NMR (CD_3CN) δ 7.82 (s, aromatic, 1 H), 7.43 (s, aromatic, 1 H), 5.69 [s, $CH(CN)_2$, 1 H], 5.63 [s, $CH(CN)_2$, 1 H], 3.75–4.37 (m, $-CH_2CH_2$, 5 H), 3.1 ppm (s, broad, OH, 1 H).

2-(2-Hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan. A mixture of 500 mg of 2-(2-hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile and 50 ml of bromine water was stirred for 30 min and filtered. The filter cake was recrystallized from benzene to give 236 mg of red crystals of 2-(2-hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan, mp 213–217 °C dec.

Anal. Calcd for $C_{14}H_7N_4BrO_2$: C, 49.00; H, 2.06; N, 16.33. Found: C, 48.86; H, 2.25; N, 16.23.

Uv (CH_3CN) 485 nm (ϵ 4461), 413 (41 521), 390 (sh, 39 805), 280 (3157).

4,4′-Bis(hydroxymethyl)tetrathiafulvalene. To a stirred slurry of 6.5 g (0.0256 mol) of lithium tri-*tert*-butoxyaluminum hydride and 30 ml of tetrahydrofuran under nitrogen cooled to −78 °C was added 1.81 g (0.00555 mol) of tetrathiafulvalenedicarbonyl chloride. The mixture was stirred for 1 h at −78 °C and then allowed to slowly warm to room temperature during which time the purple solid became amber. After 3 h, the solvent was removed in a stream of nitrogen and water was added to the residue under nitrogen. The mixture was filtered under nitrogen, and the filter cake was stirred under argon with 10% sodium hydroxide solution for 1 h and refiltered. The filter cake was extracted with methanol, and the extract was diluted with aqueous sodium hydroxide and concentrated somewhat in vacuo causing separation of rust-colored crystals which were collected by filtration and washed with water to give 368 mg of 4,4′-bis(hydroxymethyl)tetrathiafulvalene which begins to decompose at 160 °C.

Anal. Calcd for $C_8H_8S_4O_2$: C, 36.34; H, 3.05. Found: C, 36.67; H, 3.29.

NMR (Me_2SO-d_6) 6.41 (s, 2 ring H), 5.39 (t, J = 5.5 Hz, OH, 2 H), 4.15 (d, J = 5.5 Hz, $-CH_2O$, 4 H), 3.27 ppm (s, H_2O, 1 H). Addition of D_2O causes disappearance of the 5.39 and 3.27 ppm peaks and a new exchange singlet appears at 3.78 ppm while the 4.15 ppm CH_2 peak collapses to a singlet.

Tetrathiafulvalene Polyurethane (7). To a stirred, refluxing mixture of 108.9 mg of 4,4′-bis(hydroxymethyl)tetrathiafulvalene, 118 mg of 4,4′-diisocyanatotetrathiafulvalene, and 15 ml of acetonitrile under argon was added 0.1 μl of dibutyltin dilaurate catalyst. After 2 h, the mixture was filtered under argon, and the filter cake was twice mixed with acetonitrile and centrifuged to give 167 mg of brown polymer. The infrared spectrum shows carbonyl absorption at 1730 cm^{-1} and NH absorption at 3400 cm^{-1}.

Anal. Calcd for $(C_{16}H_{10}N_2S_8O_4)x$: C, 34.89; H, 1.83; N, 5.09. Found: C, 33.52, 33.47; H, 2.17, 2.16; N, 5.35, 5.30.

Reaction of Tetrathiafulvalene Polyurethane with Iodine. A mixture of 30 mg of **7**, 10 ml of acetonitrile, and 14 mg of iodine was stirred under argon for 3 h and filtered in a nitrogen atmosphere to give 35.5 mg of black polymer.

Anal. Calcd for $C_{16}H_{10}O_4S_8N_2I_2$: C, 23.88; H, 1.25; N, 3.48. Found: C, 23.94, 23.97; H, 1.56, 1.54; N, 4.16, 4.29.

Electrical resistivity of compaction 2 × 10^6 ohm cm.

Registry No.—**1**, 58268-29-4; **2**, 58312-83-7; **3**, 58312,84-8; **4**, 58268-60-3; **5**, 58268-30-7; **6**, 58268-31-8; **7**, 58268-59-0; 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dichloride, 58268-32-9; 1,4-bis(acetoxyethoxy)benzene, 47096-64-0; 2,5-bis(2-acetoxyethoxy)-*p*-xylylene dicyanide, 58268-33-0; 2,5-bis(2-hydroxyethoxy)-*p*-xylene dicyanide, 58268-34-1; 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylylene dicyanide isomer 1, 58268-35-2; 2,5-bis[2-(tetrahydro-2-pyranyloxy)ethoxy]-*p*-xylene dicyanide isomer 2, 58268-36-3; *N*-iodosuccimide, 516-12-1; 1,1′-diisocyanatoferrocene, 12288-75-4; 1,1′-bis(methoxycarbonylamino)ferrocene, 12277-09-7; 4,4′-tetrathiafulvalenedicarbonyl chloride, 58268-37-4; 4,4′-tetrathiafulvalenedicarboxylic acid, 51751-19-0; methylene chloride, 75-19-2; 4,4′-diisocyanatotetrathiafulvalene, 58268-38-5; 2-(2-acetoxyethoxy-α,α',5-tribromo-*p*-xylene, 58268-39-6; 2-(2-acetoxyethoxy)-*p*-xylene, 58268-40-9; 2-(2-acetoxyethoxy)-5-bromo-1-bromomethyl-4-dibromomethylbenzene, 58268-41-0; *N*-bromosuccinimide, 128-08-5; 2-(2-acetoxyethoxy)-5-bromo-*p*-xylene dicyanide, 58268-42-1; 2-(2-hydroxyethoxy)-5-bromo-*p*-xylylene dicyanide, 58268-43-2; 2-(2-hydroxyethoxy)-5-bromo-*p*-phenylenedimalononitrile, 58268-44-3; 4,4′-bis(hydroxymethyl)tetrathiafulvalene, 58268-45-4; 4,4′-diisocyanatotetrathiafulvalene polymer, 58268-58-9; 2,5-bis(hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan 1,1′-diisocyanatoferrocene polymer, 58298-32-1; 2,5-bis(hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan 4,4′-diisocyanatotetrathiafulvalene polymer, 58268-57-8.

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Synthesis of Halogen Substituted Bicyclo[2.1.1]hexan-2-ones

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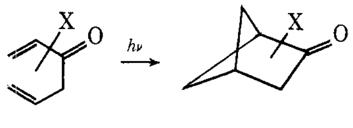
Photochemical irradiation of chlorine substituted 1,5-hexadien-3-ones has led to the synthesis of 1-chloro-, *exo*-5-chloro-, and *endo*-5-chlorobicyclo[2.1.1]hexan-2-one. The nature and utility of the photocycloaddition is discussed. Bromination of bicyclo[2.1.1]hexan-2-one has been carried out using lithium dialkylamide to form the enolate.

Strained bicyclic and polycyclic compounds continue to play an important role in the understanding of many aspects of organic chemistry,[1] including theoretical studies,[2] solvolytic reactivity,[3] thermal rearrangements,[4] and reactivity of strained σ bonds.[5] For this reason, synthetic efforts in this area have been extensive. For some time now, we and others have been interested in the chemistry of bicyclo[2.1.1]hexanes, an area far less studied than that of the homologous bicyclo[2.2.1]heptanes, owing to the ready availability of the latter. In this paper we report extension of our previously noted synthesis of bicyclo[2.1.1]hexan-2-one[6] to the preparation of functionally activated bicyclo[2.1.1]hexan-2-ones, needed for various studies, some of which are reported in the accompanying paper.[7]

Most synthetic routes to the bicyclo[2.1.1]hexane nucleus have involved either ring contractions from bicyclo[2.2.1]heptanes[1a,8] or bicyclo[3.1.1]heptanes[8g,h,9] or photochemical cycloaddition of acyclic precursors.[6,10] Other routes of less general utility include acyloin condensation of a cyclobutane precursor,[11] photochemical cyclization of aryl ketones,[12] and miscellaneous specialized reactions.[13] As we were particularly interested in studying interactions between two different functional groups on the rigid bicyclo[2.1.1]hexane nucleus, and in the use of such derivatives for the preparation of even more highly strained compounds,[7] we investigated the preparation of halogen substituted bicyclo[2.1.1]hexan-2-ones.

There are a total of five such isomers, the 1-halo, 3-halo, 4-halo, and exo and endo 5-halo derivatives. Our major effort was to extend the facile photocycloaddition of 1,5-hexadien-3-one (**1a**)[6] to halogen substituted dienones, **1b**. It was felt that such a study might also shed light on the nature of this unusual cycloaddition which has become the main synthetic route to bicyclo[2.1.1]hexanes, but which has not been extended to the preparation of other ring systems. In this regard, our results are in complete agreement with the study of Gibson and Erman,[10a] who investigated the cycloaddition of the methyl dienones **1c**.

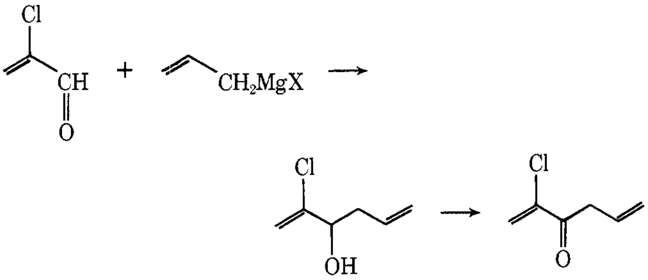


1a, X = H
b, X = Cl
c, X = CH_3

2a, X = H
b, X = Cl
c, X = CH_3

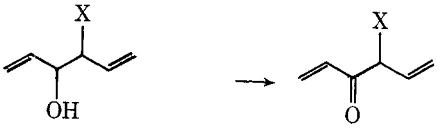
Results and Discussion

Synthesis of Precursors. The route previously used[6] for the synthesis of **1a** was applicable to only one of the halodienones, the 2-chloro isomer **4**, prepared from **3**[14] by oxidation with Jones reagent. The yield in the oxidation was low and could not be improved by excess reagent or extended reaction time, or by use of other conditions, including the Collins reagent, activate manganese dioxide, or dimethyl sulfoxide, which led to either overoxidation or no reaction. Lack of reactivity with demonstrably active manganese dioxide has precedent.[15] A cis–trans mixture of the 1-chloro isomer of **4** could be obtained from β-chloroacrolein by a similar route, but again the oxidation proceeded in low yield and the dienone underwent extensive polymerization upon photolysis. The desired products, in this case *exo*- and *endo*-5-chlorobicyclo[2.1.1]hexan-2-one, could be prepared as shown below, so that this sequence was not pursued.



3 **4**

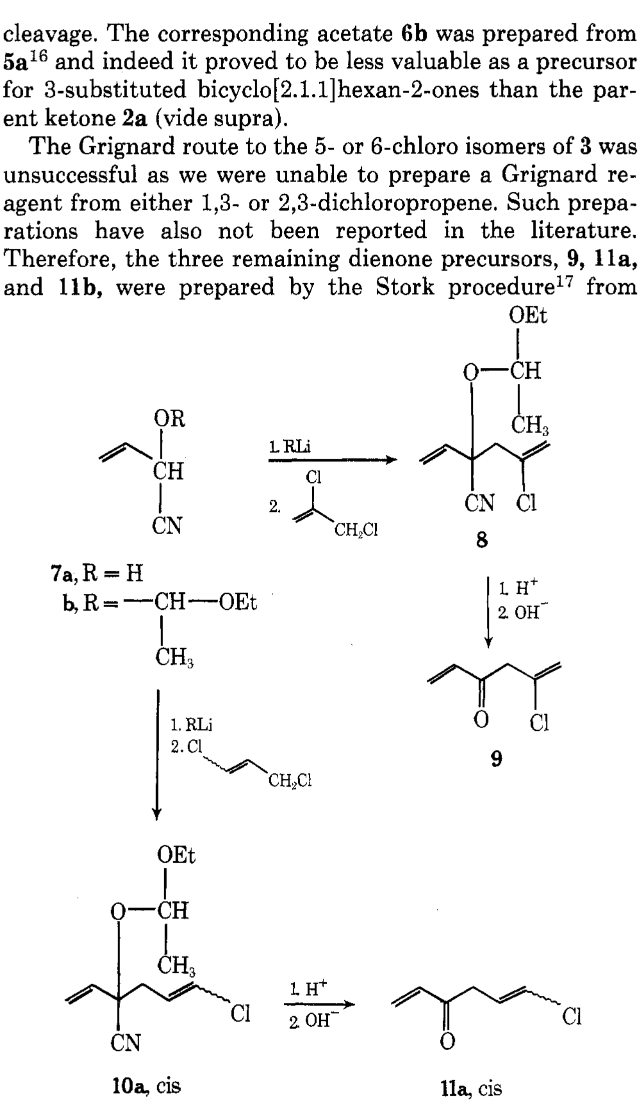
Preparation of 4-chloro-1,5-hexadien-3-one (**6a**) was not attempted since its photolysis was expected to result in α cleavage. The corresponding acetate **6b** was prepared from **5a**[16] and indeed it proved to be less valuable as a precursor for 3-substituted bicyclo[2.1.1]hexan-2-ones than the parent ketone **2a** (vide supra).



5a, X = OH (threo and erythro)
b, X = OAc (threo and erythro)

6a, X = Cl
b, X = OAc

The Grignard route to the 5- or 6-chloro isomers of **3** was unsuccessful as we were unable to prepare a Grignard reagent from either 1,3- or 2,3-dichloropropene. Such preparations have also not been reported in the literature. Therefore, the three remaining dienone precursors, **9**, **11a**, and **11b**, were prepared by the Stork procedure[17] from acrolein cyanohydrin (**7a**).[18] Treatment of **7a** with ethyl vinyl ether afforded the mixed acetal **7b** which was converted into its monoanion and alkylated with 2,3-dichloropropene to give **8**, or with 1,3-dichloropropene to give **10a** and/or **10b** depending on the stereochemistry of the starting dihalide. Hydrolysis in dilute acid generated the free cyanohydrins which were converted with base to the respective dienones, **9**, **11a**, and **11b**, all of which were irradiated without purification. Attempts at purification of the dienones led to extensive decomposition.



7a, R = H
b, R = —CH(CH$_3$)—OEt

8

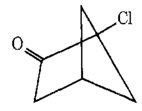
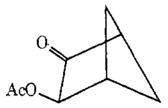
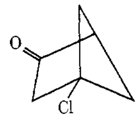
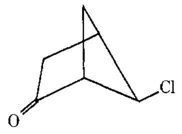
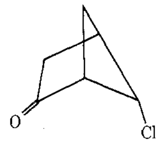
9

10a, cis
b, trans

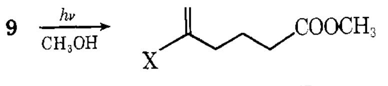
11a, cis
b, trans

Irradiation of Dienones. Results of the irradiation studies are shown in Table I. The exact conditions are given in the Experimental Section and proved important in avoiding side reactions, particularly polymerization. Hydrocarbon solvents were used generally. Methanol as a solvent resulted in some reduction of the dienones and overirradiation of the bicyclic products.[19] Reproducible quantum yields could not be obtained, possibly because of minor impurities in the difficult to purify dienones. Low, but acceptable, isolated yields of **12** and **13** were obtained and **15** and **16** were formed in satisfactory amounts. Since 3-substituted isomers related to **13** can be prepared from **2a** as described below, only the 4-chloro isomer **14** cannot be easily prepared by the photocycloaddition route, which therefore seems preferable to the alternative ring contraction of di- or trisubstituted bicyclo[2.2.1]heptanes. In all cases except **9**, side products were either very volatile or polymeric so that product isolation was not difficult, provided that photoreduction to the dienol had been avoided.

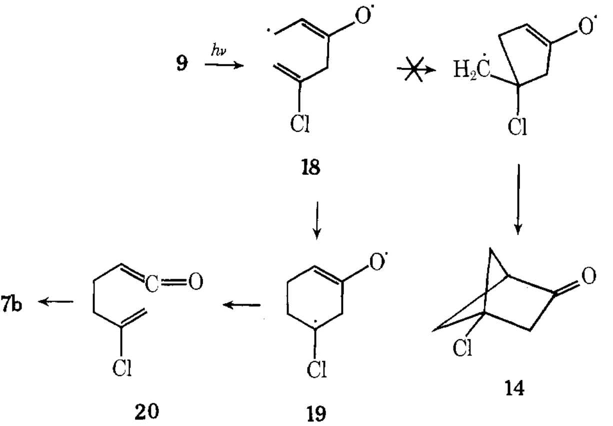
Table I. Irradiation of Dienones

Dienone	Product	Isolated yield, %
4	 12	13
6b	 13	8
9	 14	~1
11a or 11b	 15 (40%) +  16 (60%)	52

These photochemical results are in remarkable agreement with those of Gibson and Erman on the photolysis of the methyl dienones, **1c**.[10a] They also noted a low yield with the 2-methyl isomer and no cycloaddition with the 5-methyl isomer. In the latter case they detected methyl ester **17a** when the photolysis was carried out in methanol. We likewise obtained **17b** from **9** using methanol as solvent. These results are in agreement with the "biradical" mechanism for the photolysis illustrated for **9**. Excitation to **18** allows closure in either of two ways. The normal closure, predicted[20] by the "rule of five", to **14** is less favorable in this case owing to the added stabilization of **19** afforded by the halogen or methyl substituent. Fragmentation of **19** gives ketene **20** which presumably polymerizes in hydrocarbons, but affords some **17b** in methanol. It is interesting to note that Agosta[10b] observed cycloaddition upon irradiation of 5-methyl-1,5-hexadien-3-one using a uranium glass filter. In our hands the use of such a filter did not result in an increased yield of **14**. It should be noted that the structural assignment to **14** is based on its infrared spectrum (see Experimental Section).



17a, X = CH$_3$
b, X = Cl

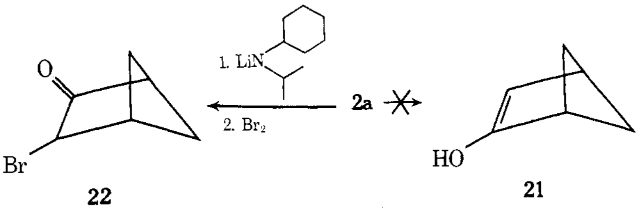


A halogen (or methyl) substituent at C-6 of the dienone should favor the normal closure, as observed. In addition, one would expect to observe the same ratio of **15:16** regardless of the stereochemistry of the starting dienone **11** since that is lost upon formation of the five-membered ring. This, again, was observed with the methyl substituent.[10a]

The remarkable similarity in product distribution from **1b** and **1c** suggests that the cyclizations occur by a similar mechanism. In the absence of more controlled experiments it is difficult to choose between a singlet and triplet pathway. Addition of standard triplet sensitizers (acetone, xanthone, acetophenone) did not affect the product distribution or approximate rate of product formation with dienones **1a**, **9**, or **11a**, though Gibson and Erman found excess acetophenone to be necessary for cycloaddition of 2,6-heptadien-4-one.[10a] Likewise piperylene did not quench the reaction, though such failure in an *intra*molecular reaction is not necessarily indicative. Perhaps the strongest suggestion for a singlet pathway is the close similarity between the methyl- and chlorodienone behavior. Were a triplet pathway involved, its facilitation due to the heavy atom effect might be expected to alter the product distribution.

Bromination of Bicyclo[2.1.1]hexan-2-one. A great deal of effort was expended in developing methods for introduction of substituents α to the carbonyl group of the parent ketone **2a**.[7] In particular, halogenation was studied as an alternative route to the 3-substituted bicyclo[2.1.1]hexan-2-ones, not easily prepared directly.

Ketone **2a** proved remarkably unreactive under a series of standard bromination conditions which readily converted camphor and norcamphor into their respective derivatives. In particular, bromination with Br$_2$–HBr either neat[21] or in acetic acid at 100 °C resulted in no reaction! Clearly formation of enol **21** is difficult, in agreement with theory.[2] Normal base conditions (*tert*-alkoxide, sodium amide, sodium hydride) followed by addition of bromine also failed to give the desired **22**. Sodium hydride, in fact, reduced **2a** to the corresponding alcohol. We were finally able to generate the enolate anion of **2a** using lithium cyclohexylisopropylamide as the base. Quenching of the anion in bromine afforded **22** in reasonable yield. Thus all of the halo-substituted bicyclo[2.1.1]hexan-2-ones except the 4 isomers are now readily available.



Experimental Section[22]

General Photolysis Conditions. The dienones were irradiated in dilute (ca. 1%) solution in pentane or in pentane–ether mixtures, using a Hanovia 450-W lamp (679 A-36) and a water-cooled quartz immersion well (no. 19434). Solutions were purged with nitrogen before photolysis and were maintained under a nitrogen atmosphere and magnetically stirred during photolysis. Irradiations were usually conducted in a hood owing to the lachrymatory nature of the dienones. Irradiations were followed by GLC using a 10-ft 5% DEGS column, monitoring disappearance of starting material and formation of product, the latter always with a longer retention time. Most solutions were irradiated for 10–20 h. Where polymer formed on the well, it was periodically removed by scraping.

1-Chlorobicyclo[2.1.1]hexan-2-one (12). A solution of 10.0 g

(0.076 mol) of 2-chloro-1,5-hexadien-3-ol[14] (**3**) in 500 ml of purified acetone was cooled to 10 °C and treated dropwise over a 30-min period with 20.6 ml (0.053 mol) of Jones reagent[23] under vigorous stirring. The solution was stirred for an additional 1 h at 10–15 °C, and 1.0 g of sodium bisulfite was added and then an excess of solid sodium bicarbonate. The solution was carefully decanted and the green residue washed with three 200-ml portions of pentane. The organic layers were combined, washed with 5% sodium bicarbonate and saturated salt solution, and dried over sodium sulfate. GLC (10 ft, 10% DEGS) showed a new peak, presumably due to **4**, with an area nine times that of unreacted **3**. The crude product has λ_{max} 230 nm (ethanol) and carbonyl absorption at 1692 cm^{-1} in the infrared. Attempts to isolate **4** led to decomposition.

This solution was added to the photolysis flask and sufficient pentane added to bring the volume to 1.9 l. Irradiation for 11.5 h was followed by GLC. Solvent was removed in vacuo to give a brown residue which was molecularly distilled to give 1.61 g of a light yellow liquid, bp 36–43 °C (0.5 mm). GLC analysis indicated that this mixture contained 15% of **3** and 85% of **12**. Pure **12** was collected by preparative GLC. Anal. Calcd for C_6H_7ClO: C, 55.09; H, 5.39; Cl, 27.25. Found: C, 54.96; H, 5.59; Cl, 27.34.

The ir spectrum shows carbonyl absorption as a doublet at 1792 and 1783 cm^{-1}. The NMR spectrum shows a complex broad pattern from 2.00 to 2.60 (6 H) and a multiplet at 2.90 ppm (1 H).

3-Acetoxybicyclo[2.1.1]hexan-2-one (13). A stirred solution of **5a**,[16] 57.0 g (0.5 mol), in 100 ml of pyridine was treated dropwise at 0 °C with 30.6 g (0.3 mol) of acetic anhydride. After storage at room temperature for 24 h the solution was poured onto ice–HCl and the product isolated with ether. The washed and dried ether was concentrated in vacuo to give a crude product which was fractionally distilled through a 24-in. Teflon spinning band column to give 40.1 g of **5b** as a mixture of threo and erythro isomers, bp 89–91 °C (9 mm), contaminated with a small amount of diacetates. This material was oxidized with Jones reagent as described above and the crude product irradiated immediately in pentane, followed by GLC. After 13.5 h the solution was worked up and distilled through the spinning band column to give, after removal of some **5b** and diacetate, the product **13** as a light yellow liquid, bp 110–113° (10 mm), yield 3.5 g (8% from **5a**). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.18; H, 6.71.

The ir spectrum (in CCl_4) shows carbonyl absorption at 1780 and 1749 cm^{-1}. The NMR shows a complex pattern from 1.45 to 2.50 (4 H), a singlet at 2.17 (3 H), a multiplet at 2.93 (2 H), and a broad singlet at 5.55 ppm (1 H).

1-(1′-Cyano-2′-propenoxy)-1-ethoxyethane (7b). Freshly distilled acrolein cyanohydrin[18] (110.0 g, 1.28 mole), *prepared and handled in a good hood,* was placed into a 500-ml three-necked flask equipped with magnetic stirrer, dry ice condenser, and an addition funnel. The cyanohydrin was stirred and acidified with 3 drops of 5% HCl. Freshly distilled ethyl vinyl ether (100 g, 1.40 mol) was then added dropwise over the next 3 h. The solution was allowed to stand at room temperature overnight, then distilled through a 6-in. Vigreux column to give **7b**, 134.6 g (69%), bp 52–56 °C (0.2–0.3 mm) [lit.[17] bp 42–45 °C (0.1 mm)]. The product is a mixture of diastereoisomers as expected.

1-(3′-Cyano-5′-chloro-1′,5′-hexadienoxy)-1-ethoxyethane (8). Lithium diisopropylamide was prepared in 400 ml of THF from 78.4 ml (0.58 mol) of diisopropylamine and 0.6 mol of *n*-butyllithium. This solution was cooled in a dry ice–acetone bath and 75.0 g (0.48 mol) of **7b** in 70 ml of hexamethylphosphoric triamide was added dropwise over 1 h. The orange solution was stirred for an additional 5 min, still at −78 °C, and then was treated dropwise with 63.9 g (0.576 mol) of 2,3-dichloro-1-propene over a 1-h period. An additional 300 ml of THF was added, stirring was continued for 2 h, and the solution then allowed to warm to room temperature.

Water (15 ml) was added and the solution concentrated (15 mm) to a black slurry which was extracted with ether. Difficulty in visualizing the separation was a problem. The ether layer was finally separated, washed, and dried. The solution was concentrated in vacuo to a dark brown residue which was dissolved in 60 ml of hexane–benzene (1:1) and passed through a chromatographic column containing 500 g of silica gel using hexane–benzene. Four 250-ml fractions were collected, combined, and distilled through a 6-in. Vigreux column to give 35.5 g (38%) of **8**, bp 75–85 °C (0.4 mm). The NMR spectrum shows a complex pattern from 1.0 to 1.5 (6 H), a multiplet at 2.8 (2 H), a multiplet at 3.4 (2 H), a quartet at 4.85 (1 H), and a complex pattern from 5.3 to 5.9 ppm (5 H). The product is the expected mixture of diastereoisomers and was used as such.

4-Chlorobicyclo[2.1.1]hexan-2-one (14). To a 250-ml flask was added 35.5 g of **8** and 85 ml of methanol. The solution was stirred and 31 ml of 5% H_2SO_4 added rapidly, followed by sufficient methanol to afford a homogeneous solution. After 30 min the solution was concentrated in vacuo, extracted with ether, washed, and dried. Removal of the ether followed by distillation afforded 18.0 g (82%) of 5-chloro-1,5-hexadien-3-one cyanohydrin, bp 75–82 °C (0.4 mm).

In a 1-l. separatory flask was placed 7.2 g of this cyanohydrin, 350 ml of ether, and 40 ml of 0.5 N sodium hydroxide. The ether was separated and treated with a second 40-ml portion of base, shaken for 10 min, separated, washed with water, and dried. This ether solution was diluted with pentane for the photolysis studies. Evaporation of a small portion of the ether gave crude **9**, infrared carbonyl at 1680 cm^{-1} and NMR absorption at 3.50 singlet (2 H), 5.33 doublet (2 H), and complex two-proton patterns at 5.81 and 6.35 ppm. Attempts to distill this material led to extensive decomposition.

The ether–pentane solution (2.1 l.) was irradiated in the usual manner. Extensive polymer buildup was noted. Disappearance of starting material was followed by GLC and was complete in 12 h. The solution was washed, dried, and evaporated to a yellow gummy residue. Molecular distillation afforded 0.38 g of a yellow oil, GLC examination of which showed two major peaks, the second of which was collected and assigned structure **14** on the basis of its intense infrared carbonyl band at 1770 cm^{-1} and consistent mass spectrum for C_6H_7ClO. The other product was not identified.

Photolysis of 9 in Methanol. A second batch of 7.2 g of 5-chloro-1,5-hexadien-3-one cyanohydrin was converted into **9** as described above. The ether solution was diluted to 2.1 l. with methanol and irradiated as before for 21 h. Solvent was removed and the residue molecularly distilled to give 0.45 g of volatile material which showed four peaks in the GLC. The major peak was collected and assigned the structure methyl 5-chloro-5-hexenoate (**17b**), based on its spectral data.

The ir spectrum shows significant bands at 3010, 1740, 1630, 1250, and 1170 cm^{-1}. The mass spectrum shows molecular ions at *m/e* 162 and 164 ($C_7H_{11}O_2Cl$). The NMR spectrum shows absorption at 1.89 (multiplet, 2 H), 2.22 (triplet, 2 H), 2.40 (triplet, 2 H), 3.55 (singlet, 3 H), and two sharp peaks at 5.14 ppm (2 H).

Two of the minor products had retention times identical with those of the products from the pentane irradiation.

1-(3′-Cyano-*trans*-6′-chloro-1′,5′-hexadienoxy)-1-ethoxyethane (10b). Compound **10b** was prepared in 39% yield exactly as described above for **8**, except that the halide used was *trans*-1,3-dichloro-1-propene.

The product, bp 78–79 °C (0.4 mm), a diastereomeric mixture, has an NMR spectrum with a multiplet at 1.2 (6 H), two doublets centered at 2.5 (2 H), a multiplet at 3.45 (2 H), a quartet at 4.8 (1 H), and a multiplet centered at 5.8 ppm (5 H).

The cis isomer **10a** was prepared in a similar manner from *cis*-1,3-dichloro-1-propene, bp 75–79 °C (0.4 mm). The NMR spectrum has a multiplet at 1.2 (6 H), a doublet at 2.75 (2 H), a complex pattern at 3.45 (2 H), a quartet at 4.8 (1 H), and a complex pattern centered at 5.8 ppm (5 H).

***trans*-6-Chloro-1,5-hexadien-3-one (11b).** Pure **10b** was converted into **11b** by treatment first with acid and then base as described above for **8**. Again, the chlorodienone proved too unstable to isolate. The crude material, **11b**, exhibits carbonyl absorption at 1670 cm^{-1} and NMR absorption at 3.33 (doublet, 2 H) and 6.05 ppm (multiplet, 5 H).

The cis isomer, **11a**, was prepared from **10a** in the same manner and has carbonyl absorption at 1670 cm^{-1} and NMR bands at 3.50 (doublet, 2 H) and complex absorption centered at 6.1 ppm (5 H).

In a similar manner a cis–trans mixture of **11a** and **11b** could be obtained from **7** using the commercially available cis–trans mixture of 1,3-dichloropropene.

***exo*- and *endo*-5-Chlorobicyclo[2.1.1]hexan-2-one (15 and 16).** A mixture of crude *trans*- and *cis*-6-chloro-1,5-hexadien-3-one [obtained from 20.6 g (0.13 mol) of its cyanohydrin] was irradiated for 7 h in 2.2 l. of 4:1 ether–pentane. Removal of solvent followed by distillation through a 2-in. Vigreux column afforded 8.97 g (52%) of a mixture of *exo*-5-chlorobicyclo[2.1.1]hexan-2-one (**15**) and its endo isomer **16**, bp 48–56 °C (1.9 mm), in a ratio (by GLC) of 2:3. The mixture was fractionally distilled through a 24-in. spinning band column to afford 2.97 g of pure exo isomer[24] [bp 44 °C (1 mm)], three fractions of mixed isomers, and a fraction of 98% pure endo isomer, **16** [bp 48 °C (1 mm)]. Anal. Calcd for C_6H_7ClO: C, 54.96; H, 5.59. Found for **15**: C, 54.97; H, 5.35. For **16**: C, 55.50; H, 5.63.

Exo isomer **15** has its infrared carbonyl absorption at 1771 cm^{-1}.

The NMR spectrum[24] shows a triplet at 1.77 (*J* = 8.0 Hz, 1 H), a doublet of doublets at 2.26 (*J* = 5, 16 Hz, 1 H), a doublet at 2.41 (*J* = 16 Hz, 1 H), a multiplet at 2.74 (2 H), a multiplet at 3.24 (1 H), and a doublet at 4.07 ppm (*J* = 8.0 Hz, 1 H).

Endo isomer **16** exhibits carbonyl absorption at 1777 cm^{-1}. Its NMR spectrum[25] shows a doublet at 1.79 (*J* = 8 Hz, 1 H), a multiplet at 1.95 (1 H), a doublet of doublets at 2.08 (*J* = 16, 3 Hz, 1 H), a doublet of doublets at 2.49 (*J* = 16, 5 Hz, 1 H), a triplet at 3.05 (2 H), and a quartet at 4.4 ppm (1 H).

Photolysis of either **11a** or **11b** under similar conditions gave the same 2:3 ratio of **15:16.** This analysis is complicated by competitive isomerization of **11b** to **11a,** and by overirradiation decomposition of the products **15** and **16.**

3-Bromobicyclo[2.1.1]hexan-2-one (22). A 1-l. three-necked flask was equipped with a mechanical stirrer, an addition funnel, a septum inlet, and a Nujol bubbler. The flask was flame dried and placed under an argon atmosphere. A solution of 14.1 g (0.1 mol) of cyclohexylisopropylamine in 300 ml of dry tetrahydrofuran was introduced into the flask which was cooled in an ice-water bath. The solution was stirred continuously and then a solution of *n*-butyllithium (0.1 mol) in hexane was added dropwise over a period of 20 min by means of a hypodermic syringe. After the addition had been completed, the solution was stirred for 10 min at 0 °C and then it was cooled to −78 °C in a dry ice-acetone bath. A solution of 4.80 g (0.05 mol) of bicyclo[2.1.1]hexan-2-one in 200 ml of dry THF was added through an addition funnel over a period of 1 h.

A 2-l. three-necked dry flask with a mechanical stirrer was charged with 54.0 g (0.3 mol) of bromine and 200 ml of dry THF under an argon atmosphere and was cooled in a dry ice-acetone bath. The enolate anion solution was added dropwise into the bromine solution over a period of 1 h. After the addition had been completed, the resulting solution was stirred for 1 h at −78 °C and then was quenched with 10 ml of concentrated hydrochloric acid. Most of the solvent was removed on a rotary evaporator and then the residue was extracted with four 200-ml portions of ether. The ether solutions were combined and washed with saturated sodium bisulfite solution and sodium chloride solution, and then dried over anhydrous sodium sulfate. After the ether had been removed on a rotary evaporator, the crude product was distilled through a 5-in. Vigreux column under reduced pressure. The product was a light yellow liquid, bp 60–66 °C (0.9 mm), yield 4.0 g (46%). Anal. Calcd for C_6H_7BrO: C, 41.17; H, 4.03; Br, 45.65. Found: C, 41.33; H, 4.09; Br, 45.70.

The NMR spectrum (in CCl_4) has signals at 1.65–1.76 (doublet of doublets, *J* = 7.0 and 7.5 Hz, 1 H), 2.03–2.14 (doublet of doublets, *J* = 7.0 and 7.5 Hz, 1 H), 2.26–2.34 (multiplet, 1 H), 2.39–2.45 (multiplet, 1 H), 2.80–3.05 (multiplet, 2 H), and 4.26 (multiplet, 1 H). The infrared spectrum (in CCl_4) shows an intense carbonyl absorption band at 1773 cm^{-1}.

3-Chlorobicyclo[2.1.1]hexan-2-one was also prepared in a similar manner, though the yield was not optimized. The NMR spectrum (in CCl_4) of the chloro ketone shows signals at 1.60 (doublet of doublets, *J* = 7.0 and 7.5 Hz, 1 H), 2.08 (doublet of doublets, *J* = 7.0 and 7.5 Hz, 1 H), 2.21 (multiplet, 1 H), 2.35 (multiplet, 1 H), 2.91 (multiplet, 2 H), and 4.12 ppm (multiplet, 1 H), and the infrared spectrum (in CCl_4) exhibits its carbonyl band at 1780 cm^{-1}. Anal. Calcd for C_6H_7ClO: C, 55.17; H, 5.40. Found: C, 54.90; H, 5.63.

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Registry No.—**3,** 58208-02-9; **4,** 58208-03-0; *threo*-**5a,** 58208-04-1; *erythro*-**5a,** 19700-96-0; *threo*-**5b,** 18654-98-3; *erythro*-**5b,** 15895-82-6; **7a,** 5809-59-6; **7b** isomer 1, 58208-05-2; **7b** isomer 2, 58208-06-3; 8 isomer 1, 58208-07-4; **8,** isomer 2, 58208-08-5; **9,** 58208-09-6; **10a** isomer 1, 58208-10-9; **10a** isomer 2, 58208-11-0; **10b** isomer 1, 58208-12-1; **10b** isomer 2, 58219-00-4; **11a,** 54096-46-7; **11b,** 54096-47-8; **12,** 58191-39-2; **13,** 58191-42-7; **14,** 58208-13-2; **15,** 54096-48-9; **16,** 54096-49-0; **17b,** 58208-14-3; **22,** 58191-34-7; ethyl vinyl ether, 109-92-2; 2,3-dichloro-1-propene, 78-88-6; 5-chloro-1,5-hexadien-3-one cyanohydrin, 58208-15-4; *trans*-1,3-dichloro-1-propene, 10061-02-6; *cis*-1,3-dichloro-1-propene, 10061-01-5; bicyclo[2.1.1]hexan-2-one, 5164-64-7; 3-chlorobicyclo-[2.1.1]hexan-2-one, 58208-16-5.

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