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SOME CYCLOADDITION REACTIONS OF HALOMETHYLENECYCLOPROPANES†

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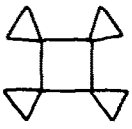
Abstract—Bromo-, chloro- and ethoxymethylenecyclopropane 3–5 undergo head to head dimer zations at 185–195° to give the corresponding 7,8-disubstituted dispiro[2.0.2.2]octanes 6–8 in high yields. Chloromethylenecyclopropane 4 undergoes cross cycloaddition reactions with near equimolar amounts of 3 and 5 to give about 50% of the corresponding mixed 7,8-disubstituted dispiro[2.0.2.2]octanes together with equal parts of 6 and 7 or 6 and 8. Bromo- and chloromethylenecyclopropane also undergo similar cross cycloaddition reactions with methylenecyclopropane to give the 7-halodispiro[2.0.2.2]octanes, but in relatively poor yields. At 190°, 4 reacts with 1,3-cyclopentadiene, furan, and 1,3-cyclohexadiene to give the products of (2+4) cycloaddition 12–14. With 2,3-dimethyl-1,3-butadiene at 190°, 4 gives the unusual products 18–20 in yields of 35%, 8% and 13%, respectively, and with acrylonitrile 4 gives exclusively 21, the product of (2+2) cycloaddition. Relative reactivities of 4 with furan, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, acrylonitrile and 1,3-cyclopentadiene were estimated as 1:2.5:2.5:4: and 50, respectively.

There has been considerable recent interest in thermally-induced cycloaddition reactions of methylenecyclopropanes. Although dichloromethylenecyclopropane undergoes head to head dimerization readily in excellent yield at 100°,[1] heating of other methylenecyclopropanes has been reported to give little or no dimer by way of (2+2) cycloaddition. Methylenecyclopropane was found to undergo only about 20% dimerization in 48 hr at 245°.[2] Biscyclopropylidene formed the thermal (2+2) cycloadduct 1 in 15% yield in 1 hr at 210°; however, methylenespiropentane 2, the product of isomerization, was formed concurrently in 40% yield.[3]



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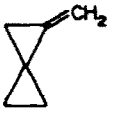

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The results for cyclopropylidenecyclobutane are apparently poor; the compound was reported to undergo thermal (2+2) cycloaddition at 210°, but no yield was given.[4] There was apparently no dimerization observed for ethylidenecyclopropane at temperatures up to 234°,[5] and Dolbier *et al.* were unable to detect any thermal (2+2) dimerization upon heating isopropylidenecyclopropane at 245° for 80 hr.[4] Benzylidenecyclopropane undergoes no reaction below 190°; above that temperature, it rearranges to 1-phenyl-3,4-dihydronapthalene with no dimerization reported.[6] Interestingly, although tetrafluoroethylene and other alkenes with a double bond substituted by 2 fluorines readily undergo thermally-induced (2+2) dimerization, perfluoromethylenecyclopropane does not dimerize on heating at 150° for 24 hr;[7] on the other hand it readily undergoes (2+4) cycloaddition reactions as well as a (2+2) cycloaddition with quadricyclene.[8] Biscyclopropylidene also undergoes mixed (2+2) cycloaddition reactions with 1,3-butadiene and 1,3-cyclohexadiene and a (2+4) cycloaddition reaction with 1,3-cyclopentadiene,[9] and dichloromethylenecyclopropane undergoes a facile (2+2) cycloaddition reaction with 1,3-butadiene.[10]

We report here our study of cycloaddition reactions of the mono-*exo*-substituted methylenecyclopropanes 3–5. These compounds are relatively easy to prepare in quantity and they appear to be useful intermediates for the preparation of dispiro[2.0.2.2]octanes, dispiro[2.0.2.2]oct-7-ene,[11] and spiro[2.3]hexanes, as well as other systems that contain a spirocyclopropane.

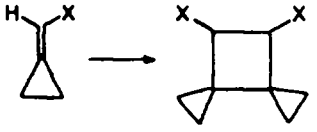
3: X = Br
4: X = Cl
5: X = OC_2H_5

Following the procedure Köster *et al.*,[12] methylenecyclopropane was brominated at −75° to obtain 1-bromo-1-bromomethylcyclopropane in 90% yield. Treatment of the dibromide with sodium amide in THF converted it in 90% yield to bromomethylenecyclopropane 3. Similarly, methylenecyclopropane was converted to 1-chloro-1-chloromethylcyclopropane in 36% yield by chlorination at −75°, and treatment of the dichloride with sodium amide in THF gave an 80% yield (at 40% conversion) of chloromethylenecyclopropane 4. When the dehydrochlorination was carried out with potassium hydroxide in ethanol, the yield of 4 was 26%, and a 25% yield of 1-chloro-1-ethoxymethylcyclopropane was also obtained. The chloroether, on treatment with sodium amide in THF, gave a 90% yield of ethoxymethylenecyclopropane 5.

On heating under autogenous pressure at 185–195° for 1.5 hr with a small amount of diphenyl ether as internal standard, 3, 4 and 5 gave 67–80% conversions to mixtures of the *cis*- and *trans*-head to head dimers, the 7,8-disubstituted dispiro[2.0.2.2]octanes 6–8 (eqn 1). The

†From the Ph.D. Dissertation of L. J. Cabral, University of California, Davis (1975).

structures of 6 and 7 were established by dehalogenation to dispiro[2.0.2.2]oct-7-ene.[11] The stereochemical assignments to the dibromides 6 were based on their relative thermal stabilities, the *cis* isomer being the less stable, and their relative reactivities with LAH,[11] the *trans* isomer being the more reactive. The ^{1}H NMR spectra of the isomers are consistent with the assigned stereochemistry. The cyclobutyl protons of the *trans* isomer are more shielded (δ 4.80 ppm) than those of the *cis* isomer (δ 5.00 ppm), which is what has been observed for the α-protons of *cis*- and *trans*-1,2-dibromocyclobutane.[13] Also, in more rigid 2,3-dihalonorbornanes and 5,6-dihalonorbornenes, it has been observed that α-protons are shielded by an eclipsing bromine or chlorine.[14] The shorter GLPC retention time of *trans*-6 relative to that of *cis*-6 is also consistent with the assigned stereochemistry.[15] The structural assignment to 8 and the stereochemical assignments to *cis*- and *trans*-7 and 8 were made on the basis of their ^{1}H NMR spectra, mass spectra, and GLPC retention times.

(1) 

6: X = Br
7: X = Cl
8: X = OC_2H_5

Almost certainly, the dimerization of 3, 4 and 5, as well as the other reactions studied that give dispiro-[2.0.2.2]octanes (see below) occur in a stepwise fashion and involve biscyclopropylcarbinyl diradicals.[16,17] No evidence was obtained from any of these reactions which indicated that any of the corresponding head to tail dimer was formed. Conversions of more than 1% to such dimers would not have gone undetected, provided that these dimers are stable under the reaction conditions. For the reactions leading to 6, 7 and 8, the *trans* isomer was favored slightly, and it made up 53–57% of the dispiro[2.0.2.2]octane.

Ethoxymethylenecyclopropane 5 gave the cleanest reaction with less than 1% of it giving product other than the dimer 8.

Compared with the thermal dimerization of the bromide 3, the chloride 4 gave a clean reaction. After 1.5 hr at *ca.* 190°, only 6% of the 4 was converted to products other than the dimer 7; and the product of isomerization, 1-chloro-2-methylenecyclopropane, made up about half of the side products. The other side products were not investigated.

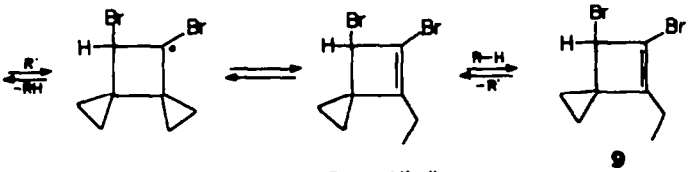
Bromomethylenecyclopropane 3 gave a number of side products that accounted for 11% of the starting 3 after 1.5 hr and >20% after 2.3 hr. These side products (Experimental) appear to arise from decomposition of the starting material and/or products in part to hydrogen bromide and subsequent reactions of hydrogen bromide with 3 and other side products. Addition of Proton Sponge (1,8-bis-(dimethylamino)naphthalene) greatly reduced the amount of side products. But because of both the slower reaction rate due to dilution of 3 and the slow decomposition of the 7,8-dibromodispiro-[2.0.2.2]octanes 6, the modified reaction conditions did not improve the yield of 6.

The most remarkable of the side products from the dimerization of 3 was identified as 5,6-dibromo-4-ethylspiro[2.3]hex-4-ene 9 on the basis of its mass spectrum and its particularly informative ^{1}H NMR spectrum. The resonance due to the methylene protons of the Et group at δ 1.95 ppm is a quartet (J = 7.0 Hz) of doublets (J = 1.5 Hz), the latter splitting due to across the ring coupling[18] with the proton at C_6 (δ 4.78 ppm, t, J = 1.5 Hz). What we believe to be the mechanism of formation of 9 is shown as eqn (2) (see Ref. 19).

The fact that 9 survived the reaction conditions might seem surprising until it is realized that (1) 3-bromocyclobutenes are *relatively* slow to solvolyze,[20] and (2) further cyclopropylcarbinyl→allylcarbinyl rearrangement of this seemingly doubly activated molecule would lead to a cyclobutadiene.

Extensive heating of mixtures of *cis*- and *trans*-6 caused significant decreases in the *cis*:*trans* ratio and extensive decomposition to a dark viscous material. On heating samples of the pure isomers in the liquid phase at 190° or 300°, it was observed that *cis*-6 was isomerized to *trans*-6. This isomerization as well as the decomposition of both isomers could come about by either free-radical pathways involving the first intermediate in eqn 2 or a carbocation pathway such as is believed to account for the isomerization of methylenecyclopropylcarbinyl chloride to 3-methylenecyclobutyl chloride in diphenyl ether at 217°.[21] A third mechanism involving partial cycloreversion to biscyclopropylcarbinyl diradicals seems unlikely because isomerization of *cis*-6 to *trans*-6 does not occur in the gas phase at 350°.

In order to estimate the relative reactivities of 3–5, reactions of *ca.* 1:1 mixtures of 3 and 4 and of 4 and 5 were investigated at 190–195°. In addition to 6 and 7 and 7 and 8, these reactions gave, respectively, *cis*- and *trans*-7-bromo-8-chlorodispiro[2.0.2.2]octane 10 and *cis*- and *trans*-7-chloro-8-ethoxydispiro[2.0.2.2]octane 11. Structural and stereochemical assignments to 10 and 11 were made on the basis of their mass and ^{1}H NMR spectra. As with 6–8, the cyclobutyl protons of the *trans* isomers were observed to be more shielded than those of the *cis* isomers. The mixed dimer made up *ca* 50% of the product from both reactions, which shows that 3, 4 and 5 react at similar rates in the thermally-induced reactions at 190–195° leading to dispiro[2.0.2.2]octanes. Thus, the 3 different substituents are about equally effective in promoting the dimerizations. The implication from this is that the transition state leading to the α,α-disubstituted biscyclopropylcarbinyl-diradical intermediate is more reactant-like than product-like. Otherwise, for example, the greater ability of chlorine than bromine in stabilizing an adjacent free-radical center[22] would lead to significantly more rapid reaction of 3 than 4. And this would have resulted in significantly less of the mixed

(2) 6 

9

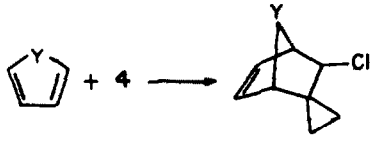
(R = Br or Alkyl)

dimer **10** than was observed from the reaction of the equimolar mixture of **3** and **4**.

Similar mixtures of bromomethylenecyclopropane **3** and methylenecyclopropane and of chloromethylenecyclopropane **4** and methylenecyclopropane (initial mole ratios: 5 to 4) on heating to 190–195° for 2 hr each gave 5:1 mixtures of the corresponding 7,8-dihalodispiro-[2.0.2.2]octanes and 7-halodispiro[2.0.2.2]octanes. No evidence was obtained from these reactions which indicated the concurrent formation of the unsubstituted dispiroöctane. These reactions, carried out with larger methylenecyclopropane: 3 or 4 ratios, appear to be the most convenient method of preparing the 7-halodispiro-[2.0.2.2]octanes (see Ref. 11).

As chloromethylenecyclopropane **4** gave much cleaner reactions than bromomethylenecyclopropane **3**, thermal cycloaddition reactions of **4** rather than the more accessible **3** were studied with a number of other reagents.

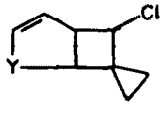
At 190°, chloromethylenecyclopropane undergoes (2+4) cycloaddition reactions with 1,3-cyclopentadiene, furan and 1,3-cyclohexadiene to give respectively, *endo*- and *exo*-8-chloro-4,7 - methanospiro[2.5]-oct-5-ene **12**, 8-chloro-4,7-epoxyspiro[2.5]oct - 5-ene **13**, and 8 - chloro-4,7-ethanospiro[2.5]oct-5-ene **14** (eqn 3).

(3) 

12: Y = CH_2; **13**: Y = O
14: Y = CH_2CH_2

The structural and stereochemical assignments to **12–14** were made on the basis of comparison of their ^1H NMR spectra with those of similarly constituted compounds.[14,23] The low-field chemical shifts and symmetrical or near symmetrical splitting patterns of the vinyl protons (analyzable under modest resolution as the AB part of an ABMN-pattern for **12** and **13**; more complex and less symmetrical for **14**) are clearly consistent with the assigned structures and inconsistent with those of products that would be expected from an alternate stepwise (2+2) cycloaddition,[23a,b] i.e. **15–17**. The splittings observed for the C_8-protons of **12** and **13** ($J < 5$ Hz) are also consistent with the assigned structures[14] and inconsistent with that expected (≥ 5 Hz)[23b] for the α-chloro protons of **15** and **16**. The stereochemical assignments were based on the generalization that an *endo* proton is more shielded than a similarly bonded *exo* proton,[14,23b] and, for **12** and **13**, that vicinal coupling of the bridgehead proton with an *exo* proton is greater than with a similarly bonded *endo* proton.[14] Interestingly, although LeBel *et al.*[14] found that spin–spin interaction between *endo* protons and bridgehead protons was ≈0 in a number of 5,6-dihalobicyclo[2.2.1]heptanes, we could detect such a coupling ($J \leq 1.6$ Hz) in *endo*-**12** and **13**.

In the absence of evidence that might be obtained through the use of N,N-di-t-butylnitroxide to trap intermediate diradicals,[24] reactions leading to **12–14** should be looked upon as concerted cycloadditions.[16] When a large excess of *cis*-1,3-diene was not used in these reactions, there was competing formation of *cis*- and *trans* - 7,8 - dichlorodispiro[2.0.2.2]octane **7**. The reaction of **4** with 1,3-cyclohexadiene gave a minor (5%) unidentified product that might be the cross (2+2) cycloaddition product **17**; 1,3-cyclopentadiene and furan gave no detectable products (<1%) with **4** other than **12** and **13**. 1,3-cyclopentadiene was the most reactive of the *cis*-1,3-dienes toward **4**, and furan was the least reactive. Use of a starting 4:1 volume ratio of *cis*-1,3-diene:**4** gave molar ratios of 98:2, 62:38 and 80:20 for **12**:**7**, **13**:**7** and **14**:**7**, respectively.



15: Y = CH_2; **16**: Y = O; **17**: Y = CH_2CH_2

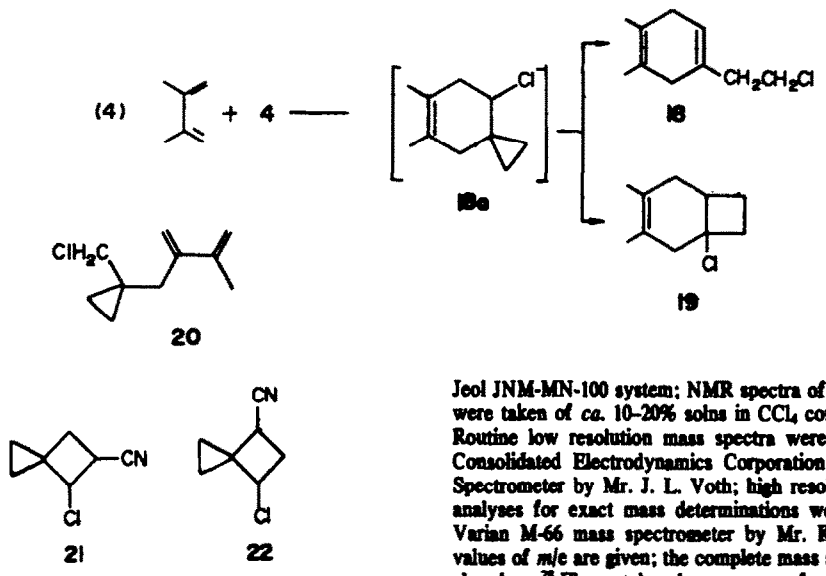
It was found that the relative amounts of *endo*- and *exo*-**12** obtained from **4** and 1,3-cyclopentadiene varied with the length of time that the reaction mixture was heated. After 10 min, when the reaction was almost complete, the *endo*-**12**:*exo*-**12** ratio was 86:14. This ratio decreased steadily to 22:78 after heating for 5.5 hr at 190°. We suspect that equilibration of *endo*- and *exo*-**12** at 190° takes place by reversal of the (2+4) cycloaddition, a pathway which has ample precedent.[25]

A 4:1 volume ratio of 2,3-dimethylbutadiene and chloromethylenecyclopropane **4**, on heating at 190° for 1 hr, gave products identified as 4 - (2 - chloroethyl) - 1,2 - dimethyl - 1,4 - cyclohexadiene **18**, 1 - chloro - 3,4 - dimethylbicyclo[4.2.0]oct - 3 - ene **19**, and 1 - chloromethyl - 1 - (2 - methylene - 3 - methylbut - 3 - en - 1 - yl)cyclopropane **20** in yields of 35%, 8%, and 13%, respectively. These structural assignments followed from mechanistic considerations and interpretation of the straightforward ^1H NMR spectra of the products. Thus, products **18** and **19** are presumed to arise via the (2+4) cycloaddition product **18a** (eqn 4), which undergoes cyclopropylcarbinyl rearrangements under the reaction conditions,[26] and compound **20** is the product of an "ene reaction."[27] (This reaction was not studied at a lower temperature, at which it might be possible to isolate **18a**.) As no other products that might be formed by a stepwise reaction involving diradicals were observed from the reaction of **4** and 2,3-dimethylbutadiene, it seems best to regard **20** as the product of a concerted process.[27]

The behavior of **4** and 2,3-dimethylbutadiene at 190° differs markedly from that of *exo*-dichloromethylenecyclopropane and 1,3-butadiene at 80°, which undergo exclusive (2+2) cycloaddition.[10] It should be noted that the higher temperature of the former reaction and the methyl substitution of the diene system increase the relative population of the *cis*-oid diene, which is required for the concerted (2+4) cycloaddition reaction.

On heating at 196° for 2 hr, a 4:1 volume mixture of acrylonitrile and chloromethylenecyclopropane **4** gave an 85% yield of a 5:4 mixture of *trans*- and *cis* - 4 - chloro - 5 - cyanospiro -[2.3]hexane **21**. The remainder of the **4** had dimerized to **7**. The ratio of **21**:**7** was almost 7:1. Note that **21** is the product that would be expected to be the principal product on the basis of a stepwise mechanism involving diradicals.[17] None of the [2+2] cycloaddition product with the alternate orientation, i.e. **22**, was detected.

The structural and stereochemical assignments to *cis*- and *trans*-**21** were made on the basis of their ^1H NMR spectra, which were incompatible with structure **22**. The major diagnostic features as to structure were the doublets, $J_r = 7.1 \pm 0.2$ Hz, observed for the C_4 protons at δ



4.58 and δ 4.68 ppm, respectively, for *cis*- and *trans*-21. The corresponding resonances of 22 are expected to be more complex.[18b] This expectation is strengthened by the observed patterns of the C_5-protons of *cis* and *trans*-21, which are strongly coupled to both vicinal methylene protons. The absolute values of the geminal coupling constants for the C_6 protons of *cis*- and *trans*-21, which are expected to be $\lesssim -11$ Hz.[18b] are apparently much greater than the corresponding chemical shifts. This simplifies the 60-MHz spectrum of *cis*-21 to an apparent quartet at δ 3.74 ppm (C_5–H) and an apparent doublet at δ 2.57 ppm (C_6–H_2). The smaller chemical shifts between the C_5- and C_6-protons of *trans*-21, which is the basis for the stereochemical assignments,[13,14] lead to slightly more complex patterns for their resonances.

The result with acrylonitrile shows that 4 (and presumably 3 and 5) can undergo a very efficient and selective (2+2) cross cycloaddition reaction with a suitably constituted alkene. However, when similar attempts were made to bring about a thermal (2+2) cycloaddition reaction of 4 with styrene or with *cis*-stilbene, all attempts were unsuccessful. It is possible that steric hindrance, which appears to play a role in preventing cycloaddition reactions of methylenecyclopropanes,[4] may have been the decisive factor in preventing cycloadditions of 4 with styrene and *cis*- and *trans*-stilbene.

An approximation was made of the relative reactivities of the compounds which underwent cross cycloaddition reactions with chloromethylenecyclopropane 4. The amount of cross cycloaddition product formed between the particular reagent and 4 was compared with the amount of dimer 7 formed in the competing reaction. The relative ability of each reagent to compete with 4 for 4 was normalized so that the least reactive reagent, furan, was assigned a relative reactivity of unity. In this way, the relative reactivities of 2,3-dimethybutadiene, 1,3-cyclohexadiene, acrylonitrile, and cyclopentadiene were estimated to be 2.5, 2.5, 4 and 50, respectively.

EXPERIMENTAL

Temps. are uncorrected. IR spectra were obtained with a Beckman IR-8 with polystyrene calibration, and only selected frequencies are reported. NMR spectra were obtained at 60 MHz with a Varian Associates A-60A system and at 100 MHz with a Jeol JNM-MN-100 system; NMR spectra of purified compounds were taken of *ca.* 10–20% solns in CCl_4 containing 1–2% TMS. Routine low resolution mass spectra were determined with a Consolidated Electrodynamics Corporation Type 21-104 Mass Spectrometer by Mr. J. L. Voth; high resolution mass spectral analyses for exact mass determinations were obtained with a Varian M-66 mass spectrometer by Mr. K. Miyano. Selected values of *m/e* are given; the complete mass spectra are recorded elsewhere.[28] Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. GLPC work was done with a Varian Aerograph Model 90-P gas chromatograph. Columns used were: *A*—5' 10% SF-96; *B*—10' 20% FFAP; *C*—3' 20% FFAP; *D*—5' 20% Carbowax 20M; columns were 3/8" O.D., and 30/60 Chromosorb W was used as the solid support. Preparative reactions, other than thermal cycloadditions (see below), were run under a positive N_2 atmosphere.

1-Chloro-1-chloromethylcyclopropane (*cf* Ref. 29). To a stirred soln of 500 ml $HCCl_3$ and 500 ml CCl_4 at −75° was added 467 g (8.65 mole) of methylenecyclopropane.[12] The reaction flask was wrapped with Al-foil, and Cl_2 was bubbled slowly into the mixture at −75° via a syringe needle until nearly all of the methylenecyclopropane had reacted (2 days). The yields of 1-chloro-1-chloromethylenecyclopropane,[29] 3-chloro - 2 - chloromethylpropene,[29,30] and 1,2,3 - trichloro - 2 - chloromethylpropene,[29,30] as estimated by NMR spectroscopy, were 36%, 48% and 7%; about 9% of the methylenecyclopropane was unreacted or unaccounted for. Preliminary distillation gave a 470-g fraction that was 70% 1 - chloro - 1 - chloromethylenecyclopropane, b.p. 127–128°, and 30% 3 - chloro - 2 - chloromethylpropane, b.p. 136–137° (lit.[31] b.p. 137–138°), which was suitable for preparation of chloromethylenecyclopropane using KOH in ethanol (see below).

Halomethylenecyclopropanes

(A) *Dehydrohalogenation with sodium amide.* To a magnetically stirred slurry of 4.0 g (0.11 mole) of sodium amide (Ventron, Alfa Inorganics) and 30 ml of THF (redistilled from LAH) was added 16.1 g (0.075 mole) of 1 - bromo - 1 - bromomethylcyclopropane.[29,32] The mixture was stirred at room temp for 1 week, when GLPC analysis (Column D at 140°) showed only a small amount of dibromide remaining. The mixture was added to 100 ml pentane and 100 ml ice water, and the phases were separated. The aqueous layer was extracted with pentane (2 × 50 ml). The pentane extracts were combined with the original pentane soln, and this soln was washed with satd NaCl soln (20 × 200 ml) to remove the THF, dried ($MgSO_4$), and distilled to give 9.0 g (90%) of 3, b.p. 106–108°, NMR δ 6.35 (p, J = 2.0 Hz, 1H), 1.20–1.40 ppm (m, 4H); IR, 1790, 1740 cm^{-1}; ms, *m/e* (rel intensity) 135 (0.8), 134 (16), 133 (0.9), 132 (17), 53 (100) [lit.[33] NMR δ 6.30–6.45 (1H), 1.25–1.45 ppm (4H)].

Essentially the same procedure, but at 40°, with 1 - chloro - 1 - chloromethylenecyclopropane gave *ca.* 80% yields of 4, based on recovery of about half of the starting dichloride.

Chloromethylenecyclopropane. b.p. 82–84°; NMR δ 6.30 (p, J = 2 Hz, 1H), 1.30 ppm (apparent d, J = 2 Hz, 4H); IR 1800, 1750 cm^{-1}; ms, *m/e* (rel intensity) 91 (0.5), 90 (9.4), 89 (1.7), 88 (29.3), 53 (100). C, 54.14; H, 5.58; Cl, 40.05 (C_4H_5Cl requires: C, 54.26; 5.69; Cl, 40.04).

(B) *Dehydrohalogenation with KOH in ethanol-preparation of*

1 - *chloro* - 1 - *ethoxymethylcyclopropane.* A soln was prepared from 250 g (3.76 mole) of 85% KOH and 750 ml of 95% EtOH and cooled to room temp. To the stirred soln was added in portions 470 g (3.76 mole) of 70% 1 - chloro - 1 - chloromethylcyclopropane: 30% 3 - chloro - 2 - chloromethylpropene. The mixture was maintained at reflux for 3 hr, 200 g (3.00 mole) of additional 85% KOH was added, and the stirred soln was maintained at gentle reflux overnight. The mixture was cooled and added to 500 ml pentane and 500 ml ice water. The phases were separated, and the aqueous phase was extracted with pentane (6 × 125 ml). The pentane solns were combined, washed with ice water (12 × 2 l), dried ($MgSO_4$) and distilled. After removal of most of the pentane at atmospheric pressure, the residue was distilled at reduced pressure. Redistillation gave 59.8 g (26%) of chloromethylenecyclopropane, b.p. 82–84°, 90 g (25%) of 1 - chloro - 1 - ethoxymethylcyclopropane, b.p. 144–146°, and 3 - ethoxy - 2 - ethoxymethylpropene, b.p. 160° (lit.[34] b.p. 160°). The chloroether and NMR δ 3.55 (s, 2H), 3.50 (q, J = 7 Hz, 2H), 1.18 (t, J = 7 Hz, 3H), and 0.85–1.0 ppm (m, 4H); ms, *m/e* (rel intensity) 136 (0.2), 134 (0.2), 108 (11), 106 (33), 80 (32), 78 (100). An elemental analysis was not obtained.

Ethoxymethylenecyclopropane 5. Using the procedure described for the preparation of bromomethylenecyclopropane, 28.7 g (0.21 mole) of 1 - chloro - 1 - ethoxymethylcyclopropane and 8.3 g (0.21 mole) of sodium amide in 100 ml THF at room temp. for 3 days gave 18.8 g (90%) of ethoxymethylenecyclopropane, b.p. 96–98°, NMR δ 6.44 (p, J = 1.8 Hz, 1H), 3.90 (q, J = 7.0 Hz, 2H), 1.22 (t, J = 7.0 Hz, 3H), 0.80–1.45 ppm (m, 4H); ms, *m/e* (rel intensity) 99 (1.7), 98 (18), 70 (30), 69 (63), 41 (100), 40 (26). C, 73.07; H, 10.21 ($C_6H_{10}O$ requires: C, 73.43; H, 10.27).

Dimerization of substituted methylenecyclopropanes

Caution! Selected, well-annealed glass tubing should be used for these and other sealed-tube reactions described here, and each sealed reaction mixture should be regarded as potentially explosive! None of the reactions described here was carried out in tubes larger than 5-mm O.D.

The following is representative. A 5-mm O.D. Pyrex glass tube was filled in part (one half to two thirds) with bromomethylenecyclopropane 3. The tube and its contents were cooled in powdered dry ice and degassed at vacuum pump pressure via a syringe needle inserted through the serum-capped top. While the vacuum was maintained, the tube was sealed using a gas–oxygen torch. The tube was placed in a wire holder and immersed in a wax bath at 187 + 2° for 2 hr. The tube was allowed to cool to room temp before opening. The contents of several tubes were combined and distilled in part at atmospheric pressure using a short-path distillation apparatus to separate the unreacted 3 and more volatile side products from the dimeric products. The components of the distillate were separated by prep GLPC (Column *B* at 80°), and the following compounds were identified by a combination of spectral methods: bromomethylenecyclopropane; 1 - bromo - 2 - methylenecyclopropane;[33] *cis*- and *trans* - 1,2 - dibromo - 1 - butene; *cis*- and *trans* - 1,2 - dibromocyclobutane;[13] 1,1 - dibromocyclobutane, dibromomethylcyclopropane; 1 - bromo - 1 - bromomethylcyclopropane; 2,4 - dibromo - 1 - butene; 1,1-dibromo - 1 - butene; and *cis*- or *trans* - 1,4 - dibromo - 1 - butene. Details of the identifications are given elsewhere.[28] The distillation residue consisted mainly of 2 compounds in a ratio of 1:0.9, which were separated by prep GLPC (Column *C* at 150°). The major compound, which had the shorter retention time, was identified as *trans*-7,8-dibromodispiro[2.0.2.2]octane: NMR δ 4.80 (s, 2H), 0.60–1.05 (m, 4H) and 0.15–0.60 ppm (m, 4H); ms, *m/e* (rel intensity) 268 (0.3), 266 (0.6), 264 (0.3), 187 (2.6), 185 (2.7), 159 (6.7), 157 (6.8), 106 (52), 105 (100), 79 (26), 78 (26), 77 (29). C, 36.19; H, 3.71 ($C_8H_{10}Br_2$ requires: C, 36.13; H, 3.79).

The other compound was *cis-7,8-dibromodispiro*[2.0.2.2]*octane*: NMR δ 5.00 (s, 2H), 0.60–1.05 (m, 4H), 0.15–0.60 ppm (m, 4H); ms very similar to that of the *trans* isomer. C, 36.32; H, 3.76.

The residue also contained 2 minor side products which were identified as 1,2,4-tribromo-1-butene [NMR, δ 6.00–6.05 (m, 1H), 2.90–3.60 ppm (m, 4H); ms, *m/e* (rel intensity) 296 (6.3), 294 (19), 292 (20), 290 (6.9), 215 (41), 213 (85), 211 (44), 134 (9.2), 133 (36), 132 (11), 131 (40)] and 5,6-dibromo-4-ethylspiro[2.3]hex-4-ene 9 [NMR δ 4.78 (t, J = 1.5 Hz, 1H), 1.95 (q, d, J = 7.0 and 1.5 Hz, 2H), 0.75–1.23 ppm (m with apparent t, J = 7.0 Hz, at δ 1.10 ppm, 7H); ms, *m/e* (rel intensity) 268 (9.3), 266 (19), 264 (9.8), 187 (18), 185 (18), 107 (12), 106 (100), 105 (56), 91 (94)].

A sealed mixture of 0.162 g (1.22 mmole) of 3, 0.012 g diphenyl ether, and 0.264 g (1.23 mmole) 1,8-bis(dimethylamino)napthalene in a 5-mm O.D. tube was heated under its own pressure in a wax bath at 187 ± 2° for a total of 4 hr. The tube was removed periodically, cooled, and the course of the reaction was determined by ^{1}H NMR analysis. The dimerization reaction was observed to occur as before, but at a significantly slower rate. For example, about 30% of the 3 remained unreacted after 2.5 hr as compared to about 10% in a typical dimerization reaction of neat bromomethylenecyclopropane (3). The tube was broken, and its contents were taken up in ether. GLPC analysis showed that dimerization to *cis*- and *trans*-6 had occurred quite cleanly. *cis*- and *trans*-1,2-dibromo-1-butene, which were prominent side products from heating neat 3, were absent. Some 1-bromo-2-methylenecyclopropane and a more volatile unidentified side product were observed together with unreacted 3.

After 2 hr at 187–189°, chloromethylenecyclopropane 4 gave a 4% conversion to 1 - chloro - 2 - methylenecyclopropane and an 80% conversion to a 1:0.9 mixture of *trans*- and *cis* - 7,8 - dichlorodispiro[2.0.2.2]octane 7. The products were isolated by prep GLPC (Column *B* at 130°).

1-*Chloro*-2-*methylenecyclopropane.* NMR δ 5.70–5.90 (m, 1H), 5.50–5.70 (m, 1H), 3.30–3.60 (m, 1H), 1.15–1.95 ppm (m, 2H); ms, *m/e* (rel intensity) 91 (0.3), 90 (5.1), 89 (1.0), 88 (16), 53 (100).

trans-7,8-*Dichlorodispiro*[2.0.2.2]*octane.* NMR 4.60 (s, 2H), 0.15–0.25 ppm (m, 8H); ms, *m/e* (rel intensity) 180 (0.04), 178 (0.2), 176 (0.3), 143 (5.3), 141 (17), 105 (100); C, 54.15; H, 5.61; Cl, 40.04 ($C_8H_{10}Cl_2$ requires: C, 54.26; H, 5.69; Cl, 40.04).

cis-7,8-*Dichlorodispiro*[2.0.2.2]*octane.* NMR δ 4.70 (s, 2H), 0.20–1.05 ppm (m, 8H); ms very similar to that of the *trans* isomer. C, 54.01; H, 5.68; Cl, 40.28.

In this and other heat-induced cycloadditions of chloromethylenecyclopropane, the amount of other observable side products formed during the 2-hr heating period accounted for <4% of the starting material.

After 2 hr at 191–193°, ethoxymethylenecyclopropane 5 gave an 83% conversion to a 1:0.76 mixture of *trans*- and *cis*-8. *Ca.* 17% of 5 remained unreacted, and there was no detectable amount of 1 - ethoxy - 2 - methylenecyclopropane present. Observable side products accounted for <1% of the starting 5. The dimeric products were separated by prep GLPC (Column *B* at 100°).

trans-7,8-*Diethoxydispiro*[2.0.2.2]*octane* NMR δ 3.91 (s, 2H), 3.00–3.80 (m, 4H), 1.12 (t, J = 7.0 Hz, 6H) and −0.15–0.90 ppm (m, 8H); ms, *m/e* (rel intensity) 196 (0.3), 195 (1.6), 139 (32), 111 (36), 95 (51), 77 (30), 67 (36), 55 (43), 53 (33), 41 (42), 39 (38), 29 (100), 27 (69), C, 73.28; H, 10.33 ($C_{12}H_{20}O_2$ requires: C, 73.43; H, 10.27).

cis-7,8-*Diethoxydispiro*[2.0.2.2]*octane.* NMR δ 4.02 (s, 2H), 3.10–3.90 (m, 4H), 1.14 (t, J = 7.0 Hz, 6H), −0.15–0.90 ppm (m, 8H); ms, indistinguishable from that of the *trans* isomer. C, 73.50; H, 10.46.

The optimum reaction times for dimerizations of 3–5 at 185–190° were estimated by following the course of the reaction in the presence of 15–20% by weight of diphenyl ether. The optimum reaction time for 3 was 1.5 hr. At that time 19% of 3 remained unreacted, and the uncorrected yield of 6 was 67%. Extended heating to 3.3 hr caused complete reaction of 3 but reduced the yield of 6 to 53%. On extended heating the *cis*-6:*trans*-6 ratio decreased: 0.91 at 0.67 hr; 0.80 at 1.5 hr; 0.64 at 3.3 hr. The uncorrected yield of 1 - bromo - 2 - methylenecyclopropane reached a maximum of 3% after 1.0 hr and declined to nil after 2.3 hr.

The optimum reaction time for 4 was 2.0 hr. At that time 15% of 4 remained unreacted, and the uncorrected yield of 7 was 78%. Extended heating to 4.0 hr reduced the amount of unreacted 4 to 8%, but the yield of 7 did not increase. The *cis*-7:*trans*-7 ratio remained constant throughout at 0.90 ± 0.02.

The optimum reaction time for 5 was 2.0–3.0 hr. At those respective times, 17% and 12% of 5 remained unreacted, and the rest had been quantitatively converted to 8.

Thermolysis of cis- *and* trans - 7,8 - *dibromodispiro*-[2.0.2.2]*octane* (6). Five -μl aliquots of pure *cis*-6 were sealed under vacuum in capillary tubes. The tubes were placed in a wire holder and immersed in a wax bath at 190 ± 2°. From time to time a capillary tube was removed from the bath, cooled, and opened, and the course and extent of reaction was determined by GLPC analysis. After 30 min, a number of products were noted including 2 with retention times identical with those of *trans*-6 and 9. After 2 hr the ratio of *cis*- to *trans*-6 was estimated as 0.42. Longer heating produced a dark viscous mass.

Five-μl aliquots of pure *trans*-6 were treated in the same manner. After 2 hr a trace of *cis*-6 could be detected together with minor amounts of other products, including 9. After 4 hr, much *trans*-6 remained unreacted, but only a trace of *cis*-6 was detectable. After 5.5 hr, the mixture was a dark viscous mass.

Five-μl aliquots of pure *cis*-6 and of pure *trans*-6 were heated at 300° ± 20° in a salt bath. Except for greatly increased reaction rates, the observations were similar to those noted at 190°.

A 340 × 26-mm quartz tube, inclined 10° from the horizontal, was placed in a 750-watt furnace. The heated length of the tube was 300 mm. The higher end of the tube was equipped with a nitrogen inlet and a small serum-capped entry port. The lower end of the tube was attached to 2 cylindrical traps in series, which were cooled with dry ice–acetone. The nitrogen flow rate was adjusted to 25 ml/min, and the tube was heated to 350 ± 5°. A solution of 50 μl of *cis*-6 in 3 ml of diphenyl ether was slowly added over 15 min by syringe through the entry port. It was allowed to flow downward into the heated portion of the tube where it immediately vaporized. All the liquid that condensed was contained in the first trap. It was dark colored and contained a fine black ppt. Analysis by GLPC indicated the presence of *cis*-6 together with a trace of *trans*-6; no other products were detectable. A similar experiment was carried out with 50 μl of *trans*-6 in 3 ml of diphenyl ether. The condensate was discolored and contained a fine black precipitate. GLPC analysis indicated that most of the *trans*-6 had passed through the hot tube unchanged; no *cis*-6 or other product was detectable.

Cross cycloaddition reactions of methylenecyclopropanes. Chloromethylenecyclopropane (300 μl) and *ca.* 400 μl of ethoxymethylenecyclopropane (equimolar amounts as determined by NMR analysis) were placed in a 5-mm O.D. glass tube. The tube was sealed under vacuum as usual and placed in a wax bath at 191–193°. At 30-min intervals the tube was removed from the wax bath and cooled, and the course and extent of reaction was estimated by NMR analysis. After heating for a total of 2 hr, the reaction mixture was analyzed by both GLPC and NMR, which showed the presence of *cis*- and *trans*-7, *cis*- and *trans*-8, and 2 new products subsequently identified as *cis*- and *trans*-11. The relative amounts of the dichloro-, diethoxy- and chloroethoxydispirooctanes were 1:1:2. Approximately 8% of the chloromethylenecyclopropane and 5% of the ethoxymethylenecyclopropane had not reacted. The new products were isolated by prep GLPC (Column *B* at 135° then 100°).

cis - 7 - *Chloro* - 8 - *ethoxydispiro*[2.0.2.2]*octane*, 11. NMR δ 4.46 (d, J = 5.2 Hz, 1H), 4.24 (d, J = 5.2 Hz, 1H), 3.00–3.90 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H), ~0.10–1.25 ppm (m, 8H); ms, *m/e* (rel intensity) 188 (0.03), 187 (0.07), 186 (0.1), 185 (0.2), 130 (92), 105 (78), 91 (50), 79 (80), 77 (84), 53 (45), 51 (58), 39 (88), 29 (100), 27 (97). C, 63.91; H, 7.90; Cl, 19.03 ($C_{10}H_{15}ClO$ requires: C, 64.34; H, 8.10; Cl, 18.99).

trans - 7 - *Chloro* - 8 - *ethoxydispiro*[2.0.2.2]*octane*, 11. NMR δ 4.42 (d, J = 4.6 Hz, 1H), 4.15 (d, J = 4.6 Hz, 1H), 3.15–3.80 (m, 2H), 1.20 (t, J = 7.0 Hz, 3H), ~0.05–1.25 ppm (m, 8H); ms indistinguishable from that of the *cis* isomer. C, 63.91; H, 7.90; Cl, 19.03.

Equimolar amounts of bromomethylenecyclopropane and chloromethylenecyclopropane (*ca.* 300 μl of each) at 194–195° for 2 hr under autogenous pressure gave a mixture of *cis*- and *trans*-6, *cis*- and *trans*-7, and 2 new products subsequently identified as *cis*- and *trans*-10. The relative molar amounts of the dibromo-, dichloro, and bromochlorodispiroöctanes were 1:1:2. About 80% of each of the halomethylenecyclopropanes were converted to dispiroöctanes, and about 14% of each remained unreacted. The new products were isolated by prep GLPC (Column *B* at 150°).

cis - 7 - *Bromo* - 8 - *chlorodispiro*[2.0.2.2]*octane*, 10. NMR δ 4.90 (d, J = 6.2 Hz, 1H), 4.72 (d, J = 6.2 Hz, 1H), 0.15–1.10 ppm (m, 8H); ms, *m/e* (rel intensity) 224 (0.1), 222 (0.3), 220 (0.2), 187 (2.5), 185 (2.6), 143 (2.0), 141 (5.5), 105 (100), 79 (40), 77 (50), 51 (50). C, 43.24; H, 4.64; total halide as % Cl, 32.05 ($C_8H_{10}BrCl$ requires: C, 43.37; H, 4.55; total halide as % Cl, 32.01).

trans - 7 - *Bromo* - 8 - *chlorodispiro*[2.0.2.2]*octane*, 10. NMR δ 4.62 (s, 2H), 0.15–1.20 ppm (m, 8H); ms indistinguishable from that of the *cis* isomer. C, 43.07; H, 4.49; total halide as % Cl 32.28.

Chloromethylenecyclopropane (250 μl) and methylenecyclopropane (*ca.* 250 μl, initial mol ratio: 1:0.83) at 191–195° for 2 hr under autogenous pressure gave a mixture of *cis*- and *trans*-7, 1 - chloro - 2 - methylenecyclopropane, and a new product subsequently identified as 7-chlorodispiro[2.0.2.2]octane. The total conversion of chloromethylenecyclopropane to dispiroöctanes was 72% as estimated by NMR and GLPC analysis, and the dichloro-:chlorodispiroöctane product ratio was 5:1. About 5% of the chloromethylenecyclopropane was converted to 1 - chloro - 2 - methylenecyclopropane, and 17% had not reacted. No dimer of methylenecyclopropane was detected in the mixture. The new product was isolated by prep GLPC (Column *B* at 150°).

7-*Chlorodispiro*[2.0.2.2]*octane*. NMR δ 4.55 (t, $J \sim 6.6$ Hz, 1H), 2.4–2.9 (AB part of ABM pattern: δ_A 2.68, δ_B 2.54, J_{AB} = 11.3 Hz, J_{AM} = 7.0 Hz, J_{BM} = 6.2 Hz), and 0.05–1.15 ppm (m, 8H); ms, *m/e* (rel intensity) 144 (0.6), 142 (1.5), 107 (19), 91 (60), 79 (100), 77 (39), 51 (40). An elemental analysis was not obtained.

Bromomethylenecyclopropane (200 μl) and methylenecyclopropane (*ca.* 200 μl, initial mol ratio 1:0.77) at 191–195° for 1.5 hr under autogeneous pressure gave a mixture of *cis*- and *trans*-6, 1 - bromo - 2 - methylenecyclopropane, and a new product subsequently identified as 7-bromodispiro[2.0.2.2]octane. The total conversion of bromomethylenecyclopropane to dispiroöctanes was 64% as estimated by NMR and GLPC analysis, and the dibromo-: bromodispiroöctane ratio was 7:1. About 4% of the bromomethylenecyclopropane was converted to 1 - bromo - 2 - methylenecyclopropane, and 28% had not reacted. No dimer of methylenecyclopropane was detected in the product mixture. The new product was isolated by prep GLPC (Column *B* at 150°).

7-*Bromodispiro*[2.0.2.2]*octane*. NMR δ 4.65 (t, $J \sim 6.6$ Hz, 1H), 2.4–3.0 (AB part of ABM pattern: δ_A 2.81, δ_B 2.64, J_{AB} = 12.3 Hz, J_{AM} = 7.2 Hz, J_{BM} = 6.2 Hz), and 0.10–1.05 ppm (m, 8H); ms, *m/e* (rel intensity) 188 (1.4), 186 (1.5), 107 (27), 91 (60), 79 (100), 77 (37), 51 (38); exact mass 186.0066 (Calc. for $C_8H_{11}Br^{79}$: 186.0044). C, 51.44; H, 5.89 ($C_8H_{11}Br$ requires: C, 51.36; H, 5.93).

Other cycloaddition reactions of chloromethylenecyclopropane 4

(A) *With* 1,3-*cyclopentadiene*. A mixture of 4 (100 μl) and 400 μl of freshly cracked 1,3-cyclopentadiene was heated under autogenous pressure at 192–198° for 1 hr and cooled. Comparison by means of NMR and GLPC analysis of the reaction mixture with one obtained by similar heating of neat 1,3-cyclopentadiene showed that it contained, in addition to cyclopentadiene condensation products, small amounts of *cis*- and *trans*-7 and 2 new products, which were isolated by prep GLPC (Column *B* at 105°) and identified as *endo*- and *exo*-12. The *endo*:*exo* ratio was, after 1 hr, 65:35, and the ratio of total 7 to total *endo*- and *exo*-12 was 2:98. The combined conversion of these products was >95%. A similar experiment was carried out, but the reaction was interrupted from time to time and the *endo*/*exo* ratio was determined by means of NMR analysis. The following data were obtained: (Table 1).

endo - 8 - *Chloro* - 4,7 - *methanospiro*[2.5]*oct* - 5 - *ene*, 12. NMR δ 5.95–6.35 (*HC* = C*H*, AB part of ABMN pattern, δ_A 6.26, δ_B 6.10 ppm, J_{AB} = 5.6 Hz, $J_{AM} \approx J_{BN} \approx 2.8$ Hz; 2H), 4.20 (C_8-*H*, J = 3.5 Hz, 1H), 3.15 ($W_{1/2}$ = 8 Hz, 1H), 2.05 ($W_{1/2}$ = 6 Hz, 1H), 1.50–1.95 (m, 2H), and 0.25–0.90 ppm ((m, 4H); ms, *m/e* (rel

Table 1.

Time (min)	*endo*/*exo*	Time (min)	*endo*/*exo*
10[a]	4.7	120	0.69
20	3.4	180	0.40
30	3.2	240	*ca.* 0.3[b]

[a]The reaction appeared to be complete. [b]The viscosity of the reaction mixture made precise NMR analysis difficult.

intensity) 157 (0.3), 156 (2.7), 155 (0.9), 154 (8.2), 119 (27), 92 (43), 91 (64), 66 (100); exact mass, 154.0526 (Calc. for $C_9H_{11}Cl^{35}$: 154.0549). C, 69.93; H, 7.36; Cl, 23.22 ($C_9H_{11}Cl$ requires: C, 69.90; H, 7.17; Cl, 22.93).

exo - 8 - *Chloro* - 4,7 - *methanospiro*[2.5]*oct* - 5 - *ene*, **12**. NMR δ 5.85–6.35 (*HC*=C*H*, AB part of ABMN pattern, δ_A 6.27, δ_B 6.01 ppm, $J_{AB} \approx 5.4$ Hz, $J_{AM} \approx 2.4$ Hz, $J_{BN} \approx 3.0$ Hz, 2H), 3.50 (C$_8$-*H*, d, $J = 1.6$ Hz, 1H), 3.05 ($W_{1/2} = 8$ Hz), 1.66 (broad d, $J \approx 9$ Hz, with fine structure, 1H), 0.20–1.40 ppm (m, 4H); ms indistinguishable from that of the *endo* isomer; exact mass, 154.0536. C, 69.93; H, 7.23; Cl, 23.06.

(B) *With furan.* A mixture of **4** (100 μl) and 400 μl of furan (freshly distilled from LAH) was heated under autogenous pressure at 192–198° for 1 hr and cooled. The mixture was taken up in CCl_4 and filtered using positive pressure to remove a white gelatinous material, presumed to be polyfuran, which formed during the reaction. Analysis of the CCl_4 soln by means of NMR and GLPC showed the presence of *cis*- and *trans*-**7** and 2 new products, which were isolated by prep GLPC (Column *B* at 150°) and identified as *endo*- and *exo*-**13**. The *endo*:*exo* ratio was 73:27; and the ratio of total dichlorodispiroöctane to total chlorospiroöctane was 62:38. The combined conversion of **4** to these products was >90%.

endo - 8 - *Chloro* - 4,7 - *epoxyspiro*[2.5]*oct* - 5 - *ene*, **13**. NMR δ 6.23–6.54 (*HC*=C*H*, AB part of ABMN pattern, δ_A 6.42, δ_B 6.33 ppm, $J_{AB} = 5.7$ Hz, $J_{AM} \cong J_{BN} \cong 1.2$ Hz), 4.97 (C$_8$-H, d, $J =$ 4.2 Hz, broadened, 1H); 4.11 and 4.08 (apparent broadened *s* and sharp d, $J \cong 4$ Hz, respectively, 2H), and 0.25–1.10 ppm (m, 4H); ms, *m/e* (rel intensity) 158 (7.8), 156 (26), 127 (69), 121 (39), 91 (88), 77 (49), 68 (100); exact mass, 156.0356 (Calc. for $C_8H_9Cl^{35}O$: 156.0342). C, 61.32; H, 5.95; Cl 22.17 (C_8H_9ClO requires: C, 61.35; H, 5.79; Cl, 22.64).

exo - 8 - *Chloro* - 4,7 - *epoxyspiro*[2.5]*oct* - 5 - *ene*, **13**. NMR δ 6.20–6.60 (*HC*=C*H*, AB part of ABMN pattern, δ_A 6.50, δ_B 6.28 ppm, $J_{AB} = 5.7$ Hz, $J_{AM} \cong J_{BN} \cong 1.3$ Hz), 4.87 (C$_8$-H, narrow m, $W_{1/2} = 3.5$ Hz, 1H), 4.11 (narrow m, $W_{1/2} = 2.5$ Hz, 1H), 3.55 (s, 1H), 0.20–1.40 ppm (m, 4H); ms very similar to that of the *endo* isomer; exact mass: 156.036. An elemental analysis was not obtained.

(C) *With 1,3-cyclohexadiene.* A mixture of **4** (100 μl) and 400 μl of 1,3-cyclohexadiene was heated under autogenous pressure at 192–198° for 1 hr and cooled. Comparison by means of NMR and GLPC analysis of the reaction mixture with one obtained by similar heating of neat 1,3-cyclohexadiene showed that it contained *cis*- and *trans*-**7** and 3 additional products, one of which was formed in minor amounts and was not investigated further. One of the 2 major products was isolated by prep GLPC (Column *B* at 120°) and identified as *exo*-**14**. NMR δ 5.40–6.35 (m, 2H), 4.50 (d, $J = 7.9$ Hz, 1H), 2.95–3.60 (m, 1H), 2.30–2.90 (m, 1H), 1.85–2.30 (m, 2H), 1.20–1.60 (m, 2H), and 0.30–0.95 ppm (m, 4H); ms, *m/e* (rel intensity) 170 (0.9), 169 (0.4), 168 (2.8), 133 (31), 127 (76), 106 (69), 105 (53), 91 (100), 81 (74), 79 (92); exact mass, 168.0716 (Calc. for $C_{10}H_{13}Cl^{35}$: 168.0706); C, 71.37, H, 8.01; Cl, 19.98 ($C_{10}H_{13}Cl$ requires: C, 71.21; H, 7.77; Cl, 21.04).

The other major product was not obtained free of 1,3-cyclohexadiene dimer. The NMR and mass spectra of the impure material were completely consistent with the *endo*-**14** structure. If this structural assignment is correct, and the doublet, $J =$ 5.5 Hz, at δ 4.10 ppm is due to the proton α to the chlorine, then the ratio of total **7** to total **14** was *ca.* 1:4, and the *endo*:*exo* ratio (after 1 hr), was *ca.* 5:4. Only a trace of **4** remained unreacted, and its conversion to the 4 major products was estimated as >90%.

(D) *With 2,3-dimethyl-1,3-butadiene.* In each of 4-, 5-mm O.D. glass tubes was placed 100 μl of **4** and 400 μl of 2,3-dimethyl-1,3-butadiene. The tubes were sealed under vacuum as usual, heated at 188–192° for 1 hr, cooled and opened. Comparison by means of NMR and GLPC analysis of the reaction mixture with one obtained by similar heating of neat 2,3-dimethyl-1,3-butadiene showed that it contained *cis*- and *trans*-**7** (est. yield by GLPC: 24%) together with several new products in substantially different amounts. The 2 major products (est. yields by GLPC: 35% and 13%), subsequently identified as **18** and **20**, were purified by prep GLPC (Column *B* at 110° and at 135°). A smaller amount of a third product (est. yield by GLPC: 8%) was isolated and analyzed as a mixture with *trans* - 7,8 - dichlorodispiro-[2.0.2.2]octane. The spectral data obtained by correcting the spectra of the mixture for the presence of the dispiro compound indicated that it was **19** [NMR δ 2.55–3.0 (m, 1H), 2.3–2.5 (m, 2H), 2.0–2.25 (m, 2H), 1.2–1.95 ppm (m, with s at δ 1.75, 10H); ms, *m/e* (rel intensity) 173 (0.9), 172 (8.3), 171 (2.9), 170 (25), 135 (14), 107 (100)].

At least 5 other minor products (total est. yield by GLPC: <5%) were noted by GLPC, and at least 2 of these were isolated as a mixture with a very minor $C_{12}H_{20}$ product. The $C_{12}H_{20}$ product appears to be 1,2,5,6-tetramethyl-1,5-octadiene[35] [NMR δ 2.22 and 1.58 ppm, singlets, intensity ratio 2:3; ms, *m/e* 165:164 intensity ratio 0.136:1.00]. The mass spectrum of this mixture indicated the presence of at least 1 compound with the molecular formula $C_{10}H_{15}Cl$.

About 15% of the chloromethylenecyclopropane remained unreacted.

4 - (2 - *Chloroethyl*) - 1,2 - *dimethyl* - 1,4 - *cyclohexadiene* **18**. NMR δ 5.41 (narrow unresolved m, $W_{1/2} = 5$ Hz, 1H), 2.49 (t, $J = 7.2$ Hz, 2H), 2.38 and 2.50 (apparent *t*, $J = 7.2$ Hz, and s, 6H), and 1.60 ppm (s, 6H); ms, *m/e* (rel intensity) 173 (1.2), 172 (10), 171 (3.7), 170 (32); 135 (1.1), 119 (64), 107 (100), 91 (56); exact mass, 170.0855 (Calc. for $C_{10}H_{15}Cl^{35}$: 170.0862). An elemental analysis was not obtained.

1 - *Chloromethyl* - 1 - (2 - *methylene* - 3 - *methylbut* - 3 - *en* - 1 - *yl*)*cyclopropane* **20**. NMR δ 5.04–5.17 (m, 2H), 4.83–5.04 (m, 2H), 3.37 (s, 2H), 2.48 (s, 2H), 1.88 (s, 3H), and 0.53 ppm (s, 4H); ms, *m/e* (rel intensity) 172 (3.7), 170 (12), 135 (42), 107 (60), 105 (34), 93 (100), 91 (80), 77 (77), 65 (31), 53 (58), 51 (40), 41 (84), 39 (88), 27 (55). An elemental analysis was not obtained.

(E) *With acrylonitrile.* A mixture of 200 μl of **4**, 800 μl of acrylonitrile, and a trace of hydroquinone was heated under autogenous pressure at 194–198° for 2 hr. Comparison by means of NMR and GLPC analysis of the reaction mixture with one obtained by similar heating of neat acrylonitrile showed that it contained *cis*- and *trans*-**7** and 2 new major products, which were isolated by prep GLPC (Column *D* at 145°) and subsequently identified as *cis*- and *trans*-**21**. The ratio of *cis* to *trans* cycloadduct after 2 hr was 0.8:1.0, and the ratio of total **21** to total **7** was 87:13. The total conversion to these products was >80%, and 13% of **4** remained unreacted.

cis - 4 - *Chloro* - 5 - *cyanospiro*[2.3]*hexane*, **21**. NMR (60 MHz) δ 4.58 (d, $J = 7.1$ Hz, 1H), 3.74 (apparent q, $J = 7.1$ Hz, 1H), 2.57 (apparent d, $J = 7.0$ Hz, 2H), 0.51–1.21 ppm (m, 4H); ms, *m/e* (rel intensity) 143 (0.32), 142 (1.5), 141 (0.8), 140 (4.1), 106 (44), 105 (37), 88 (33), 79 (100), 78 (37), 77 (30), 54 (61), 53 (53), 52 (36), 51 (39); exact mass of M-1, 140.0281 (Calc. for $C_7G_7NCl^{35}$: 140.0267). C, 59.09; H, 5.64; N, 9.66; Cl, 25.55 (C_7H_8ClN requires: C, 59.37; H, 5.69; N, 9.89; Cl, 25.04).

trans - 4 - *Chloro* - 5 - *cyanospiro*[2.3]*hexane*, **21**. NMR (60 MHz) δ 4.68 (d, $J = 7.0$ Hz, 1H), 3.05–3.60 (7 lines at 185, 193, 195, 200, 203, 210 and 213 Hz from TMS, 1H) 2.20–2.72 (3 principal lines at 144, 146 and 154 cps from TMS, rel intensities 1:1.1:2.9, 2H), and 0.35–1.20 ppm (m, 4H); ms indistinguishable from that of the *cis* isomer; exact mass of M-1, 140.0286; C, 59.50; H, 5.62; N, 9.50; Cl, 24.66.

Other attempted cross cycloaddition reactions with chloromethylenecyclopropane. Attempts to effect cycloaddition reactions of **4** with *cis*- and *trans*-stilbene, styrene, isocrotyl bromide, and isocrotyl chloride at *ca.* 190° gave no observ-

able cycloaddition products. Details of these attempts are given elsewhere.[28]

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