The Photolysis of Bicyclo[5.2.1]decan-10-ones[1]

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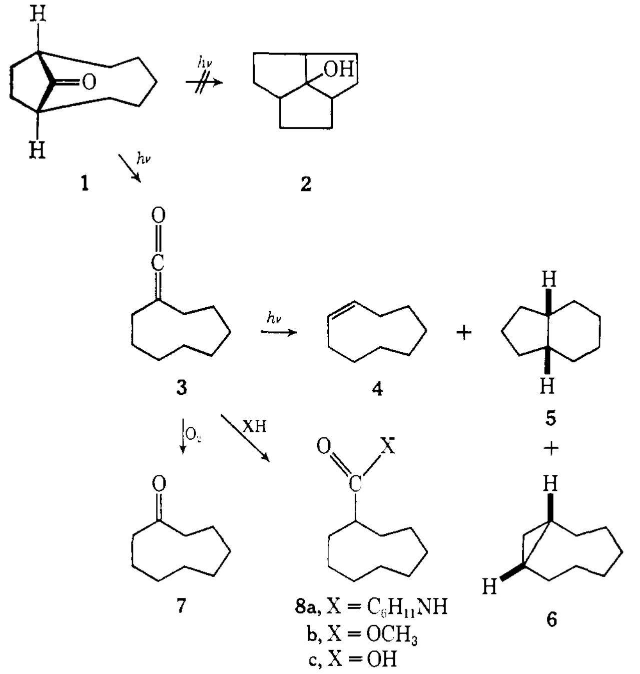
Abstract: An investigation of the photolysis of bicyclo[5.2.1]decan-10-one (**1**) and 1,7-dimethylbicyclo[5.2.1]-decan-10-one (**16**) has shown that, while the initial scission occurs between the carbonyl carbon and the α-carbon, the ensuing steps differ for the two ketones. Compound **1**, containing α-hydrogens, undergoes transannular hydrogen migration to yield a ketene which, in turn, is susceptible to further photolysis and yields *cis*-cyclononene (**4**), *cis*-bicyclo[4.3.0]nonane (**5**), and *cis*-bicyclo[6.1.0]nonane (**6**). Compound **16**, containing no α-hydrogens, undergoes decarbonylation to yield *cis*-1,7-dimethylbicyclo[5.2.0]nonane (**18**), 2,8-dimethylnona-1,8-diene, and a mixture of isomeric $C_{11}H_{20}$ monoolefins (**19, 20, 21**). The monoolefins are thought to arise *via* initial production of a dimethylcyclononenecarboxaldehyde, formed *via* intramolecular hydrogen migration in the initially formed biradical **26**.

The temporal congruence of publications concerning the preparation of bicyclo[5.2.1]decan-10-one[3] and the photoisomerization of monocyclic ketones to bicyclic alcohols[4] suggested the possibility of the chemical congruence of the systems described therein, *viz.*, a photochemical isomerization of **1** to **2**. However, when **1** was dissolved in a hydrocarbon solvent and irradiated in an inert atmosphere, no evidence for any hydroxyl-containing material in the product was obtained.[5] Instead, the mixture has been shown to contain octamethyleneketene (**3**)[5] and three isomeric C_9H_{16} compounds.[6] The C_9H_{16} compounds are secondary photolysis products of the initially formed ketene which is the result of a homolytic cleavage between the carbonyl carbon and the α-carbon in **1** followed by transannular migration of an α-hydrogen. With the knowledge that a methyl group is far less likely than hydrogen to undergo transannular migration, different products might be expected from 1,7-dimethylbicyclo[5.2.1]-decan-10-one (**16**) where ketene formation should be precluded. It is the purpose of this paper to compare and contrast the photoinduced decompositions of the parent ketone **1** and its dimethyl analog **16**.

Photochemistry of Bicyclo[5.2.1]decan-10-one (1). Irradiation of a pentane solution of **1** was carried out until almost all of the starting material had been consumed (45 hr in a representative case), and the bright yellow solution[7] was then exposed to air to convert the ketene to cyclononanone.[8] Evaporation of the solvent and separation by column chromatography yielded a $C_9H_{16}O$ ketone, already identified in previous work as cyclononanone (**7**)[5] which is formed *via* air oxidation of the ketene **3**, and a C_9H_{16} hydrocarbon fraction. Vapor phase chromatographic (vpc) separation of the latter yielded three materials which were identified, by comparison with known compounds and with data in the literature, as *cis*-cyclononene (**4**), *cis*-bicyclo[4.3.0]-nonane (**5**), and *cis*-bicyclo[6.1.0]nonane (**6**), obtained in a ratio of 8.3:7.5:1.0 (Scheme I). To provide conclusive proof that the previously alleged[5] bicyclo[5.2.0]-nonane (**12**) is not a product of photolysis, an unequivocal synthesis of this material was undertaken. Employing a modification of a published procedure,[9] bicyclo[5.2.0]non-1(9)-ene-9-carboxamide (**9**) was prepared and subjected to a Hofmann rearrangement to yield the ketone **10**, and **10** was reduced by the Wolff-Kishner method to the desired hydrocarbon **11**. Alternatively, the amide **9** was reduced to the saturated analog **12**, subjected to a Hofmann rearrangement, methylated, quaternized, and decomposed to yield the olefinic mixture **13**, the reduction of which then yielded **11** (Scheme II). The hydrocarbon so obtained has a

Scheme I



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[1] This work was supported, in part, by Grant No. DA ARO(D)-31-124-G533 from the U. S. Army Research Office.

[2] National Institutes of Health Predoctoral Fellow, 1963–1966.

[3] C. D. Gutsche, T. D. Smith, M. F. Sloan, J. J. Quarles van Ufford, and D. E. Jordan, *J. Amer. Chem. Soc.*, 80, 4117 (1958).

[4] M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 302 (1958).

[5] C. D. Gutsche and C. W. Armbruster, *Tetrahedron Lett.*, 1297 (1962).

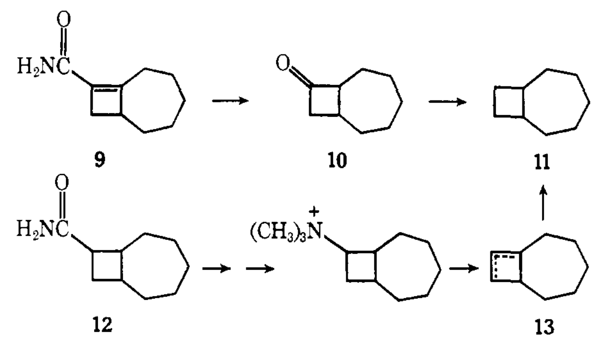
[6] For a preliminary communication of these results, see C. D. Gutsche and J. W. Baum, *Tetrahedron Lett.*, 2301 (1965).

[7] Monomeric dialkylketenes are characterized by a bright yellow color (H. Staudinger, "Die Ketene" in "Chemie in Einzeldarstellungen," Vol. 1, J. Schmidt, Ed., Verlag von Ferdinand Enke, Stuttgart, Germany, 1912, p 99).

[8] One of the characteristic chemical properties of monomeric dialkylketenes is the formation, upon exposure to air, of a peroxide which is unstable and which decomposes to a ketone, carbon dioxide, and polymeric material (H. Staudinger, K. Dyckerhoff, H. W. Klever, and L. Ruzicka, *Chem. Ber.*, 58, 1079 (1925)).

[9] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 2165 (1964).

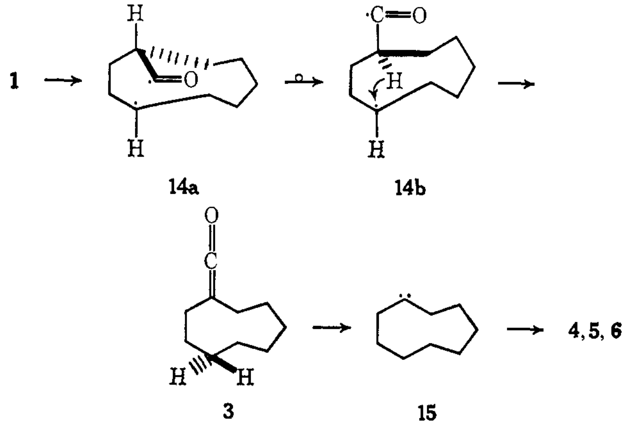
Scheme II



different vpc retention time from that of hydrocarbons **4** and **6** and a sufficiently different infrared spectrum from that of **4**, **5**, and **6** to leave no doubt concerning its absence as a detectable product from the photolysis of **1**.

The presence of octamethyleneketene in the photolysis mixture, established by infrared measurements in the earlier work,[5] was further substantiated by carrying out an irradiation in the presence of cyclohexylamine and isolating a 91% yield of N-cyclohexylcyclononanecarboxamide (**8a**).[10,11] Ketenes have been observed in a variety of photochemical processes,[12] and their formation can be interpreted in terms of an intramolecular hydrogen atom migration in the initially formed biradical **14**, as illustrated in Scheme III. Somewhat

Scheme III



surprising in the case of the ketene **3**, however, is its tendency to undergo further photolysis to the compounds **4**, **5**, and **6**. Although the vapor phase photoinduced decomposition of ketene itself to methylene is a well-known process, the condensed phase production of carbenes by photolysis of ketenes is represented in the literature only by the conversions of dimesitylketene and diphenylketene to tetramesitylethylene[13] and tetraphenylethylene,[14] respectively. Nevertheless, it seems quite probable that hydrocarbons **4**, **5**, and **6** are the result of a photoinduced conversion of **3** to octamethylenecarbene (**15**) followed by collapse of **15** to stable products. To support this contention, a sample of authentic octamethyleneketene (**3**)[15] was subjected to the same photolysis conditions that had been used with **1**. As indicated in Table I, almost identical product distributions were obtained from the photolyses of **1** and **3**, although these differed to some extent from that of the tosylhydrazone-derived carbene.[16] On the premise that the most readily formed hydrocarbon is **5**, the conclusion follows that the carbene produced by photolysis of **3** is more energetic and less discriminate than the carbene produced by pyrolysis of the sodium salt of the tosylhydrazone of cyclononanone.

Table I. Hydrocarbon Product Distribution as a Function of Carbene Source

Source of carbene	Cyclononene, %	Bicyclo-[4.3.0]-nonane, %	Bicyclo-[6.1.0]-nonane, %
Bicyclo[5.2.1]decan-10-one (**1**)	50	45	6
Octamethyleneketene (**3**)	50	44	6
Cyclononanone tosylhydrazone	22	66	10

The present work indicates that the major photolysis pathway for bicyclo[5.2.1]decan-10-one (**1**) involves fission of the C-1 to C-10 bond followed by transannular hydrogen migration to form a ketene (**3**). It has been pointed out that for this migration to occur it is necessary that the biradical undergo a conformational change to bring the migrating hydrogen into proper juxtaposition with the carbonyl carbon.[17] It is interesting, therefore, that other intramolecular hydrogen migrations which would not require significant conformational changes, *i.e.*, those which would lead to aldehyde formation, do not take place. The olefin **4** could, of course, have its genesis in the decarbonylation of an aldehyde formed by one of these alternate pathways. It seems very unlikely that this is the case, however, in the light of the almost identical product distributions of **4**, **5**, and **6** when ketone **1** and ketene **3** are the starting materials. Whether this selectivity is to be ascribed to the relative abilities of the methynyl radical at C-1 and the carbonyl radical at C-10 to abstract hydrogen or whether other factors also intervene is not yet known. Whatever the reason, it appears that the ketene pathway is strongly favored if α-hydrogen atoms are present and that to preclude this pathway, substituents other than hydrogen must be placed at these positions. Accordingly, the α,α'-dimethyl analog of **1** has been investigated.

Photochemistry of 1,7-Dimethylbicyclo[5.2.1]decan-10-one (16). Since bicyclo[5.2.1]decan-10-one (**1**) is an enolizable ketone,[18] bridgehead methylation can be effected to give the 1,7-dimethyl analog **16** in reasonable

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(10) Similarly, an irradiation carried out in methanol solution produced methyl cyclononanecarboxylate (**8b**) in good yield. The synthetic utility of this reaction was demonstrated by carrying it out on a large scale with a sample of crude **1** (once-distilled; *ca.* 90% pure) and obtaining cyclononanecarboxylic acid (**8c**), after hydrolysis of **8b**, in 25% over-all yield from cyclohexanone. Another recent example illustrating the usefulness of the photochemical cleavage reaction is the conversion of bicyclo[9.4.1]hexadecan-16-one to methyl cyclopentadecanecarboxylate in 73% yield.[11]

(11) H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron Lett.*, 779 (1967).

(12) See G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965), for a comprehensive review of these reactions.

(13) H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

(14) H. Nozaki, M. Nakano, and K. Kondō, *Tetrahedron*, **22**, 477 (1966).

(15) We are indebted to Professor J. L. E. Erickson of Louisiana State University for a generous gift of this material.

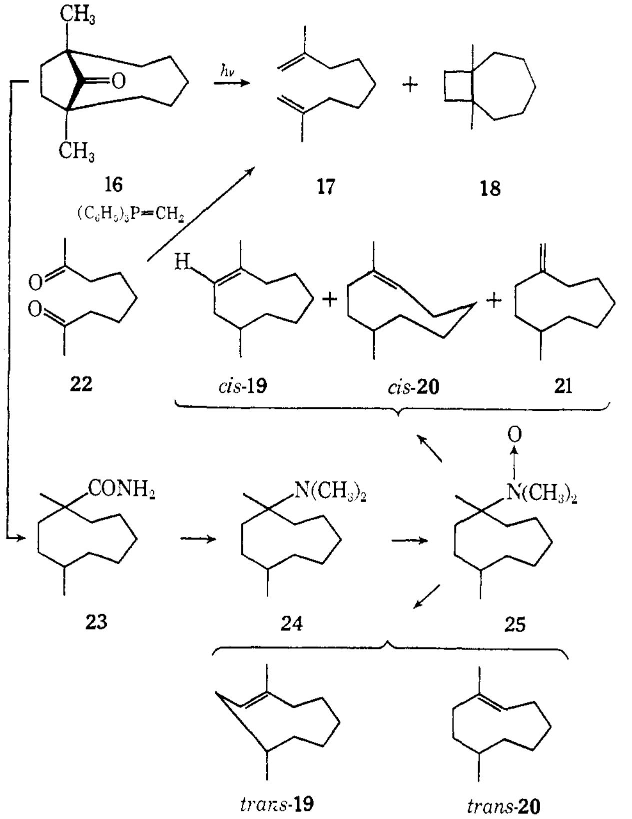
(16) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961).

(17) R. C. Cookson, *Pure Appl. Chem.*, **9**, 575 (1964).

(18) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

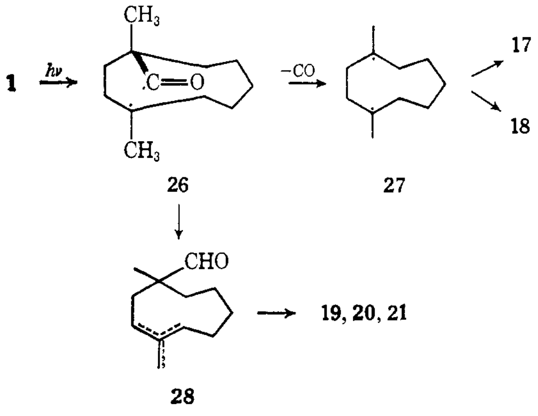
yield. Irradiation of **16** in a pentane solution under an inert atmosphere proceeds with the evolution of carbon monoxide and yields a mixture of products (Scheme IV). The volatile portion, amounting to *ca.* 30% of the starting material, was subjected to preparative-scale vpc separation, and three fractions were collected (designated as α fraction (1 part), β fraction (2.2 parts), and γ fraction (1.6 part)). The α fraction had an analysis compatible with a $C_{11}H_{20}$ formula, possessed infrared absorptions characteristic for a $R_2C{=}CH_2$ group, and showed nmr resonances characteristic for two identical methyl groups and four vinyl protons. Confirmation of the structure **17**, suggested by these data, was obtained in the conversion of the known diketone, nonan-2,8-dione (**22**), to 2,8-dimethylnona-1,8-diene (**17**), identical in all respects with the α fraction from the photolysis. The β fraction, obtained as a low-melting solid, had an analysis compatible with a $C_{11}H_{20}$ formula, gave no evidence in the infrared or nmr spectrum for any unsaturation, and showed the presence of two identically situated methyl groups in the nmr spectrum. These data are commensurate with, although by no means definitive for, a *cis*-1,7-dimethylbicyclo[5.2.0]nonane (**18**) structure. The mass spectrum, also, is interpretable in terms of this structure, and the marked similarity between the cracking patterns of **17**, **18**, and 1,2-dimethylcycloheptene serve to substantiate this assignment. Considerable effort was expended in attempted syntheses of **18**, but unfortunately none of these succeeded and the structural assignment must remain tentative. The γ fraction, shown by analytical vpc to be a mixture, had an analysis compatible with a $C_{11}H_{20}$ formula, possessed infrared bands characteristic of a $R_2C{=}CH_2$ group, and showed nmr resonances for $CH_3C{=}$ protons, $C{=}CH_2$ protons, and $CH{=}CH$ protons. On the assumption that the olefins **19**, **20**, and **21** comprise this mixture, a calculation from the areas under the nmr curves indicated 94% **19** + **20** and 6% **21** to be present. To verify this structural assignment, an authentic synthesis of the olefin mixture was undertaken *via* a Haller–Bauer cleavage of the ketone **16**, a Hofmann rearrangement of the resulting 1,4-dimethylcyclononanecarboxamide (**23**) to a urethan which was reduced and methylated to yield the amine **24**, conversion of the amine to the amine oxide **25**, and pyrolysis of the amine oxide to furnish a mixture which could be separated by vpc into two fractions, one containing the *exo*-methylene compound **21** and the *cis* isomers of **19** and **20**, and the other containing the *trans* isomers of **19** and **20**. Spectral and vpc comparisons of the first fraction with the photolysis-derived products showed them to be identical.

Scheme IV



With bicyclo[5.2.1]decan-10-one (**1**) as well as its dimethyl analog **16**, the initial point of scission upon irradiation appears to be between the carbonyl carbon and the α-carbon. In the case of **1** the resulting biradical undergoes, as the apparently exclusive process, a transannular hydrogen migration to yield the ketene **3**. Such a process is precluded in **16**, however, and other pathways become available to the biradical **26**. One of these involves the extrusion of carbon monoxide to give a second biradical (**27**) which can either collapse to the bicyclic compound **18** or disproportionate to the acyclic diene **17**; apparently, the former pathway is slightly preferred. Alternatively, the biradical **26** can engage in intramolecular hydrogen abstraction reactions to produce the olefinic aldehydes **28**. Although none of these could be detected in the final photolysis product, the presence of **28** during the course of the photolysis was demonstrated by carrying out a reaction in a degassed and sealed thin-wall nmr tube. Periodic examination of the contents of the nmr tube during the course of the photolysis showed a progressive diminution of the resonances associated with the methyl groups at C-1 and C-7 of the starting material and the appearance of a weak band at δ 9.40 ppm which persisted until almost all of the starting material had been consumed. It seems probable that this band arises from an aldehyde, presumably **28**, which maintains a low steady-state concentration through formation from **16** and depletion to **19**, **20**, and **21** (Scheme V). The decarbonylation of aldehydes and ketones is a well-known pathway for vapor phase photolyses[19] and has

Scheme V



also been demonstrated in a few cases for condensed phase photolyses.[20]

The substitution of methyl for hydrogen at the α position of **1** precludes, as anticipated, the ketene formation and requires that other pathways be followed. However, these do not include the kind of transannular reaction that originally aroused our interest in the photolysis of these bicyclic systems. Possibly, the reason lies in the strain of the cyclopentanone ring which seeks relief in bond scission before transannular C–C bonding can take place. If this be the case, it might be predicted that the cyclization of a bridged ring bicyclic ketone to a tricyclic alcohol should find a more favorable example in 1,9-dimethylbicyclo[7.3.1]tridecan-13-one, a compound in which the carbonyl function is in a six-membered ring and in which the corresponding tricyclic alcohol would contain three six-membered rings.

Experimental Section[21]

Photolysis of Bicyclo[5.2.1]decan-10-one (1) in an Inert Solvent. The apparatus employed for the photolyses consisted of a water-jacketed quartz well (carrying a Hanovia 8A36, 100-W, medium-pressure mercury arc lamp) placed in a cylindrical vessel of a dimension such that 150–200 ml of solution filled the vessel to a level above that of the lamp in the well. The vessel was equipped with one outlet which allowed aliquot samples to be withdrawn during the photolysis and another outlet to which was attached a condenser and an apparatus for evacuating the system and subsequently filling it with an inert gas. A solution of 2.50 g (0.0164 mol) of bicyclo[5.2.1]decan-10-one (**1**) in 180 ml of purified *n*-pentane was irradiated in an atmosphere of nitrogen, and 2–5-ml aliquot samples were periodically withdrawn and analyzed by vpc and by infrared spectroscopy. After 45 hr the starting material had been completely consumed, whereupon the bright yellow reaction mixture was exposed to air and concentrated at aspirator pressure to leave 2.5 g of a yellow oil. Chromatography on a water-jacketed 1.1 × 37 cm column of Woelm neutral alumina using *n*-pentane (40 ml) as the elutrient carried the hydrocarbons through the column and left the ketone, previously identified as cyclononanone, behind. The *n*-pentane was removed by evaporation, and the residue was separated by preparative-scale vpc on column no. 4[21] to yield three compounds. The most volatile of these comprised 45% of the mixture and was unreactive toward bromine in carbon tetrachloride or potassium permanganate in acetone. It was identified as *cis*-bicyclo[4.3.0]nonane (**5**) by comparison of its vpc retention time and its infrared and nmr spectra with those of an authentic sample.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.80; H, 13.03.

The next most volatile component, comprising 6% of the mixture, was identified as *cis*-bicyclo[6.1.0]nonane (**6**) by a comparison of its vpc retention time and its infrared spectrum with those of an authentic sample.[22] The least volatile component, comprising 50% of the mixture, readily decolorized solutions of bromine in carbon tetrachloride and potassium permanganate in acetone. It was identified as *cis*-cyclononene (**4**) by a comparison of its infrared spectrum with one published in the literature[23] and by an nmr spectrum which is compatible with this structure.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.85; H, 13.23.

Photolysis of Bicyclo[5.2.1]decan-10-one (1) in the Presence of Cyclohexylamine. A 2.50-g (0.0164 mol) sample of **1** and 3.25 g (0.0328 mol) of cyclohexylamine (distilled from potassium hydroxide) were dissolved in 150 ml of cyclopentane (Phillips, spectrograde) and irradiated in an atmosphere of nitrogen for 20 hr. Unreacted amine was removed by extraction with dilute hydrochloric acid, and the product was worked up to yield 3.76 g (91%) of N-cyclohexylcyclononanecarboxamide (**8a**) as a tan solid, mp 128–138.° Sublimation and several recrystallizations from aqueous ethanol yielded colorless needles, mp 154–154.5°.

Anal. Calcd for $C_{16}H_{29}NO$: C, 76.44; H, 11.63. Found: C, 76.37; H, 11.84.

Photolysis of Bicyclo[5.2.1]decan-10-one (1) in Methanol Solution. A 49.0-g sample of **1** (estimated by vpc to be 90% pure) was dissolved in 1750 ml of anhydrous methanol and placed in a 2-l. three-necked flask equipped with a center neck capable of accepting the quartz immersion well. The solution was irradiated for 60 hr, concentrated to 150 ml, treated with a solution of 36.2 g of potassium hydroxide in 50 ml of water, and refluxed overnight. The mixture was worked up to yield 34.9 g of a viscous, yellow liquid which, upon distillation through a 22-cm Vigreux column, gave 29.9 g (55%) of cyclononanecarboxylic acid (**8c**) as a pale yellow liquid, bp 134° (5 mm) (lit.[24] bp 114–115° (0.1 mm)).

Photolysis of Octamethyleneketene (3). A solution containing 0.200 ml of octamethyleneketene (**3**)[15] in 180 ml of *n*-pentane was irradiated in an atmosphere of nitrogen for 3.5 hr, by which time a vpc and infrared analysis of an aliquot indicated complete decomposition of the ketene. The pentane was removed, and the residue was analyzed by vpc on column no. 4[21] and shown to contain 44% of *cis*-bicyclo[4.3.0]nonane (**5**), 6% of *cis*-bicyclo[6.1.0]nonane (**6**), and 50% of *cis*-cyclononene (**4**).

1,7-Dimethylbicyclo[5.2.1]decan-10-one (16). Following a published procedure for methylation reactions,[25] a 0.100-mol sample of sodium hydride, washed free from mineral oil, was suspended in 50 ml of dry benzene and 75 ml of reagent grade dimethylformamide contained in a 500-ml round-bottomed flask. To the stirred suspension a solution of 3.805 g (0.025 mol) of bicyclo[5.2.1]decan-10-one (**1**) in 25 ml of anhydrous benzene was added all at once. The mixture was stirred for 5 hr at room temperature, cooled to 0°, and treated with 15 g (0.100 mol) of methyl iodide. After the reaction mixture had been stirred at room temperature for 2 days, the excess sodium hydride was decomposed with water, and the product was isolated in the usual fashion to give, after distillation through a short column, 3.691 g (82%) of colorless oil, bp 129–135° (32 mm). A vpc analysis of this material on column no. 1[21] showed that it contained 2% of a material which lacks a carbonyl absorption in the infrared and which may be a product of O-methylation, 5% of starting ketone, 10% of 1-methylbicyclo[5.2.1]decan-10-one, and 81% of 1,7-dimethylbicyclo[5.2.1]decan-10-one (**16**). The monomethyl compound was isolated as a colorless oil: $\bar{\nu}^{\text{liq}}$ (cm^{-1}) 1735 (cyclopentanone carbonyl), 1370 (C–CH_3); nmr (CCl_4) (ppm), 3-proton singlet at 0.97 (CH_3 at C-1), 15-proton multiplet at 1.25–2.50.

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(19) For a good review of the photochemistry of aldehydes and ketones see J. N. Pitts and J. K. S. Wan in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 823.

(20) A particularly pertinent example which appeared during the course of this work involves the photolysis of 7,7,9,9-tetramethylbicyclo-[4.3.0]nonan-8-one which yields *cis*-7,7,8,8-tetramethylbicyclo[4.2.0]-octane (*i.e.*, a product comparable to **18**), *cis*-1-isopropylidene-2-isopropylcyclohexane (*i.e.*, a product comparable to **19**, **20**, and **21**), and 2,9-dimethyldeca-2,8-diene (*i.e.*, a product comparable to **17**) (J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966)).

(21) All melting points and boiling points are uncorrected. The infrared spectra were measured on a Perkin-Elmer Infracord instrument. The nmr spectra were measured on a Varian HA-60 and A-60A spectrometers; the resonances are expressed in parts per million downfield shift from tetramethylsilane, present as an internal reference. Microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria, and by Microtech Laboratories, Skokie, Ill. Vpc analyses were performed on units containing thermistor detectors and using the following columns: column no. 1, a 0.25 in. × 16 ft column packed with 15% w/w neopentylglycol sebacate polymer on 40–50 mesh type ABS Anakrom (a product of Analytical Engineering Laboratory, Inc., Hamden, Conn.); column no. 2, a 0.25 in. × 6 ft column packed with 5% w/w Dow No. 710 Silicone oil on 40–50 mesh type ABS Anakrom; column no. 3, 0.25 in. × 3 ft column packed with 30% w/w Carbowax 400 containing 52% w/w silver nitrate on 80–100 mesh type RZ Gaschrom (a product of Applied Science Laboratories, State College, Pa.); column no. 4, a 0.25 in. × 16 ft column packed with 20% w/w Carbowax 1540 on 60–70 mesh type RZ Gaschrom; column no. 5, 0.25 in. × 12 ft column packed with 60% w/w commercial tricresylphosphate on 30–60 mesh Firebrick; column no. 6, a 0.5 in. × 9 ft column packed with 15% w/w Dow No. 710 Silicone oil on 40–50 mesh type ABS Anachrom. The percentage compositions of mixtures analyzed by vpc were calculated from peak area measurements (peak height times width at half-height) and are uncorrected for differences in heat capacities.

(22) We are indebted to Dr. C. W. Armbruster for a sample of this material, prepared from *cis*-cyclooctene and methylene iodide by the Simmons–Smith procedure (H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 80, 5323 (1958)).

(23) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, 74, 3643 (1952).

(24) K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953).

(25) F. J. Marshall and W. M. Cannon, *J. Org. Chem.*, **21**, 245 (1956).

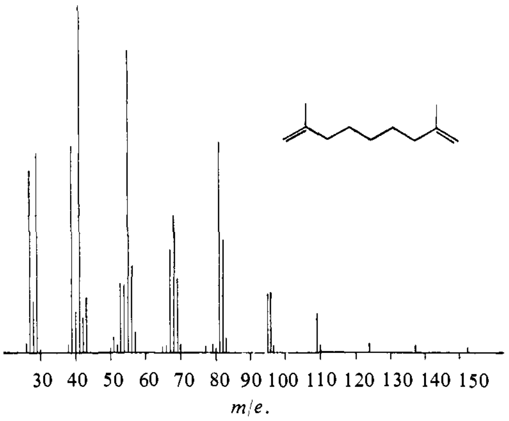

Figure 1. Mass spectrum of 2,8-dimethylnona-1,8-diene (**17**).

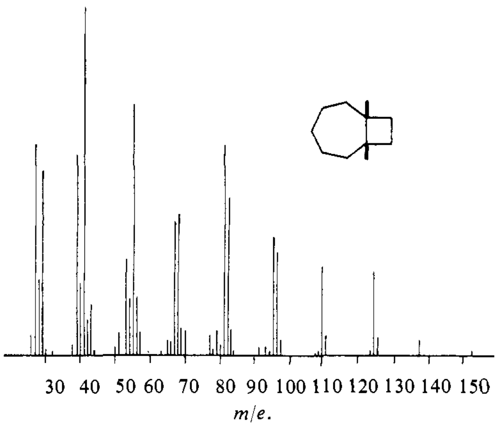

Figure 2. Mass spectrum of *cis*-1,7-dimethylbicyclo[5.2.0]nonane (**18**).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.38; H, 10.74.

The dimethyl compound **16**, also isolated as a colorless oil, failed to form carbonyl derivatives with semicarbazide, hydroxylamine, or 2,4-dinitrophenylhydrazine: $\bar{\nu}^{\mathrm{liq}}$ (cm^{-1}) 1735 (cyclopentanone carbonyl), 1370 (C–CH$_3$): nmr (CCl$_4$) (ppm), 6-proton singlet at 0.95 (CH$_3$ at C-1 and C-7), 14-proton multiplet at 1.30–2.40.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.82; H, 11.30.

Photolysis of 1,7-Dimethylbicyclo[5.2.1]decan-10-one (16). A 2.928-g sample of **16** dissolved in 200 ml of purified *n*-pentane was irradiated in the apparatus described above for 22 hr in an atmosphere of nitrogen. The pentane was removed under vacuum, and the residue was distilled through a short column to give 0.939 g (39%) of material boiling up to 150° (30 mm) and shown by vpc analysis on column no. 1[21] and by infrared analysis to be composed of hydrocarbons. A nonvolatile residue of 1.620 g remained, and 0.130 g of material was held up in the distillation apparatus. Separation of the volatile constituents by vpc on column no. 4[21] gave three fractions, the most volatile of which was obtained as a colorless, mobile liquid and identified as 2,8-dimethylnona-1,8-diene (**17**) on the basis of its spectral characteristics and by comparison with an authentic sample: $\bar{\nu}^{\mathrm{liq}}$ (cm^{-1}), 3140 (vinyl C–H), 1655 (olefin), 1378 (C–CH$_3$), 889 (C=CH$_2$); nmr (CCl$_4$) (ppm), 6-proton multiplet at 1.17–1.63 (CH$_2$ at C-4, C-5, C-6), 6-proton singlet at 1.70 (CH$_3$ at C-2 and C-8), 4-proton multiplet at 1.79–2.21 (CH$_2$ at C-3 and C-7), 4-proton doublet with J = 1.0 Hz at 4.64 (H$_2$C=C).

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.55; H, 13.27.

The second component was obtained as colorless crystals, mp 37–38°, and was assigned the structure *cis*-1,7-dimethylbicyclo[5.2.0]nonane (**18**): $\bar{\nu}^{\mathrm{liq}}$ (cm^{-1}) 3010 (s), 2740 (w), 1455 (vs), 1375 (s), 1300 (m), 1250 (m), 1220 (m), 1190 (m), 1130 (m), 1115 (m), 1080 (w), 1040 (w), 1010 (m), 970 (m), 928 (w), 900 (w), 838 (m), 788 (w), 738 (w); nmr (CCl$_4$) (ppm), 6-proton singlet at 1.05 (CH$_3$), 8-proton multiplet at 1.10–2.00 (CH$_2$ at C-2, C-6, C-8, C-9), 6-proton sharp resonance at 1.62 (CH$_2$ at C-3, C-4, C-5).[26]

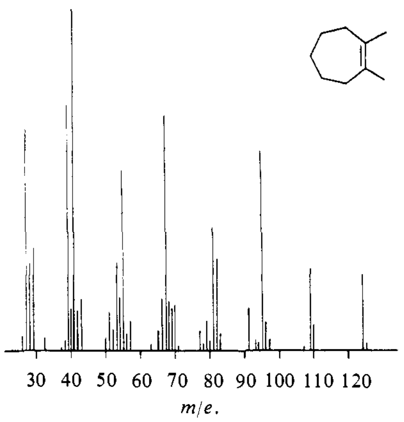

Figure 3. Mass spectrum of 1,2-dimethylcycloheptene.

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.93; H, 13.25.

The mass spectra of **17**, **18**, and 1,2-dimethylcycloheptene are shown in Figures 1, 2, and 3.[27] The highest boiling component was obtained as a colorless, mobile liquid identified as a mixture of *cis*-1,4-dimethylcyclononene (**19**), *cis*-1,7-dimethylcyclononene (**20**), and 1-methylene-4-methylcyclononane (**21**) on the basis of its spectral characteristics and by comparison with a mixture prepared by an unambiguous route: $\bar{\nu}^{\mathrm{liq}}$ (cm^{-1}), 1671 (olefin), 1641 (olefin), 1420–1500 (a group of bands in this region correlates with *cis* medium ring olefins),[28] 1372 (C–CH$_3$), 879 (C=CH$_2$); nmr (CCl$_4$) (ppm), a pair of doublets between 0.75 and 1.03 with J = 5.8 Hz (CH_3CH in **19** and **20**), multiplet at 1.03–1.77 (CH$_2$ at C-4, C-5, C-6, C-7, and C-8 in **19**, **20**, **21** and C-3 in **21**), singlet at 1.67 (CH$_3$C= at C-1 in **19**, **20**), multiplet at 1.87–2.67 (CH$_2$C= at C-3 and C-9 in **19** and C-2 and C-9 in **20**), broad singlet at 4.81 (CH$_2$=C in **21**), multiplet at 4.91–5.41 (CH=C in **19**, **20**). The region 4.80–5.50 was scanned at higher gain on an expanded scale, and area calculations indicated that the mixture contained 94% of **19** + **20** and 6% of **21**.

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.83; H, 13.24.

Synthesis of Authentic Samples and Comparison Products for Photolysis Reactions. ***cis*-Bicyclo[5.2.0]nonane (11).** Following literature directions,[9] bicyclo[5.2.0]non-1(9)-ene-9-carboxamide (**9**) was prepared from the reaction of the enamine of cycloheptanone with acrylonitrile. A 5.0-g (0.030 mol) sample of this material was dissolved in 50 ml of anhydrous methanol, cooled to −70°, and treated slowly (to maintain the temperature of −20 to −15°) with 47.3 ml of a 0.704 *M* solution of sodium hypochlorite (Chlorox solution) containing 1.3 g of sodium hydroxide. After then allowing the solution to warm to 0° for 30 min and heating to 60–65° for 15 min it was cooled to room temperature, acidified to pH 1–2, and refluxed for 22 hr. The product was worked up, and the crude material was distilled through a short-path apparatus to yield 1.75 g of material boiling up to 130° (0.30 mm). A portion of this fraction was purified by vpc on column no. 1[21] and yielded a compound, presumably **10**, having a strong infrared absorption at 1785 cm^{-1}, characteristic for the cyclobutanone ring. A 0.500-g sample of the purified material was treated with sodium ethoxide (from 0.146 g of sodium dissolved in 4.8 ml of ethanol) and 0.188 g of anhydrous hydrazine for 12 hr at 160°. The product consisted of 0.246 g of a colorless, mobile liquid from which a pure sample of **11** was separated by vpc on column no. 1.[21] It is interesting to note that none of the columns used separated *cis*-**11** from *cis*-**5** including column no. 5[21] which sufficed for the separation of *cis*-**11** from *trans*-**11**.[29]

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[26] In accordance with the observations of W. B. Moniz and J. A. Dixon (*J. Amer. Chem. Soc.*, **83**, 1671 (1961)), the sharp resonance at this position is ascribed to the conformational mobility of these positions in the *cis*-bicyclo[5.2.0]nonane ring system.

[27] We are indebted to Dr. O. P. Tanner and Mr. M. T. Jackson of the Central Research Laboratories of Monsanto Co. for their assistance in obtaining the mass spectra using a CEC 21-104 instrument.

[28] A. C. Cope, E. Ciganek, C. F. Howell, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **82**, 4663 (1960), and references cited therein.

[29] N. L. Allinger, M. Nakasaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

The infrared spectrum of this material is identical with that of material prepared by an alternative route.[30] As an alternate procedure for converting **9** to **11**, a 5.00-g sample of the unsaturated amide **9** was reduced with hydrogen in the presence of 5% platinum-on-carbon catalyst to yield 4.07 g (81%) of colorless plates, mp 201.5–203° (lit.[9] mp 205.5°). This material was dissolved in 60 ml of anhydrous methanol, treated with a sodium methoxide solution (from 1.13 g of sodium in 30 ml of methanol) and 3.94 g of bromine, and heated for 10 min on the steam bath. The resulting urethan was hydrolyzed by refluxing overnight with concentrated hydrochloric acid, and the reaction mixture was processed to give 2.5 g (76%) of 8-aminobicyclo[5.2.0]nonane as a pale yellow oil. Following a literature procedure,[31] this material was treated with 4.15 g of 98% formic acid and 3.22 g of 37% aqueous formaldehyde solution. The reaction mixture was heated on the steam bath for 24 hr, cooled, and acidified, and the formic acid and formaldehyde were removed under aspirator vacuum. The residue was made basic with aqueous hydroxide, and the product was isolated and treated with 10 ml of methyl iodide to yield 3.6 g of 8-trimethylammoniumbicyclo[5.2.0]nonane iodide as a colorless solid. The methiodide was dissolved in 80 ml of aqueous methanol (1:3) and stirred for 1 hr with moist silver oxide prepared from 6.21 g of silver nitrate.[32] The oxidant was removed, and the product was pyrolyzed at 140° (50 mm) in an atmosphere of nitrogen to yield 0.138 g (6.3% based on starting amine) of a colorless oil which was indicated by vpc analysis to consist of a mixture of isomeric olefins (**13**). Palladium-on-carbon-catalyzed hydrogenation of the olefin mixture yielded the hydrocarbon **11** as a colorless oil possessing an infrared spectrum identical with that of **11** obtained from **9** *via* the alternative route as well as with **11** obtained from a different synthetic route.[30]

2,8-Dimethylnona-1,8-diene (17). Using a literature procedure as a model,[33] a solution of dimethyl cadmium (from 29.3 g of anhydrous cadmium chloride) in 150 ml of anhydrous benzene was treated with pimeloyl chloride (from 5.0 g of pimelic acid) in 50 ml of benzene. The mixture was allowed to stand at room temperature overnight and was then worked up to give 5.0 g of a yellow oil which was shown by vpc on column no. 1[21] to contain 65% of nona-2,8-dione (**22**), 30% of 2-methyl-2-hydroxynonan-8-one, and 5% of 2,8-dimethylnona-2,8-diol. Recrystallization from petroleum ether (bp 63–68°) effected only partial purification and gave 1.036 g of a first crop of colorless crystals, mp 36–42° (lit.[34] mp 49–50°) containing 78% of **22** and 22% of the hydroxy ketone, and 1.052 g of a second crop containing 70% of **22** and 30% of the hydroxy ketone. This second crop was dissolved in 5 ml of anhydrous ether and added to a solution of the Wittig reagent prepared by the action of butyllithium on 5.79 g of triphenylmethylphosphonium bromide suspended in 20 ml of anhydrous ether.[35] The mixture was stirred at −10° for 15 min and then refluxed overnight on a water bath. The reaction mixture was worked up, and the crude product was chromatographed on alumina (Alcoa F-20) using petroleum ether (bp 63–69°) as the elutrient. The first 50 ml of eluate was concentrated, and the residue was purified by vpc on column no. 1[21] to give 0.081 g of 2,8-dimethylnona-1,8-diene (**17**), identical in vpc retention time and infrared spectra with the sample obtained *via* photolysis of **16**.

***cis*-1,4-Dimethylcyclononene (19), *cis*-1,7-Dimethylcyclononene (20), and 1-Methylene-4-methylcyclononane (21).** A solution of 9.0 g (0.050 mol) of 70% pure 1,7-dimethylbicyclo[5.2.1]decan-10-one (**16**) (bp 97–105° (14 mm)) in 100 ml of dry, reagent grade xylene was added dropwise over a 20-min period to a stirred, refluxing suspension of 4.5 g of sodium amide in 250 ml of xylene. The mixture was then cooled, 100 ml of water was added dropwise, and the product was isolated in the usual fashion as 7.9 g of a viscous, brown oil. On standing overnight, the oil deposited 1.74 g (18%) of 1,4-dimethylcyclononanecarboxamide (**23**) as pale tan crystals, mp 90–91.5°. Two recrystallizations from cyclohexane–chloroform gave material with mp 92–93°; $\tilde{\nu}^{KBr}$ (cm^{-1}) 3440 (N–H), 1730 (amide), 1705 (amide), 1380 (C–CH$_3$).

Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 72.80; H, 11.64; N, 6.83.

A solution of 2.261 g (11.5 mmol) of the carboxamide in 10 ml of anhydrous methanol was treated with sodium methoxide (from 0.53 g of sodium in 11 ml of methanol) and 1.84 g (11.5 mmol) of bromine, and the mixture was refluxed for 12 hr and then worked up to yield the crude urethan, mp 57–60°. Following a literature procedure,[36] a solution of 1.8 g of the crude urethan in 50 ml of anhydrous ether was added dropwise to a suspension of 0.53 g of lithium aluminum hydride in 50 ml of anhydrous ether. The mixture was then refluxed for 15 hr and worked up to give 2.6 g of N-methyl-1,4-dimethylcyclononylamine. This was converted to the dimethyl compound **24** following a published procedure using formic acid and formaldehyde[37] and yielded 1.956 g of product as a colorless oil. Treatment of an ethereal solution of a 0.976-g sample of this material with 10 ml of methyl iodide yielded, after 7 days at 0°, 1.351 g (85%) of N,N,N-trimethyl-1,4-dimethylcyclononylammonium iodide which could be recrystallized from absolute methanol to yield a white, microcrystalline powder, mp 262–264°.

Anal. Calcd for $C_{14}H_{30}NI$: C, 49.45; H, 8.91; N, 4.13. Found: C, 49.70; H, 8.75; N, 4.05.

Employing a procedure described by Cope and coworkers,[28] a 0.960-g sample of N,N-dimethyl-1,4-dimethylcyclononylamine was converted into the amine oxide by treatment with 30% hydrogen peroxide, and the amine oxide was pyrolyzed at 150–175° to give 0.555 g of a colorless, mobile oil. By vpc on column no. 3[21] the product was separated into two fractions. The more readily eluted fraction was shown, on the basis of infrared and nmr spectral data, to be comprised of *cis*-1,4-dimethylcyclononene (**19**), *cis*-1,7-dimethylcyclononene (**20**), and 1-methylene-4-methylcyclononane (**21**); the less readily eluted fraction was shown to be comprised of *trans*-**19** and *trans*-**20**.[38] A comparison of the vpc, infrared, and nmr characteristics of the more readily eluted fraction with that obtained from the photolysis of **16** showed the two to be qualitatively identical with only small quantitative differences in the isomer ratios.

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[30] We are indebted to Professor Allinger for making available to us a copy of the spectrum of **11** prepared by the procedure described in ref 29.

[31] J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, 71, 3925 (1949).

[32] B. Helferich and W. Klein, *Ann.*, **450**, 219 (1926).

[33] D. A. Shirley, *Org. Reactions*, 8, 28 (1954).

[34] F. S. Kipping and W. H. Perkin, *J. Chem. Soc.*, **55**, 336 (1889).

[35] G. Wittig and U. Schollkopf, *Org. Syn.*, 40, 66 (1966).

[36] F. Wessely and W. Swoboda, *Monatsh.*, **82**, 621 (1951).

[37] H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Amer. Chem. Soc.*, **55**, 4571 (1933).

[38] The nmr spectrum of the *trans* isomers resembles, in general, that of the *cis* isomers. The major difference between the two is the somewhat broader multiplet in the δ 1.07–1.80 region (CH$_2$ groups in ring) which presumably arises from the greater rigidity of the *trans*-cyclononene system