The Addition of Unsaturated Carbenes to Cyclic Dienes. Intramolecular Trapping of Trimethylenemethane Diradicals[1]

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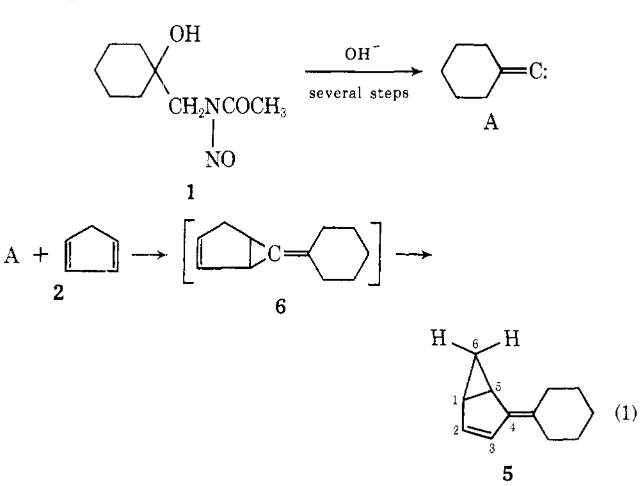
The addition of cyclohexylidenecarbene (A) generated *in situ* by alkaline treatment of 1-(*N*-nitrosoacetylaminomethyl)cyclohexanol (1) to cyclopentadiene (2), 1,4-cyclohexadiene (3), and bicyclo[2.2.1]heptadiene (4) yields 4-cyclohexylidenebicyclo[3.1.0]hex-2-ene (5), 7-cyclohexylidenebicyclo[4.1.0]hept-3-ene (8), and 3-cyclohexylidenetricyclo[3.2.1.$0^{2,4}$]oct-6-ene (9), respectively, in 65–76% yields. On heating at 150° 9 rearranges to 3-cyclohexylidenetetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (10). Oxidation of 10 yields tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octan-3-one (16).

The tendency of methylenecyclopropanes to afford a trimethylenemethane diradical on heating represents a phenomenon long of interest.[3] Methods of preparing the requisite precursors, methylenecyclopropanes, have been summarized.[4] In addition to the methods mentioned, the addition of unsaturated carbenes, generated from nitrosoxazolidones, to olefins provides another route.[5] We undertook the work herein described to see whether an unsaturated carbene would react in a 1,2 (or other) manner with cyclic dienes and to observe any thermal rearrangements of the addition products.

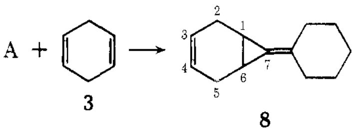
In order to generate an unsaturated carbene, A, we chose the procedure in which a solution of the diene and 1-(*N*-nitrosoacetylaminoethyl)cyclohexanol (1) containing a catalytic amount of Aliquat 336[6] is treated with aqueous sodium hydroxide.[7] The dienes were cyclopentadiene (2), 1,4-cyclohexadiene (3), and bicyclo[2.2.1]heptadiene (4).

In the reaction involving 2 (eq 1) there was obtained a 76% yield of 4-cyclohexylidenebicyclo[3.1.0]hex-2-ene (5),[8] a compound which cannot be initially formed by a 1,2 or a 1,4 addition to the diene. We believe 5 is formed by a 1,2 addition to yield 6-cyclohexylidenebicyclo[3.1.0]hex-2-ene (6), which is thermally unstable and rearranges readily to 5. In our first experiment no attempt was made to keep the temperature down during distillation of the product. On repetition involving a work-up in which the temperature was never higher than about 30°, the product was still entirely 5. Thus 6 rearranges readily to 5. The driving force for this trimethylenemethane diradical type rearrangement undoubtedly stems both from the steric strain in 6 and from the formation of the conjugated diene system in 5. We see no route by which the reactants can go directly to 5.[9]



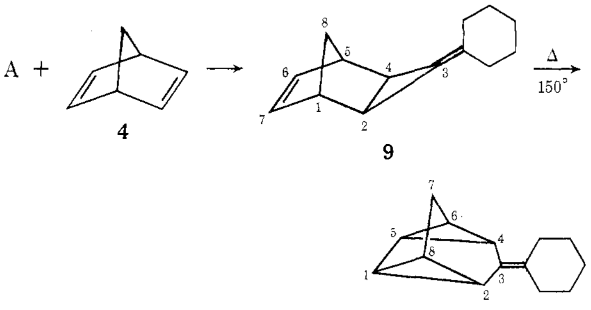
1 A 2 6 5 (1)

In the reaction involving 3 (eq 2) there was obtained a 65% yield of 7-cyclohexylidenebicyclo[4.1.0]hept-3-ene (8),[8] a compound which proved stable thermally at temperatures as high as 185°. At higher temperatures a complex mixture of hydrocarbons which was not studied in detail resulted.[10] If a trimethylenemethane diradical is formed, the olefinic bond present is not well enough oriented for homoallylic participation to allow for rearrangement.



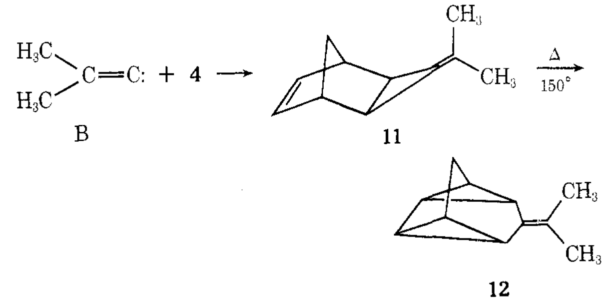
3 8 (2)

In the reaction involving 4 (eq 3) there was obtained a 69% yield of 3-cyclohexylidenetricyclo[3.2.1.$0^{2,4}$]oct-6-ene (9).[8] On heating to 150° for 20 min rearrangement of 8 to 3-cyclohexylidenetetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (10) resulted. No change in 10 resulted on longer heating at 190–200°.



4 9 10 (3)

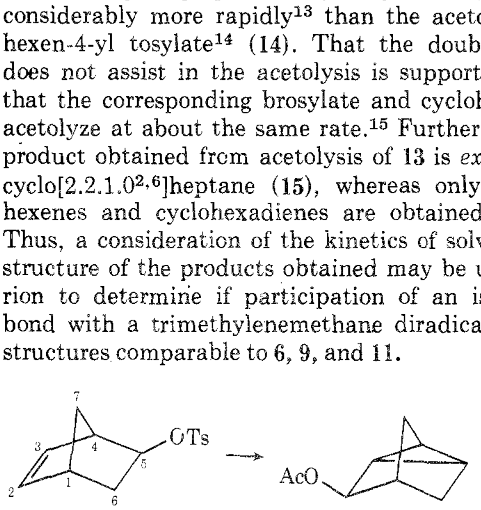
While our work was in progress the synthesis of 3-isopropylidenetricyclo[3.2.1.$0^{2,4}$]oct-6-ene (11) in 12% yield by the addition of isopropylidenecarbene (B) to 4 as well as the flash thermolysis of 11 at 400° to give 3-isopropylidenetetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (12) was reported.[11] We had also prepared 11 in 35% yield (not maximized) and shown that heating at 150° for 20 min converted 11 smoothly to 12 (eq 4).



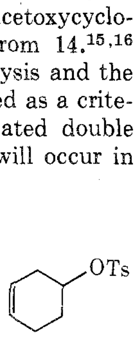
B 11 12 (4)

We believe the rearrangements of 9 to 10 and of 11 to 12 occur by trimethylenemethane diradical paths as the concerted cycloaddition alternative would involve a forbidden $_{\sigma}2_s + _{\pi}2_s$ process.[12]

The facile participation of the 6,7-double bond of **9** in the trimethylenemethane diradical type rearrangement of **9** to **10** as contrasted to the lack of participation of the 3,4-double bond of **8** may be parallel to the acetolysis of *exo*-bicyclo[2.2.1]hept-2-en-5-yl tosylate (**13**), which occurs considerably more rapidly[13] than the acetolysis of cyclohexen-4-yl tosylate[14] (**14**). That the double bond in **14** does not assist in the acetolysis is supported by the fact that the corresponding brosylate and cyclohexyl brosylate acetolyze at about the same rate.[15] Furthermore the main product obtained from acetolysis of **13** is *exo*-7-acetoxytricyclo[2.2.1.0^{2,6}]heptane (**15**), whereas only acetoxycyclohexenes and cyclohexadienes are obtained from **14**.[15,16] Thus, a consideration of the kinetics of solvolysis and the structure of the products obtained may be used as a criterion to determine if participation of an isolated double bond with a trimethylenemethane diradical will occur in structures comparable to **6**, **9**, and **11**.



13 **15**



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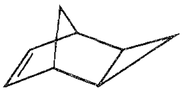
Our results with the rearrangement of **9** to **10** may be compared with similar studies of intramolecular trapping of 1,3 diradicals[17] as pointed out by a referee. Interestingly, the rearrangement of tricyclo[3.2.1.0^{2,4}]oct-6-ene (**16**) to **17** takes place only on photolysis and not on pyrolysis,[17b] in contrast to the thermal rearrangement of **9** to **10**. On pyrolysis **16** gave three products,[17b] none of which was **17**.



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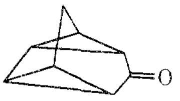

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On oxidation **10** yields tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octan-3-one (**18**), a ketone previously prepared[18] by an entirely different route.

In conclusion we would like to emphasize that by the reaction of cyclic dienes with unsaturated carbenes of type A products in the polycyclic hydrocarbon area may readily be synthesized in one step. Furthermore, since such methylenecyclopropyl structural units undergo thermal homolytic cleavage to trimethylenemethane diradicals, new complex polycyclic hydrocarbons may easily be obtained. The combination of these two steps allows for the elaboration of molecules which otherwise would require multiple step synthesis. Many interesting products may be predicted by proper choice of dienic and polyenic systems.

Experimental Section

Product Analysis. Glpc analyses were performed on a Wilkens Aerograph Model A-700; column (10 ft × ¼ in.): 30% SE-30, 45/60 a/w Chromosorb A, helium flow 25 ml/min. Proton magnetic resonance (pmr) spectra were recorded on an A-60 nmr spectrometer, Varian Associates, Palo Alto, Calif. All samples were dissolved in carbon tetrachloride (CCl_4); tetramethylsilane (TMS) was used as an internal standard; chemical shifts are reported in δ values (TMS = 0.0). Melting and boiling points are uncorrected. Melting points were taken with a Thomas-Hoover melting point apparatus. All boiling points are approximate since the material was rapidly distilled in order to avoid unwanted thermal rearrangements.

The *in situ* generation of all alkylidenecarbenes described here follows a general procedure which begins with the nitrosation of 1-(acetylaminomethyl) alcohols.

1-(*N*-Nitrosoacetylaminomethyl)cyclohexanol (1). A solution prepared by bubbling gaseous nitrosyl chloride into 100 ml of cooled glacial acetic acid until 13.2 g (0.2 mol) had been absorbed was added dropwise during 45–60 min to a solution of 17.1 g (0.1 mol) of 1-(*N*-acetylaminomethyl)cyclohexanol,[7] 20 g of freshly fused potassium acetate, and 2 g of phosphorus pentoxide in 100 ml of glacial acetic acid cooled to part crystallization. After 2 hr the mixture was allowed to warm to room temperature and was then poured onto ice and methylene chloride. The organic layer was separated and washed thrice with ice–water. The combined aqueous fractions were neutralized with sodium bicarbonate and back-extracted with methylene chloride. The organic portions were combined and washed with cold saturated $NaHCO_3$ solution, cold saturated NaCl solution, and filtered through a cone of anhydrous Na_2SO_4 into a flask immersed in an ice bath. The methylene chloride was removed under reduced pressure at or below room temperature to afford 19 g (95%) of **1** as a yellow oil which had no NH absorption in the ir spectrum and a strong band at 5.75 μ. These nitroso compounds should be used immediately or stored for up to 1 week in methylene chloride solution in the freezing compartment of a refrigerator.

Generation of Cyclohexylidene Carbene A; Isolation of Addition Products. In a typical reaction a stirred solution held at −10 to −5° of **1** prepared from 4.3 g (25 mmol) of 1-(*N*-acetylaminomethyl)cyclohexanol and 1 g of Aliquat 336[6] in 50 ml of olefin was treated dropwise over 30 min with a solution of 1.2 g (30 mmol) of sodium hydroxide in 3 ml of water. The theoretical volume of nitrogen was collected over water during the addition of the base. The reaction mixture was diluted with ether and shaken with saturated NaCl. The organic layer was filtered through a cone of anhydrous Na_2SO_4, and the solvent was fractionally distilled at atmospheric pressure in a small total-reflux partial-takeoff column in order to recover excess olefin. The residue was chromatographed through 50 g of Woelm neutral alumina (column 250 × 23 mm) with 250 ml of pentane to remove Aliquat 336. The solvent was then fractionally distilled at atmospheric pressure, and the residue was distilled at reduced pressure to afford the carbene adduct. Yields are based on isolated material obtained after distillation and calculated from the amount of 1-(acetylaminomethyl) alcohol used.

When addition products from alkylidene carbenes and valuable olefins are required, moderate yields (40–50%) may be obtained by using only 2 equivalents of olefin in pentane as the solvent. Furthermore since all solvent removal processes involve fractional distillation, the excess olefin may be recovered.

4-Cyclohexylidenebicyclo[3.1.0]hex-2-ene (5). The above procedure[19] [from 50 mmol of 1-(*N*-acetylaminomethyl)cyclohexanol] afforded 6.1 g (76%) of **5**; bp 125–130° (25 mm); uv max (cyclohexane) 260 mμ (ϵ 24,500) [lit.[20] uv max (ethanol) 257 mμ (ϵ 12,780)]; pmr 6.00 (m, 2, vinyl), 2.22 and 2.05 (m, 6, allylic), 1.58 (m, 6, aliphatic), 0.82 (triplet of doublets, 1, exo cyclopropyl), and 0.15 (q, 1, endo cyclopropyl); mass spectrum *m/e* 160.

Anal.[21] Calcd for $C_{12}H_{16}$: C, 90.0; H, 10.0. Found: C, 90.3; H, 10.0.

The above procedure was repeated except that the cyclopentadiene was diluted with an equal volume of pentane (to reduce dimerization) and the reaction mixture was never warmed above 30°. The solvents were evaporated at reduced pressure at or below room temperature. The final product (5.2 g, 65%), which was not distilled (pmr analysis showed no dicyclopentadiene), was identical with the **5** obtained above. The lower yield is due to the loss incurred when the fractional distillation of solvent and excess cyclopentadiene was omitted. Since the primary adduct is apparently not stable at room temperature or somewhat lower we made no further efforts to elucidate its structure.

The structure of **5** was elucidated[22] by recording the pmr spectrum on an HA 100 nmr in frequency sweep mode, locked internally on chloroform. Since irradiation at 0.82 and 0.15 had no effect on the vinyl hydrogens (6.00), structure **6** is eliminated. Furthermore, the cyclopropyl hydrogens of **6** are allylic and are not expected to display such high-field signals as those observed. Structure **7** (in ref 9) is eliminated by the lack of symmetry observed in the pmr and by the fact that it has no cyclopropyl hydrogens.

7-Cyclohexylidenebicyclo[4.1.0]hept-3-ene (8). The above general procedure was used (for a 25-mmol run) to afford 2.8 g (65%) of **8**: bp 85–95° (1 mm); pmr 5.38 (m, 2, vinyl), 2.30 and 2.19 (m, 8, allylic), 1.50 and 1.38 (m, 8, aliphatic and allylic cyclopropyl); mass spectrum *m/e* 174.

Anal. Calcd for $C_{13}H_{18}$: C, 89.7; H, 10.4. Found: C, 89.7; H, 10.3.

3-Cyclohexylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (9). The above general procedure was used (for a 25-mmol run) to afford 3.2 g (69%) of **9**: bp 75-80° (<1 mm); pmr 6.20 (t, 2, H_6 and H_7, see numbering in **9**, eq 3), 2.83 (m, 2, H_1 and H_5), 2.12 (m, 4, allylic on the cyclohexylidene fragment), 1.51 (m, 6, aliphatic on the cyclohexylidene fragment), 1.38 (d, 2, H_2 and H_4), and 0.93 (m, 2, H_8). Further structure proof was based on the product obtained from the thermal rearrangement and subsequent oxidation to LeBel and Liesemer's ketone.[18]

3-Isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (11) was prepared according to the general procedure (50-mmol run) except 5,5-dimethyl-*N*-nitrosooxazolidone[5a] was used as the isopropylidenecarbene precursor to afford 2.90 g (35%) of **11**: bp 35° (<1 mm); pmr 6.28 (t, 2, H_6 and H_7), 2.88 (m, 2, H_1 and H_5), 1.75 (t, 6, allylic methyls), 1.40 (broad singlet, 2, H_2 and H_4), 0.98-0.88 (m, 2, H_8); these data agree with those reported.[11]

Thermal Treatment of 8. Heating **8** neat for 10 min or 1 hr below 180° had no effect on the pmr spectrum. When **8** was heated at 195°, it quickly darkened. After 10 min the vinyl and allylic signals in the pmr spectrum changed, the vinyls moved to δ 5.95-5.80 and the allylic signals became very broad. Glpc indicated that a good portion of the material was no longer volatile and the volatile material contained several components.

3-Cyclohexylidenetetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (10). A sample of **9** was heated for 20 min at 150° to afford **10** (quantitative by glpc): bp 110-115° (1 mm); pmr 2.3 (m, 4), series of peaks between 2.0 and 1.2 (14 H), no signals below 2.4; mass spectrum *m/e* 186.

Anal. Calcd for $C_{14}H_{18}$: C, 90.3; H, 9.7. Found: C, 90.6; H, 9.5.

Tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octan-3-one (18). To a well-stirred mixture of 186 mg (1 mmol) of **10** and 6 drops of Aliquat-336[6] in 2 ml of benzene and 4 ml of water was added 634 mg (4 mmol) of potassium permanganate. The suspension was stirred for 2 hr at room temperature, excess sodium sulfite was added, and the suspension was diluted with ether and vacuum filtered through Celite (analytical filter aid) to remove manganese dioxide. The organic layer was washed with water, saturated sodium chloride solution, and filtered through a cone of anhydrous sodium sulfate. Fractional distillation of the solvents afforded an oil which contained 72 mg of **18** (60%) and cyclohexanone. The tetracyclic ketone was shown to be identical with an authentic sample provided by Dr. LeBel: mp 68-70°; mmp 67-69°; ir (CCl_4) 1730 cm^{-1} (C=O); mass spectrum *m/e* 120 [lit. mp 69-71°; ir (CCl_4) 1730 cm^{-1}]; both ketones had identical fragmentation patterns in the mass spectrum.

3-Isopropylidenetetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (12). A sample of **11** was heated for 20 min at 150° to afford **12** (quantitative by glpc): pmr 1.70 (s, 6, allylic methyls), series of multiplets from 2.09 to 1.35 (8 H), no absorption below δ 2.10; these data compare with those in the literature;[11] mass spectrum *m/e* 146; the compound decolorizes Br_2 in CCl_4.

Registry No.—**1**, 37150-64-4; **2**, 542-92-7; **3**, 628-41-1; **4**, 121-46-0; **5**, 50277-68-4; **8**, 50277-69-5; **9**, 50277-70-8; **10**, 50277-71-9; **11**, 50277-72-0; **12**, 42038-54-0; **18**, 873-36-9; A, 20693-98-5; B, 26265-75-8; 1-(*N*-acetylaminomethyl)cyclohexanol, 37150-63-3.

References and Notes

(1) This work was supported by Grant No. 12445 from the National Science Foundation.
(2) This work formed part of the Ph.D. Thesis of M. C. V. Z., The Ohio State University, 1973.
(3) For reviews, see F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970), and P. Dowd, *Accounts Chem. Res.*, **5**, 242 (1972).
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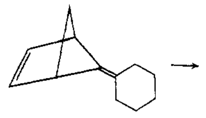
(6) Aliquat 336 is methyltricaprylammonium chloride. Our procedure is based on the phase transfer principle of C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971).
(7) M. S. Newman and Z. ud Din, *J. Org. Chem.*, **38**, 547 (1973).
(8) The proof of structure is given in the Experimental Section.
(9) An alternate, less likely route involves the 1,4 addition of A to **2** to yield 5-cyclohexylidenebicyclo[2.1.1]hex-2-ene (**7**), which could undergo a suprafacial [1,3] sigmatropic rearrangement to give **5**.



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Such a rearrangement has shown to occur in the parent case at about 150° by F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968); see also W. R. Roth and A. Friedrich, *ibid.*, 2607 (1969), and S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969), for other examples.
(10) For the formation of dimers from a trimethylenemethane diradical, see J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Amer. Chem. Soc.*, **93**, 1544 (1971).
(11) R. Bloch, F. Leyendecker, and N. Toshima, *Tetrahedron Lett.*, 1025 (1973). The exo structure for **11** was established by spin-decoupling experiments. We assume **9** to be exo because of the similarity of the nmr data.
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(13) The calculated value at 25° is given by S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, **78**, 592 (1956).
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(19) The dicyclopentadiene which formed during the course of the reaction and work-up was removed by heating the residue obtained after chromatography at 180° and fractionally distilling the cyclopentadiene formed.
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(21) Chemical analyses were performed by The M.H.W. Laboratories, Garden City, Mich. 48135.
(22) We would like to thank Mr. Michael Geckle for performing the spin-decoupling experiments and discussing the results.

Cycloadditions of Pentamethyleneketene. Spiro[5.3]nonanes

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Cycloaddition reactions of pentamethyleneketene to cyclopentadiene, dihydropyran, tetramethylallene, diisopropylcarbodiimide, *N-tert*-butylbenzylimine, and chloral have been investigated as routes to spiro compounds. Pentamethyleneketene is formed *in situ* from the triethylamine dehydrochlorination of cyclohexanecarboxyl chloride and the zinc dehalogenation of α-bromocyclohexanecarboxyl chloride. Dimerization is a serious competing reaction and reactive cycloaddition partners are necessary to successfully compete for the ketene.

The preparation and dimerization of pentamethyleneketene from cyclohexanecarboxyl chloride was reported about 20 years ago.[1] The preparation of this ketene by cracking cyclohexanecarboxylic acid anhydride and prop-