**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 $\delta$ 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 $\delta$ 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.

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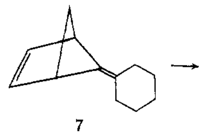
(8) The proof of structure is given in the Experimental Section.

(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**.



7

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.

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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.

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# Cycloadditions of Pentamethyleneketene. Spiro[5.3]nonanes

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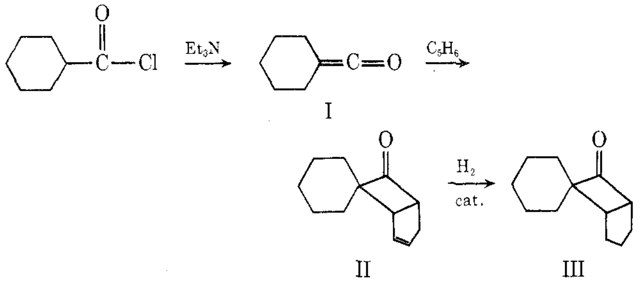
Cycloaddition reactions of pentamethyleneketene to cyclopentadiene, dihydropyran, tetramethylallene, diisopropylcarbodiimide, *N-tert*-butylbenzylimine, and chloral have been investigated as routes to spiro compounds. Pentamethyleneketene is formed *in situ* from the triethylamine dehydrochlorination of cyclohexanecarboxyl chloride and the zinc dehalogenation of $\alpha$-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 properties of the ketene have recently been described.[2] There have been several recent reports on the dimerization and trimerization of this ketene and the chemistry of these oligomers.[3-5] However, cycloaddition reactions of the ketene have not received much attention. Wasserman and coworkers have just recently described the cycloaddition of pentamethyleneketene and ethoxyacetylene to yield a thermally unstable cycloadduct.[6] The cycloaddition of this ketene and sulfur dioxide has also been recently reported.[7]

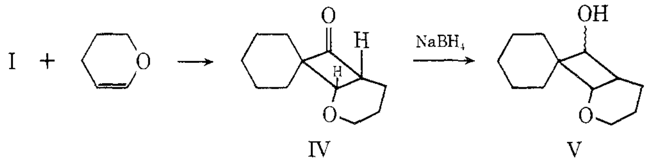
Pentamethyleneketene (I) is quite susceptible to dimerization; *e.g.*, the reaction of cyclohexanecarboxyl chloride with triethylamine produces a good yield of the dimer, dispiro[5.1.5.1]tetradecane-7,14-dione. Therefore, it seemed desirable to effect *in situ* cycloadditions with reactive unsaturated compounds to successfully compete with the dimerization process. This is also the case with $\beta,\gamma$-unsaturated pentamethyleneketene.[8]

We now wish to report on some *in situ* cycloaddition reactions of pentamethyleneketene to yield spiro[5.3]nonanes.

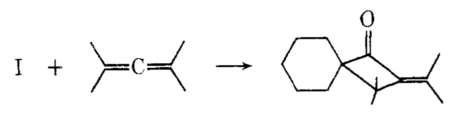
The dehydrochlorination of cyclohexanecarboxyl chloride with triethylamine in the presence of cyclopentadiene resulted in a 65% yield of the spiro[5.3]nonane (II) accompanied by some ketene dimer. The optimum conditions appear to be the dropwise addition of the acid halide to a refluxing solution of triethylamine and cyclopentadiene in benzene and continued refluxing for about 20 hr. A reaction time of this length is necessary because the ketene is slowly formed from the acid halide and amine under these conditions. The use of chloroform as a solvent reduces the reaction time to about 8 hr. Complete separation of this cycloadduct from the dimer was not achieved. Consequently, hydrogenation to the corresponding saturated ketone, III, resulted in a compound which could be purified.



The cycloaddition of pentamethyleneketene with dihydropyran occurred readily and the cycloadduct was isolated in 67% yield (IV). This adduct was also difficult to separate from the ketene dimer and was reduced with sodium borohydride to the corresponding alcohol V, which was easily separated from the ketene dimer and thus completely characterized. Although two regioisomers of this cycloadduct are possible, only one was detected. The presence of the bridgehead protons in the nmr at $\delta$ 4.1 and 3.3 dictates that the isomer indicated is the one produced.[9] This is quite consistent with numerous other ketene cycloadditions where some charge separation in the transition state is indicated.



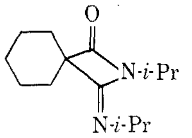
Tetramethylallene cycloadded to pentamethyleneketene to yield an $\alpha,\beta$-unsaturated spiro[5.3]nonane (VI) in 60% yield which was easily purified by recrystallization. Only one regioisomer was detected and this was the expected $\alpha,\beta$-unsaturated adduct, which is the only regioisomer that has been detected in these cycloadditions.[10]



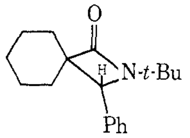
VI

We also investigated the cycloaddition of ethoxyacetylene with pentamethyleneketene and found that while the cycloaddition occurred the cycloadduct was thermally unstable (decomposition occurred upon vacuum distillation) as reported by Wasserman and coworkers.[6]

The *in situ* cycloaddition of pentamethyleneketene with diisopropylcarbodiimide and *N-tert*-butylbenzylimine was also effected. These reactive imino compounds yielded the expected spiroimino-$\beta$-lactam in 51% yield (VII) and the spiro-$\beta$-lactam in 48% yield (VIII).

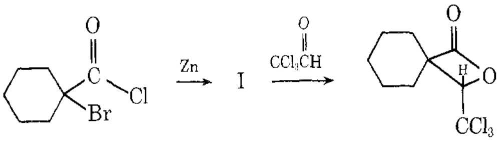


VII



VIII

The dehydrochlorination of cyclohexanecarboxyl chloride in the presence of chloral did not produce the expected spiro 2-oxetanone. Triethylamine readily reacts with chloral, which complicates this *in situ* cycloaddition, and numerous attempts with simultaneous and various orders of additions were unsuccessful. However, the zinc dehalogenation of $\alpha$-bromocyclohexanecarboxyl chloride in the presence of chloral produced a 45% yield of the spiro-2-oxetanone (IX). This 2-oxetanone was quite resistant to decarboxylation, as are other 4-trichloromethyl-2-oxetanones.[11] This method of generating pentamethyleneketene offers the advantage of not having a reactant which reacts with chloral, and also the by-product in this reaction, zinc halide etherate, activates the carbonyl compound for cycloaddition. The ketene dimer is also produced by this method of generation.



IX

The attempted cycloaddition of cyclohexene with pentamethyleneketene by both the dehydrohalogenation and dehalogenation methods were unsuccessful. It should be emphasized that all the successful cycloadditions described above involve activated unsaturated compounds. Pentamethyleneketene undergoes cycloaddition with activated unsaturated compounds readily but the reaction is always accompanied with ketene dimer. Consequently, if unactivated olefins such as cyclohexene are employed, dimerization occurs completely at the expense of cycloaddition with the olefin. Other unsaturated compounds which were investigated with little or no success included phenylacetylene, 5-methylene-2-norbornene, ethyl thioisocyanate, quinone, *p*-chlorobenzaldehyde, and *N*-phenylbenzalaniline.

In summary, the generation of pentamethyleneketene by the dehydrohalogenation and/or dehalogenation method in the presence of reactive unsaturated compounds gives a good yield of the [2 + 2] cycloaddition product, which is a spiro[5.3]nonane. All cycloadditions are accompanied by ketene dimer. Unactivated or less reactive cycloaddition partners do not successfully compete with the dimerization process.

## Experimental Section

Proton nmr spectra were recorded on Jeolco Minimar 60-MHz and Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and $CCl_4$ as the solvent unless otherwise noted. Solvents and triethylamine were distilled from sodium and stored over Linde type 4-A molecular sieve. Tetramethylallene was obtained by the $AlC_3$-catalyzed rearrangement of the tetramethylcyclobutadione dimer of dimethylketene followed by pyrolysis over a hot wire. *N-tert*-Butylbenzylimine was prepared from benzaldehyde and *tert*-butylamine according to standard procedure.

**General Procedure for Preparation of Pentamethyleneketene by the Dehydrohalogenation Method.** A solution of 0.1 mol of cyclohexanecarboxyl chloride in 50 ml of dry benzene was added dropwise to a refluxing solution of 0.15 mol of triethylamine and 0.2–0.3 mol of an unsaturated compound in 150 ml of dry benzene. After completion of the addition, refluxing was continued for about 20 hr. The amine salt was removed by filtration and washed with benzene. Concentration afforded the crude cycloadduct. Vacuum distillation or recrystallization resulted in purification of the pentamethyleneketene adduct.

**Pentamethyleneketene Cyclopentadiene Adduct (II).** This adduct was obtained in 65% yield at 67–69° (0.1 mm): ir 1767 (C=O), and 1601 cm$^{-1}$ (C=C); nmr $\delta$ 1.50 (m, 10 H), 2.42 (m, 2 H), 3.15 (m, 1 H), 3.75 (two t or three d, 1 H), and 5.70 (m, 2 H).

After two distillations, this adduct contained a small amount of the ketene dimer as an impurity. Consequently, the cycloadduct was hydrogenated in ethanol under 50 psi of hydrgoen employing platinum oxide as a catalyst. An 80% yield of the saturated spiro ketone (III) resulted at 57–58° (0.08 mm): nmr $\delta$ 1.7 (m, 16 H), 2.52 (two t or three d, 1 H), and 3.65 (two t or three d, 1 H).

*Anal.* Calcd for $C_{12}H_{18}O$: C, 80.89; H, 10.11. Found: C, 80.63; H, 9.75.

**Pentamethyleneketene Dihydropyran Cycloadduct (IV).** This cycloadduct was produced in 67% yield at 90–92° (0.2 mm): ir 1767 cm$^{-1}$ (C=O); nmr $\delta$ 1.60 (m, 14 H), 3.30 (two d or three t, 2 H), 3.80 (two t or three d, 1 H), and 4.10 (d, 1 H).

This compound was also contaminated with the ketene dimer and was reduced with sodium borohydride in ethanol. The corresponding alcohol (V) was recrystallized from ether: mp 53–55°; ir 3450 cm$^{-1}$ (OH); nmr $\delta$ 1.42 (m, 14 H), 2.1–2.6 (s, H of OH), 2.43 (m, 1 H), 3.30 (m, 1 H), and 3.80 (m, 3 H).

*Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.46; H, 10.21. Found: C, 73.28; H, 9.99.

**Pentamethyleneketene Tetramethylallene Cycloadduct (VI).** A 60% yield of a crystalline solid which was recrystallized from ethanol was obtained: mp 47–48°; ir 1725 (C=O) and 1639 cm$^{-1}$ (C=C); nmr $\delta$ 1.28 (s, 6 H), 1.84 (s, 3 H), 2.08 (s, 3 H), and 1.25–2.0 (m, 10 H); the three singlets are out of the multiplet at 1.25–2.0. The chemical shift values for the unequivalent methyl protons attached to the vinyl linkage and the equivalent methyl protons on the $\beta$ carbon are in excellent agreement with other tetramethylallene ketene cycloadducts.[10,11]

**Pentamethyleneketene Diisopropylcarbodiimide Cycloadduct (VII).** This adduct was prepared in 51% yield and was recrystallized from ether: mp 83–85°; ir 1818 (C=O) and 1686 cm$^{-1}$ (C=N); nmr $\delta$ 1.20 (d, 6 H), 1.48 (d, 6 H), 1.94 (m, 10 H), and 3.80 (m, 2 H).

*Anal.* Calcd for $C_{14}H_{24}ON_2$: C, 71.19; H, 10.18; N, 11.86. Found: C, 71.31; H, 10.56; N, 11.36.

**Pentamethyleneketene *N-tert*-Butylbenzylimine Adduct (VIII).** The cycloadduct was obtained in 48% yield and was recrystallized from ether: mp 105–106°; ir 1748 cm$^{-1}$ (C=O); nmr ($CDCl_3$) $\delta$ 1.30 (s)and 1.60 (m) (accounts for 19 H), 4.35 (s, 1 H), and 7.30 (s, 5 H).

*Anal.* Calcd for $C_{18}H_{25}NO$: C, 79.70; H, 9.22; N, 5.16. Found: C, 80.00; H, 9.03; N, 5.08.

**Pentamethyleneketene Chloral Adduct (IX).** To a mixture of 0.3 mol of activated zinc and 0.2 mol of freshly distilled chloral in 100 ml of dry ether containing a trace of $AlCl_3$ with vigorous stirring was added dropwise a solution of 0.1 mol of $\alpha$-bromocyclohexanecarboxyl chloride in 15 ml of ether. After the addition was complete, the reaction mixture was refluxed for 24 hr. The unreacted zinc was removed by filtration and the filtrate was concentrated on a rotatory evaporator. The residue was extracted with three 50-ml portions of $CCl_4$ to extract the cycloadduct from the zinc halide etherate. The combined extracts were concentrated and distilled under vacuum. The condensate solidified and was recrystallized from ethanol: mp 77–78°; ir 1837 cm$^{-1}$ (C=O); nmr $\delta$ 1.80 (m, 10 H) and 4.57 (s, 1 H).

*Anal.* Calcd for $C_9H_{11}Cl_3O_2$: C, 41.94; H, 4.27. Found: C, 41.78; H, 3.93.

**Acknowledgments.** The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

**Registry No.**—I, 22589-13-5; II, 50515-89-4; III, 50515-91-8; IV, 50515-90-7; V, 50515-92-9; VI, 50515-93-0; VII, 50515-94-1; VIII, 50515-95-2; IX, 50515-96-3.

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