentially only normal disproportionation and coupling products.

Since the discovery of proximity effects in the reactions of medium-sized carbocyclic compounds,[4] a considerable amount of research has been conducted in order to explore the scope of such effects. However, most of the work done up until the present time has been concerned with the reactions of medium-sized ring compounds which proceed through ionic intermediates. Until quite recently, no research had been carried out in the area of free radical reactions of medium-sized cycloalkyl rings. However, in the last few years, a number of papers have appeared describing the reactions of free radical species of medium-sized ring compounds. Dowbenko has reported[5] the novel addition of various free radical species to *cis,cis*-1,5-cyclooctadiene with subsequent transannular ring closure to form *cis*-bicyclo[3.3.0]octane derivatives. Cope, *et al.*, have recently described the transannular hydrogen abstraction by the intermediate alkoxy radical formed during decomposition of 1-methylcyclooctyl hypochlorite.[6] The paper by Traynham and Couvillon,[7] in which they describe the radical addition of carbon tetrachloride to *cis*-cyclooctene to yield transannular product, best illustrates a 1,5-hydrogen atom shift which is analogous to the 1,5-hydride shift characteristic of ionic reactions of medium-sized ring compounds.

In a somewhat different vein, we completed a study of the reactions of some simple medium-sized cycloalkyl radicals in order to determine whether ring closure products could arise from a transannular disproportionation reaction. This paper describes some of the results obtained in this study.

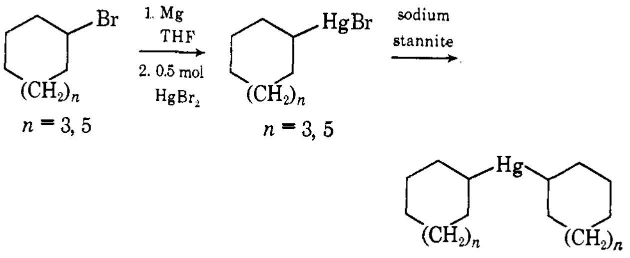
Results and Discussion

For this investigation, it was decided to utilize the azo and dialkylmercury compounds corresponding to the cyclooctyl and cyclodecyl ring systems. The choice of the azo and mercury compounds was indicated by the known ease of homolytic cleavage of the carbon–nitrogen or carbon–mercury bond under pyrolytic or photolytic conditions.[8] The availability of intermediate starting materials and our prior experience with the possible reaction products governed our choice of the cyclooctyl and cyclodecyl ring systems as models for this investigation. Azocyclooctane (**1**) and azocyclodecane (**2**) were prepared in good yields as shown in the reaction scheme



1, $n = 3$
2, $n = 5$

The analogous mercury compounds, dicyclooctylmercury (**3**) and dicyclodecylmercury (**4**), were readily prepared as indicated.



3, $n = 3$
4, $n = 5$

The photolysis of azocyclooctane in pentane solution (using a Hanau H-81 mercury arc lamp) proceeded smoothly to give a 71% yield of disproportionation and coupling products as indicated in Table I. However, the pyrolysis of this compound in benzene solution at 260° (under nitrogen pressure) gave only a 28% yield of products (see Table I) in addition to 45% of a nitrogen-containing polymer. Previous attempts to pyrolyze this azo compound by dropping it through a hot tube at temperatures ranging from 350 to 480° gave very

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[1] Previous paper in this series, A. C. Cope and S. S. Hecht, *J. Am. Chem. Soc.*, **89**, 6920 (1967).

[2] Deceased June 4, 1966.

[3] (a) National Science Foundation Cooperative Predoctoral Fellow, 1959–1960. (b) To whom inquiries should be addressed at the Esso Agricultural Products Laboratory, Linden, N. J.

[4] (a) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5882 (1952); (b) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

[5] R. Dowbenko, *J. Am. Chem. Soc.*, **86**, 946 (1964).

[6] A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, *ibid.*, **87**, 3111 (1965).

[7] J. G. Traynham and T. M. Couvillon, *ibid.*, **89**, 3205 (1967).

[8] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954, and references cited therein.

Table I. Per Cent Yields of Products from Cyclooctyl Compounds

Decomposition of	Cyclooctane	*cis*-Cyclooctene	*cis*-Bicyclo[3.3.0]octane	Bicyclooctyl	Pentylcyclooctane
1 (photolysis)	19.0	15.5	1.2	31.5	3.6
1 (pyrolysis)	7.3	2.0	0.07	18.5	
3 (photolysis)	23.5	23.5	0.0	49.5	2.3
3 (pyrolysis)	16.2	14.3	0.0	44.3	2.7

complex product mixtures which were inseparable using gas chromatographic techniques. Distillation of the azo compound through a hot tube heated to 270–340° (under high vacuum) gave a less complex reaction mixture but always resulted in about 90% recovery of starting material. The conditions which were finally chosen for the pyrolysis of this compound were the optimal ones obtainable with respect to the product yield and the simplicity of the product mixture.

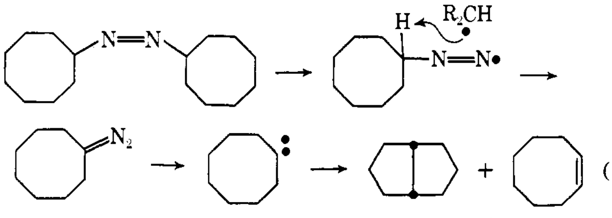
Table II. Per Cent Yields of Products from Cyclodecyl Compounds

Decomposition of	Cyclodecane	*trans*-Cyclodecene	*cis*-Cyclodecene	*cis*-Bicyclo[5.3.0]decane	*cis*-Decalin	*trans*-Decalin	Bicyclodecyl	Pentylcyclodecane
2 (photolysis)	19.1	3.4	20.2	2.5	0.5	0.2	19.3	5.8
2 (pyrolysis)	32.0	3.8	0.64	11.2	3.2	7.0	5.0	
4 (photolysis)	30.0	29.5	3.5	0.0	0.0	0.0	20.5	1.5
4 (pyrolysis)	28.0	8.1	16.7	0.2	0.0	0.0	35.0	4.0

The photolysis and pyrolysis of dicyclooctylmercury proceeded smoothly to give high yields of disproportionation and coupling products derived from intermediate cyclooctyl radicals (see Table I).

Included in the decomposition products from the photolysis and pyrolysis of azocyclooctane was a small amount of *cis*-bicyclo[3.3.0]octane. Work in these laboratories[9] and by Friedman and Shechter[10] has indicated that generation of cyclooctyl carbene from diazocyclooctane yields a large percentage of *cis*-bicyclo[3.3.0]octane.

It seems quite possible that the presence of *cis*-bicyclo[3.3.0]octane in our product mixtures could be due to an analogous process, namely, the generation of diazocyclooctane from a radical intermediate as outlined in eq 1. Alternately, the formation of the bicyclooctane could be attributed either to an intramolecular transannular disproportionation reaction (eq 2) or to the formation of cyclooctyl carbene followed by intramolecular ring closure (eq 3). Since the decomposition of dicyclooctylmercury yielded no bicyclo[3.3.0]octane, however, the processes described in eq 2 and 3 become less tenable. One would expect that both dicyclooctylmercury and azocyclooctane should yield a bicyclooctane product if either of the latter two processes were the true pathway. As Table I indicates, all reactions which were carried out in pentane solution yielded small amounts of a pentylcyclooctane fraction.



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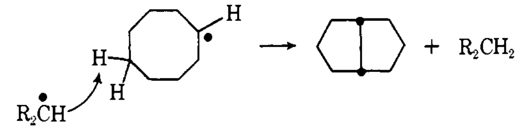

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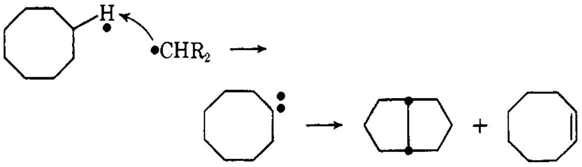
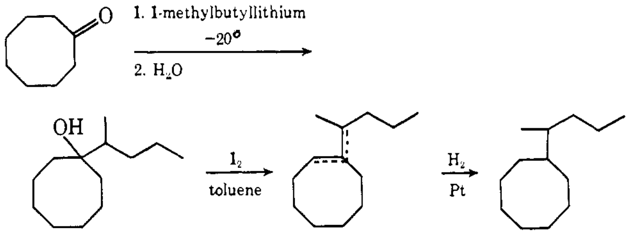


(3)

This is not unreasonable for a radical reaction carried out in pentane solvent. The identification of this C_{13} hydrocarbon fraction was accomplished by synthesizing 1-methylbutylcyclooctane (**5**) and showing that its retention time on a gas chromatography column and its infrared spectrum were virtually identical with the suspected pentylcyclooctane component. It is probable that the pentylcyclooctane fraction is a mixture of isomers and this is substantiated by the fact that the main peak on a gas chromatograph has two small ridges indicative of a mixture of isomers.



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Significant amounts of bicyclodecanes were obtained from the photolysis and especially from the pyrolysis of azocyclodecane (see Table II). It is likely that the formation of *cis*- and *trans*-decalin as well as *cis*-bicyclo[5.3.0]decane occurs by one of the mechanisms proposed for the corresponding cyclooctyl system.

The photolysis and pyrolysis of dicyclodecylmercury proceeded in good yield to give the product mixtures shown in Table II. As in the case of the dicyclooctylmercury reactions, virtually no transannular products were formed. The pyrolysis of dicyclodecylmercury did give a maximum 0.2% yield of *cis*-bicyclo[5.3.0]decane but no other unusual products were found. In the decomposition studies in which pentane was used as a solvent, a small amount of a pentylcyclodecane fraction was found and identified by infrared spectrum comparisons with authentic pentylcyclodecane and gas chromatography retention time comparisons. Several

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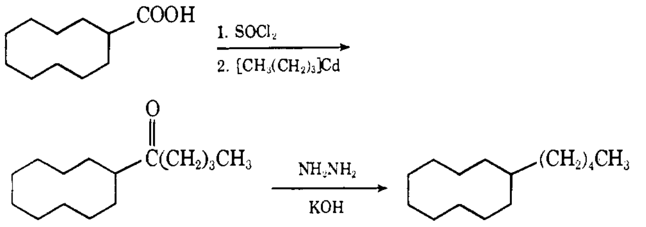
[9] A. C. Cope, M. Brown, and G. L. Woo, unreported observations.

[10] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, 83, 3159 (1961).

unsuccessful attempts were made to synthesize a representative pentylcyclodecane. The reaction of 1-methylbutyllithium, pentyllithium, and pentylmagnesium bromide with cyclodecanone gave none of the desired tertiary alcohol. The reaction of the Wittig reagent derived from pentyltriphenylphosphonium bromide with cyclodecanone gave none of the desired C_{15} olefin; recovered cyclodecanone and a small amount of low-boiling hydrocarbon were the only products obtained. In all of these reactions of strongly basic intermediates with cyclodecanone it appears that the ketone was converted to the corresponding enolate and this in turn reverted to cyclodecanone upon hydrolysis. A successful synthesis of pentylcyclodecane (**6**) was carried out.



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The decomposition of the two azo compounds and the two dialkylmercury compounds generally resembles a conventional free radical process. However, the generation of bicyclic hydrocarbons from the photolysis or pyrolysis of azocyclooctane and azocyclodecane may very likely be the result of a carbene insertion reaction as described earlier. On the other hand, a transannular disproportionation reaction cannot be ruled out as the mechanism by which these bicyclic hydrocarbons are formed. The formation of a greater relative percentage of bicyclic C_{10} hydrocarbons from azocyclodecane as contrasted with the formation of bicyclic C_8 hydrocarbons from azocyclooctane is not unexpected in view of the relatively greater ease of ring closure of the cyclodecane ring system. Further research in the chemistry of medium-sized cycloalkyl radicals should help us to understand some of the anomalies present in systems of this type.

Experimental Section[11,12]

N,N′-Dicyclooctylhydrazine Monohydrochloride. To a cold solution of 3.83 g of anhydrous hydrazine, 30 ml of absolute ethanol, and 24 ml of glacial acetic acid was added 30.0 g of cyclooctanone. The resulting solution was transferred to a 1-l. metal hydrogenation bomb containing 0.4 g of platinum oxide and a solution of 60 ml of absolute ethanol and 15 ml of glacial acetic acid. Reductive alkylation of this system proceeded smoothly at 20–30 psi of hydrogen and room temperature, and the reaction was complete in 3 hr. The platinum catalyst was separated by filtration and 100 ml of concentrated hydrochloric acid was slowly added to the previously cooled filtrate. The resulting white precipitate was collected on a filter and the filtrate was concentrated under reduced pressure with a rotary concentrator, yielding additional product. Recrystallization of the crude product from ethanol-acetone yielded 25 g (73%) of a product as long, colorless needles, mp 192–195° dec. A second recrystallization from ethanol-acetone gave analytically pure N,N′-dicyclooctylhydrazine monohydrochloride as colorless needles, mp 216–218.8° (sample introduced at 180°).

Anal. Calcd for $C_{16}H_{33}N_2Cl$: C, 66.66; H, 11.46; N, 9.72; Cl, 12.28. Found: C, 66.49; H, 11.28; N, 9.86; Cl, 12.04.

N,N′-Dicyclodecylhydrazine Monohydrochloride. To a cold solution of 2.68 g of anhydrous hydrazine, 25 ml of absolute ethanol, and 15 ml of glacial acetic acid was added 27.7 g of cyclodecanone.[13] The resulting system was reductively alkylated as described in the synthesis of N,N′-dicyclooctylhydrazine monohydrochloride and the reduction was complete in 4.5 hr. The crude hydrazine salt was recrystallized once from ethanol–acetone, yielding 20.5 g (73%) of fluffy white needles, mp 165–169°. Several further recrystallizations from ethanol–acetone yielded pure N,N′-dicyclodecylhydrazine monohydrochloride, mp 164.2–167° (sample introduced at 155°).

Anal. Calcd for $C_{20}H_{41}N_2Cl$: C, 69.66; H, 11.90; N, 8.12; Cl, 10.30. Found: C, 69.94; H, 11.98; N, 8.09; Cl, 10.11.

Azocyclooctane (1). To a suspension of 3 g of N,N′-dicyclooctylhydrazine monohydrochloride in 60 ml of water was added a solution of 0.8 g of potassium hydroxide in 25 ml of water, and the mixture was shaken vigorously for 15 min in a separatory funnel. The free hydrazine was extracted with four 30-ml portions of ether and the ether solution was then extracted with a small portion of water and dried over magnesium sulfate. Evaporation of the ether yielded a semisolid residue which was dissolved in 50 ml of reagent benzene. To this solution was added 8.0 g of yellow mercuric oxide, and the resulting suspension was stirred at room temperature for 3 hr. Filtration of the mixture and evaporation of the benzene under reduced pressure using a rotary concentrator yielded 2.34 g (90%) of azocyclooctane as a yellow oil which solidified, mp 36–39°. Three recrystallizations from absolute methanol at −80° gave analytically pure azocyclooctane as almost colorless granules, mp 43.6–44.2°. The ultraviolet spectrum of this compound shows a broad peak (330–390 mμ) with λ_{max} 358 mμ (log ϵ 1.28).

Anal. Calcd for $C_{16}H_{30}N_2$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.77; H, 12.00; N, 11.50.

Azocyclodecane (2). To a suspension of 2.0 g of N,N′-dicyclodecylhydrazine monohydrochloride in 100 ml of water was added a solution of 0.36 g of potassium hydroxide in 30 ml of water. A 30-ml portion of ethanol was then added to enhance the solubility of the hydrazine salt and the mixture was shaken vigorously in a separatory funnel for a 20-min period. Extraction of the free hydrazine with ether and oxidation of this hydrazine with mercuric oxide as described in the synthesis of azocyclooctane yielded 1.3 g (73%) of a pale yellow oil. Recrystallization of this oil from acetone–methanol at −15° gave colorless platelets which melted upon warming to room temperature. Two further recrystallizations from acetone–methanol at −15° gave pure azocyclodecane as colorless plates, mp 22–24° uncor. The ultraviolet spectrum of this compound showed λ_{max} 364 mμ (log ϵ 1.11).

Anal. Calcd for $C_{20}H_{38}N_2$: C, 78.43; H, 12.42; N, 9.15. Found: C, 78.58; H, 12.79; N, 9.48.

Cyclooctylmercuric Bromide. To the filtered Grignard reagent prepared from 14.4 g of clean magnesium turnings and 39 g of cyclooctyl bromide[14] in 320 ml of dry tetrahydrofuran was added dropwise a solution of 60 g of mercuric bromide in 150 ml of dry tetrahydrofuran. The addition took 1.5 hr during which time the temperature gradually rose to about 50°. The grayish white suspension which formed was stirred overnight at room temperature under a nitrogen atmosphere. The reaction mixture was then poured into 1 l. of water containing 60 ml of glacial acetic acid and the product was extracted with four 200-ml portions of chloroform. The chloroform extracts were washed three times with water, dried over magnesium sulfate, and filtered. The chloroform was then removed under reduced pressure with a rotary concentrator. The white solid residue remaining was recrystallized from acetone–water to yield 27.5 g of product as white needles. Concentration of the mother liquors yielded an additional 17 g of product giving a total yield of 44.5 g (62%), mp 88–93°. Two further recrystallizations from acetone–water yielded pure cyclooctylmercuric bromide as colorless needles, mp 97.4–98.4°.

Anal. Calcd for $C_8H_{15}HgBr$: C, 24.54; H, 3.84; Br, 20.43. Found: C, 24.52; H, 3.81; Br, 20.23.

Cyclodecylmercuric Bromide. To the filtered Grignard reagent prepared from 1.66 g of clean magnesium turnings and 5.0 g of

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(11) Melting points are corrected unless otherwise stated and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

(12) Gas chromatography was carried out with 190 × 0.8 cm Pyrex columns containing 25–30% by weight liquid stationary phase on 60–80 or 80–100 mesh Johns-Manville Chromosorb. Samples were eluted with helium gas at 15 psi and detected by use of a thermal conductivity cell.

(13) A. C. Cope, J. W. Barthel, and R. D. Smith, *Org. Syn.*, **36**, 14 (1956).

(14) R. Willstatter and E. Wasser, *Chem. Ber.*, **43**, 1181 (1910).

cyclodecyl bromide[15] in 75 ml of dry tetrahydrofuran was added a solution of 8.3 g of mercuric bromide in 25 ml of dry tetrahydrofuran. A 3.9-g (41%) yield of product was obtained by following the procedure used in the preparation of cyclooctylmercuric bromide. Recrystallization from methanol–water gave pure cyclodecylmercuric bromide as colorless needles, mp 126.8–127.8°.

Anal. Calcd for $C_{10}H_{19}HgBr$: C, 28.58; H, 4.53; Br, 19.10. Found: C, 28.84; H, 4.57; Br, 19.28.

Dicyclooctylmercury (3) was synthesized using a modification of the method of Winstein and Traylor.[16] To a solution of sodium stannite (made from 19.1 g of stannous chloride dihydrate in 100 ml of water followed by the addition of 6 *N* sodium hydroxide solution until the white precipitate just disappeared) in 500 ml of water was added 10 g of cyclooctylmercuric bromide and the resulting suspension was stirred at high speed (1800 rpm) for 7 hr in the dark under a nitrogen atmosphere. The solution was then extracted with four 100-ml portions of pentane and the pentane extracts were washed with three small portions of water and dried over magnesium sulfate. The pentane was removed under reduced pressure and 4.72 g of crude semisolid product remained. Recrystallization of this material from ethyl acetate–methanol at 0° yielded 3.42 g (63%) of pure dicyclooctylmercury, mp 49.0–50.0°. This compound is very unstable to light and gradually turns gray even if kept in a refrigerator in the dark.

Anal. Calcd for $C_{16}H_{30}Hg$: C, 45.42; H, 7.15. Found: C, 45.26; H, 7.03.

Dicyclodecylmercury (4). A 5.0-g sample of cyclodecylmercuric bromide was suspended in a sodium stannite solution and stirred at high speed in the manner described for the synthesis of dicyclooctylmercury. Extraction of the product with pentane and finally recrystallization from ethyl acetate–methanol at 0° gave an analytically pure sample, mp 41.8–42.5°. This compound is also very unstable to light and must be used immediately.

Anal. Calcd for $C_{20}H_{38}Hg$: C, 50.55; H, 7.88. Found: C, 50.24; H, 7.85.

1-(1-Methylbutyl)cyclooctanol. To the lithium reagent prepared from 1.4 g of finely divided lithium wire and 25 g of 2-bromopentane in 100 ml of dry ether was added a solution of 7.55 g of cyclooctanone in 20 ml of dry ether at −20°. The solution was kept at −20° for a 1-hr period and then allowed to warm to room temperature. The mixture was then hydrolyzed with water and extracted with three 50-ml portions of ether. The ether extracts were dried over magnesium sulfate and filtered, and the ether was removed under reduced pressure with a rotary concentrator. Distillation of the product mixture gave mainly unreacted cyclooctanone (40% recovery) and 2.64 g of a colorless liquid, bp 70–100° (0.25 mm), which appeared to be a mixture of cyclooctanone and the desired tertiary alcohol. Chromatography on 60 g of Woelm activity I neutral alumina yielded another 1.2 g of cyclooctanone and 956 mg (18%) of crude tertiary alcohol. Distillation of this material through a semimicro column yielded 842 mg of 1-(1-methylbutyl)cyclooctanol, bp 81–82° (0.3 mm), $n^{25}D$ 1.4815–1.4823.

Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.63; H, 13.00.

Dehydration of 1-(1-Methylbutyl)cyclooctanol. A 0.80-g sample of tertiary alcohol was dissolved in 40 ml of toluene and 40 mg of iodine was added to the mixture. The mixture was then refluxed for 24 hr and the water formed was removed by the use of a Dean–Stark trap. The toluene solution was then washed with water and 5% sodium thiosulfate solution, dried over sodium sulfate, and finally distilled through a semimicro column under reduced pressure; 398 mg (55%) of product, bp 44° (0.3 mm), was obtained. An analytical sample of the olefin had bp 44° (0.3 mm), $n^{25}D$ 1.4738.

Anal. Calcd for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.76; H, 13.37.

1-Methylbutylcyclooctane (5). A 0.213-g sample of the mixture of C_{13} olefins was hydrogenated over 0.2 g of prereduced platinum oxide in 10 ml of glacial acetic acid. Neutralization of the acetic acid solution with cold sodium hydroxide solution and extraction with pentane yielded 167 mg (79%) of colorless hydrocarbon. Chromatography on 5 g of Woelm activity I neutral alumina and elution with pentane yielded analytically pure 2-cyclooctylpentane, $n^{25}D$ 1.4641.

Anal. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.53; H, 14.48.

Pentyltriphenylphosphonium Bromide. Triphenylphosphine (26.2 g) was dissolved in 40 ml of dry benzene and pentyl bromide (15.1 g) was added dropwise. The resulting solution was refluxed for 42 hr during which time the crystalline phosphonium salt began to precipitate. Filtration of the salt, followed by drying in a desiccator, yielded 26 g of thick colorless crystals. To the benzene filtrate was added an additional 2 g of pentyl bromide and this solution was refluxed for an additional 36 hr, yielding 3.3 g of crystalline phosphonium salt. The total yield of phosphonium salt was 29.3 g (71%) of colorless crystals, mp 157–165°. Two recrystallizations from acetone–petroleum ether yielded analytically pure product, mp 166.8–167.4°.

Anal. Calcd for $C_{23}H_{27}PBr$: C, 66.70; H, 6.52; Br, 19.30. Found: C, 66.51; H, 6.13; Br, 19.08.

Butyl Cyclodecyl Ketone. To a solution of dibutylcadmium (prepared from 6.7 g of butyl bromide, 3.6 g of magnesium turnings, and 5.0 g of anhydrous cadmium chloride) in 40 ml of dry benzene was added dropwise a solution of cyclodecanecarbonyl chloride (prepared by refluxing 3.03 g of cyclodecanecarboxylic acid[17] with 5 ml of thionyl chloride for a 1-hr period followed by removal of excess thionyl chloride under reduced pressure) in 8 ml of benzene. The resulting mixture was heated at 60–80° for 3.5 hr and then cooled and hydrolyzed with 150 ml of 10% aqueous hydrochloric acid. The aqueous layer was extracted with two 40-ml portions of benzene and the combined benzene extracts were extracted with three 50-ml portions of 10% sodium hydroxide solution and finally with three 50-ml portions of water and dried over magnesium sulfate. Removal of the benzene through a 45-cm Vigreux column under reduced pressure yielded 3.55 g of a slightly yellow liquid. Chromatography on 100 g of Merck activity III neutral alumina and elution with pentane gave 3.43 g of crude ketone as a colorless liquid, bp 96–101° (0.4 mm), $n^{25}D$ 1.4740–1.4751. An analytical sample had bp 99–101° (0.4 mm), $n^{25}D$ 1.4751.

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.64; H, 12.22.

Pentylcyclodecane (6). To a solution of 30 ml of diethylene glycol, 4.0 g of hydrazine hydrate (85%), and 1.5 g of potassium hydroxide was added 0.500 g of butyl cyclodecyl ketone, and the resulting mixture was heated at 100° for 0.5 hr, 190° for 1 hr and 220° for 3 hr. The mixture was then cooled, diluted with 100 ml of water, and extracted with three 100-ml portions of ether. The ether extracts were washed with water and dried over magnesium sulfate. After removal of the ether by distillation at atmospheric pressure, the residue was chromatographed on 30 g of Woelm activity I neutral alumina. Elution with pentane yielded 158 mg (34%) of pentylcyclodecane, $n^{25}D$ 1.4680–1.4682.

Anal. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37. Found: C, 85.54; H, 14.16.

Photolysis Procedures. All photolysis experiments were carried out in a 500-ml Kjeldahl flask fitted with a nitrogen inlet tube through the bottom of the flask and with a 24/40 standard taper joint as a side arm into which was inserted a Graham coil water condenser. The light source was a Hanau H-81 mercury arc lamp (Quarzlampen Gesellschaft, Hanau, West Germany) which was connected in series to two 100-ohm Dividohm resistances (Ohmite, 200 W) which in turn were connected to a 110–220-V transformer. In all experiments 450 ml of pentane (purified by chromatography on silica gel) was used as the solvent. A slow stream of prepurified nitrogen was allowed to flow through the system in each photolysis to prevent any air from entering the system. After completion of a photolysis reaction, the pentane solvent was removed by distillation at atmospheric pressure through a 25 × 2 cm column packed with glass helices. The C_8 or C_{10} hydrocarbon fraction was then distilled at 25–40° (10 mm) or 30–70° (0.5 mm), respectively. These products were trapped with a Dry Ice–acetone bath. The high-boiling residue from each photolysis was then chromatographed on 28–200 mesh Davison silica gel. During the photolysis of the azo compounds, polymer continually formed on the surface of the lamp, necessitating interruption of the reaction at 5-hr intervals for removal of polymer with acetone. All hydrocarbon products were identified by collection from a gas chromatography column and comparison of their infrared spectra with authentic spectra (unless otherwise noted).

A. Photolysis of Azocyclooctane. A 2.00-g sample of azocyclooctane was irradiated for a period of 42 hr and yielded, after distillation, 576 mg (36.4% based on unrecovered azocyclooctane) of a

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(15) A. T. Blomquist, A. E. Burger, and A. C. Sucsy, *J. Am. Chem. Soc.*, 74, 3636 (1952).

(16) S. Winstein and T. G. Traylor, *ibid.*, 78, 2597 (1956).

(17) L. Ruzicka, P. Barman, and V. Prelog, *Helv. Chim. Acta*, 34, 401 (1951).

colorless liquid. Gas chromatography of this material using a 4-methyl-4-nitropimelonitrile (NMPN) column at 30° indicated the presence of 52.8% cyclooctane, 43% *cis*-cyclooctene, and 3.3% *cis*-bicyclo[3.3.0]octane. Chromatography of the oily residue which remained (1.209 g) on 36 g of silica gel and elution with pentane yielded a fraction which after distillation through a short path at 150–200° (0.3 mm) yielded 547 mg (34.6% based on unrecovered azocyclooctane) of a colorless oil. Gas chromatography using a silicone grease column at 230° showed the presence of bicyclooctyl (89.8%) and a pentylcyclooctane fraction (10.2%). Elution of the chromatogram with pentane containing 5% ether followed by distillation through a short path at 125–135° (0.3 mm) yielded 194 mg of a slightly yellow oil which crystallized upon being seeded with a crystal of authentic azocyclooctane (9.7% recovery of starting material). Trace amounts of cyclooctanone were also eluted from the column with pentane containing 40% ether.

B. Photolysis of Azocyclodecane. A 2.031-g sample of azocyclodecane was irradiated for a period of 45 hr and yielded, after distillation, 785 mg (46% based on unrecovered azocyclodecane) of a colorless liquid. Gas chromatography using an NMPN column at 70° showed the presence of 41.5% cyclodecane, a mixture of *cis*- and *trans*-cyclodecene (51.5%), *cis*-bicyclo[5.3.0]decane (5.4%), 1% *cis*-decalin, and 0.5% *trans*-decalin. The cyclodecene mixture was shown to consist of 43.8% *cis* olefin and 7.7% *trans* olefin by gas chromatography using a silver nitrate–tetraethylene glycol column at 93°. It was necessary to collect the *cis*-bicyclo[5.3.0]decane on a silicone oil column at 130° to ensure separation from the other components. The *cis*-decalin could not be collected because of separation difficulty but it was identified by comparison of its retention time on four gas chromatography columns [NMPM, TCEP, silver nitrate–tetraethylene glycol (shoulder), and silicone oil (shoulder)] with authentic *cis*-decalin. Chromatography of the high-boiling residue (1.054 g) on 30 g of silica gel and elution with pentane yielded a fraction which after distillation through a short path at 200–300° (0.3 mm) yielded 435 mg (25.4% based on unrecovered azocyclodecane) of a light yellow oil. Gas chromatography using a silicone grease column at 230° showed the presence of bicyclodecyl (77%) and a pentylcyclodecane fraction (23%). Elution with pentane containing 2–5% ether yielded 117 mg of azocyclodecane (5.8% recovery) which solidified upon cooling below 25°. Cyclodecanone (0.3%) was also eluted from the chromatogram with pentane containing 10% ether.

C. Photolysis of Dicyclooctylmercury. A 1.75-g sample of dicyclooctylmercury was irradiated for a 1-hr period and distillation of the product mixture yielded 434 mg (47.2%) of a C_8 hydrocarbon fraction. Gas chromatography using an NMPN column at 30° indicated the presence of 50% cyclooctane and 50% *cis*-cyclooctene. The colorless residue (506 mg) was chromatographed on 20 g of silica gel and elution with pentane yielded 477 mg (51.8%) of a colorless oil. Gas chromatography of this material using a silicone grease column at 230° showed the presence of 95.5% bicyclooctyl and 4.5% of a pentylcyclooctane fraction.

D. Photolysis of Dicyclodecylmercury. A 0.900-g sample of dicyclodecylmercury was irradiated for a 1-hr period and yielded, after distillation, 328 mg (62.5%) of a colorless liquid which was shown to consist of 47.7% cyclodecane, 46.8% *cis*-cyclodecene, and 5.5% *trans*-cyclodecene by gas chromatography using a silver nitrate–tetraethylene glycol column at 90°. Chromatography of the high-boiling residue (203 mg) on 6 g of silica gel and elution with pentane yielded 160 mg of a yellow oil. Distillation of this material through a short path at 200–300° (0.3 mm) yielded 116 mg (22.1%) of an almost colorless oil. Gas chromatography using a silicone grease column at 230° showed the presence of bicyclodecyl (93.1%) and a pentylcyclodecane fraction (6.9%).

Pyrolysis Procedures. All pyrolysis experiments were carried out in a 150-ml Pyrex glass bomb liner that was fitted into an appropriate stainless steel high-pressure bomb. The compound to be pyrolyzed was dissolved in 40–50 ml of a suitable solvent (benzene for the pyrolysis of the azo compounds and pentane for the pyrolysis of the mercury compounds) and the entire system was flushed eight to ten times with prepurified nitrogen. Finally, the system was pressured to 500–600 psi with nitrogen and heating of the bomb was begun. After completion of a pyrolysis, the solvent was removed by distillation and identification of the product mixture was then undertaken. Products were identified as described in the section on photolysis procedures.

A. Pyrolysis of Azocyclooctane. A 1.20-g sample of azocyclooctane was pyrolyzed at 260° for a period of 1.5 hr. Distillation afforded 100 mg of C_8 hydrocarbons consisting of 78.3% cyclooctane, 21% *cis*-cyclooctene, and 0.7% *cis*-bicyclo[3.3.0]octane as shown by gas chromatography on an NMPN column at 30°. The *cis*-bicyclo[3.3.0]octane was identified only by comparison of its retention time on four gas chromatography columns (NMPN, TCEP, silicone oil, and silver nitrate–tetraethylene glycol (shoulder)). Chromatography of the high-boiling residue (0.773 g) on 22 g of silica gel and elution with pentane yielded 218 mg of a yellow oil. Rechromatographing on 10 g of Woelm activity I neutral alumina and elution with pentane yielded 194 mg (19%) of bicyclooctyl as a colorless oil. In addition, a total of 45% of a nitrogen containing polymer was eluted from the chromatogram.

B. Pyrolysis of Azocyclodecane. A 1.963-g sample of azocyclodecane was pyrolyzed at 220° for a period of 120 hr. Distillation afforded 1.025 g (57.6%) of C_{10} hydrocarbons. Gas chromatography of this mixture using an NMPN column at 60° showed the presence of 55.5% cyclodecane, a mixture of 7.7% *cis*- and *trans*-cyclodecene, 5.6% *cis*-decalin, 12.1% *trans*-decalin, and 19.3% *cis*-bicyclo[5.3.0]decane. The mixture of cyclodecenes was shown to amount to 1.1% *cis* olefin and 6.6% *trans* olefin by gas chromatography using a silver nitrate–tetraethylene glycol column at 90°. Identification of *cis*-decalin and *cis*-bicyclo[5.3.0]decane involved collecting these two components together on a silicone oil column and then recollecting each component separately on an NMPN column at 60°. The high-boiling residue (0.582 g) was chromatographed on 20 g of silica gel and elution with pentane yielded 218 mg of a dark yellow oil. Rechromatographing of 150 mg of this oil on 10 g of Woelm activity I neutral alumina and elution with pentane yielded 67 mg of colorless oil identified as bicyclodecyl (5%).

C. Pyrolysis of Dicyclooctylmercury. A 0.800-g sample of dicyclooctylmercury was pyrolyzed at 150° for 21 hr. Distillation yielded 130 mg (30.6%) of C_8 hydrocarbons shown to consist of 53.8% cyclooctane and 46.2% *cis*-cyclooctene by gas chromatography using an NMPN column at 30°. The high-boiling residue was then chromatographed on 8 g of silica gel and elution with pentane yielded 200 mg (47.1%) of a colorless oil. Gas chromatography of this oil on a silicone grease column at 196° showed the presence of bicyclooctyl (94.2%) and a pentylcyclooctane fraction (5.8%).

D. Pyrolysis of Dicyclodecylmercury. A 1.10-g sample of dicyclodecylmercury was pyrolyzed at 150° for 24 hr. Distillation yielded 349 mg (53.3%) of a mixture of C_{10} hydrocarbons shown to consist of 52.8% cyclodecane, 15.2% *cis*-cyclodecene, 31.6% *trans*-cyclodecene, and 0.4% *cis*-bicyclo[5.3.0]decane by gas chromatography using a silver nitrate–tetraethylene glycol column at 85°. The *cis*-bicyclo[5.3.0]decane could be identified only by its retention time on four gas chromatography columns (NMPN, TCEP, silver nitrate, and silicone oil). Chromatography of the high-boiling residue (286 mg) on 9 g of silica gel yielded 258 mg of material (eluted with pentane) shown to consist of a mixture of 89.7% bicyclodecyl and 10.3% of a pentylcyclodecane fraction by gas chromatography using a silicone grease column heated to 260°.