Chemistry of *gem*-Dihalocyclopropanes. XXII. Intramolecular Addition of Cyclopropylidenes to Aliphatic and Aromatic Double Bonds. A Synthesis of 2-Alkenyltropones

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Skattebøl, L., Nilsen, N. O. and Myhren, F., 1986. Chemistry of *gem*-Dihalocyclopropanes. XXII. Intramolecular Addition of Cyclopropylidenes to Aliphatic and Aromatic Double Bonds. A Synthesis of 2-Alkenyltropones. – Acta Chem. Scand. B 40: 782–790.

Substituted *gem*-dibromocyclopropanes containing a vinylic or phenolic ether oxygen α to the cyclopropane ring undergo intramolecular cycloaddition as well as ring opening to allenes when treated with methyllithium. Cycloaddition of derivatives with a vinyl ether moiety gave rise to 2-oxatricyclo[4.1.0.$0^{4,6}$]heptanes while from the phenolic ethers, 11-oxatricyclo[5.4.0.$0^{7,9}$]undecatrienes were obtained. The latter rearranged thermally to the corresponding 2-alkenyltropones. The proportion of cycloaddition products formed was influenced by the reaction temperature. The cycloaddition of 7-bicyclo[4.1.0]heptylidene to anisole gave the corresponding spirononatriene among other products.

Reaction with π bonds to form three-membered rings is characteristic of carbene intermediates.[1] Cyclopropylidenes are no exception although only a few examples of the addition to π bonds to form spiropentanes have been recorded.[2,3,4] Furthermore, the success of this reaction seems dependent on the way the cyclopropylidene is formed. When generated from *gem*-dibromocyclopropanes and alkyllithium in the presence of alkenes or aromatic compounds, the addition does not generally occur; other reactions such as ring opening and insertion are preferred. However, intramolecular addition[3,4] becomes competitive provided the double bond is structurally 5,6-related to the carbenyl carbon. Thus, reactions of 1.1-dibromo-2-(3-butenyl)cyclopropane (*1a*) and the dimethyl analogue (*1b*) with methyllithium at −78 °C gave substantial amounts of the spiropentanes *2* besides the allenes *3*, whereas the homologue *4* gave rise to the allene *5* as major product,[3] (Scheme 1). Furthermore, replacing the double bond in *1a* with a benzene ring, as in compound *6*, resulted in ring opening to the allene *7* as the only observed reaction (see below).

Increased nucleophilicity of the double bond should enhance the rate of addition. This is achieved by attaching an oxygen function to the double bond as in vinyl and phenolic ethers, and the present work reports on the successful addition of cyclopropylidenes to such double bonds.

Results

The vinyl ethers *8* (Scheme 2) were prepared in about 50 % yields from the corresponding *gem*-dibromocyclopropanemethanol derivatives and ethyl vinyl ether by ether exchange.[5] The vinyl ether *9* was obtained in low overall yield from 3-buten-1-ol and dibromocarbene, generated by the phase transfer method,[6] followed by ether exchange. The aromatic ethers *10a, b* and *d* (Scheme 3) were prepared by replacing the exocyclic halogen of compounds *11* with the respective aryloxy group. The reactions were very slow, requiring several days for completion at 70 °C in methanol or dimethylsulfoxide/acetonitrile as sol-

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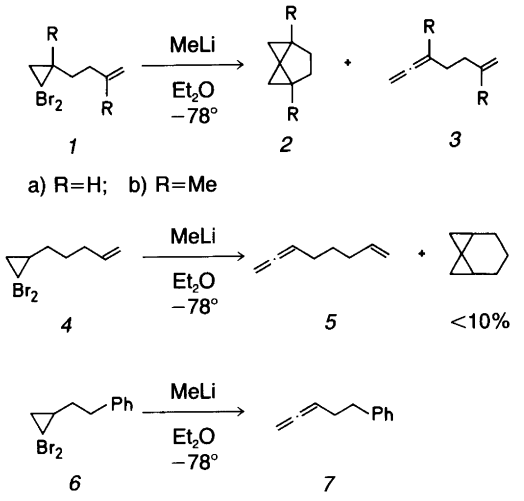


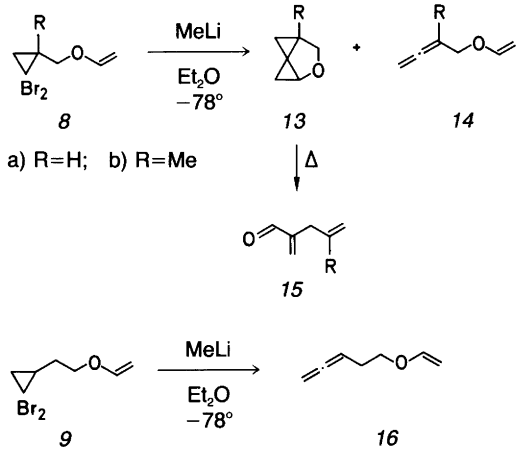
Scheme 1.

vents and in the presence of sodium iodide. The yields varied from 26 to 65 %. Compounds *10c* and *12* were prepared from the corresponding olefins by addition of dibromocarbene, generated by the phase transfer method. These reactions gave only moderate yields as well.

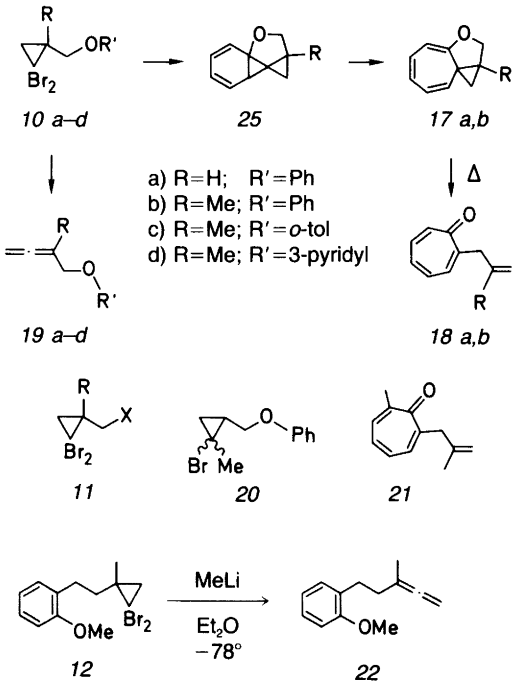
Reactions with methyllithium were carried out in the usual way by adding the organometallic reagent to an ethereal solution of the *gem*-dibromocyclopropane derivative kept at −78 °C. Care was exercised during work-up to avoid heating the reaction mixture above 0 °C and the crude product was analyzed immediately by GLC and NMR spectroscopy. However, partial polymerization during work-up of some of the reaction mixtures seemed unavoidable and isomerization on GLC analysis was encountered as well. We therefore relied mainly on NMR data for estimating the proportion of each component of the reaction mixtures.

Results from reactions of the vinyl ethers are depicted in Scheme 2. Reactions of the ethers *8* gave very similar results; approximately 7:1 mixtures of the 2-oxatricycloheptanes *13* and the allenes *14* were obtained in almost quantitative yields. The isomers were separated by preparative GLC and characterized on the basis of spectroscopic evidence. The tricyclic compound *13b* rearranged partly on the GLC column to the aldehyde 4-methyl-2-methylene-4-pentenal (*15b*). A similar rearrangement was also observed for *13a,* but not to the same extent. Small amounts of 2-methylene-4-pentenal (*15a*) were formed on GLC analysis of the reaction mixture from *8a*. It is interesting to note that the reaction product from the *gem*-dibromocyclopropane derivative *9* and methyllithium consisted of the allene *16* only.

In Scheme 3, the results from reactions of the aromatic ethers are summarized. The phenyl ether *10b* reacted with methyllithium at −78 °C to give a product which by GLC consisted of two compounds. These could be separated by preparative GLC sufficiently pure for structural determination. The major component (67 %) was a slightly yellow liquid that exhibited an UV maximum at 342 nm. According to the IR spectrum, the compound contained double bonds which were not aromatic. The ^{1}H NMR spectrum revealed the presence of a methyl group as a singlet, five olefinic protons, as well as one high and one low field AB quartet due to four methylene protons. This information suggested the structure 9-methyl-11-oxatricyclo[5.4.0.0^{7,9}],undeca-1,3-5-triene *17b* which was subsequently confirmed by the ^{13}C NMR spectrum, from which, the resonance due to the spiro carbon was too weak for definite recognition. The only previously known derivatives with this oxatricycloundecane skeleton have been described by Toda *et al.*[7] The tricyclic compound was thermally unstable and complete conversion to the tropone *18b* took



Scheme 2.



10 a–d 25 17 a,b

19 a–d 18 a,b

11 20 21

12 22

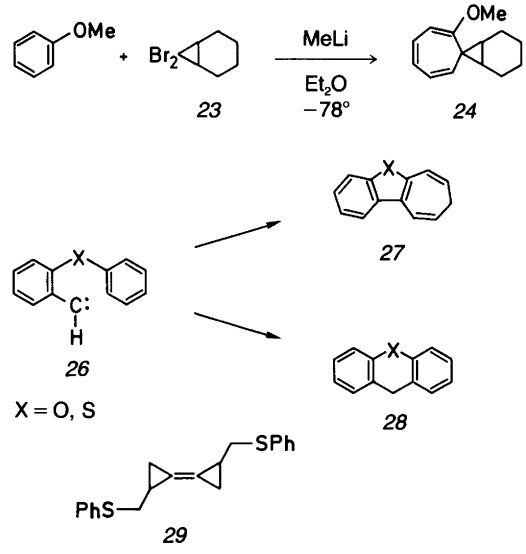
Scheme 3.

place in the gas chromatograph with an injection temperature of 195 °C. In the ^{1}H NMR spectrum of *18b*, the allylic methyl and methylene protons appeared as singlets at δ 1.74 and 3.37 ppm, respectively, while the five cyclic olefinic protons gave rise to resonances in the aromatic region characteristic of tropone derivatives.[8] The minor component (33 %) of the reaction mixture was identified spectroscopically as the allene 2-methyl-1-phenoxy-2,3-butadiene (*19b*).

A similar reaction with compound *10a* afforded a mixture of four products according to GLC analysis. The major component (59 %) was isolated by preparative GLC and identified spectroscopically as the tricyclic compound *17a*. It rearranged thermally to the tropone *18a*. The second component (29 %) was shown to be the allene *19a*. The last two components (12 %) of the mixture had very close retention times on the GLC column and could not be separated individually but as a 85:15 mixture of stereoisomeric 1-bromo-1-methyl-2-phenoxymethylcyclopropanes *20*. In the ^{1}H NMR spectrum, the methyl protons appeared at 1.84 and 1.82 ppm, respectively, for the two isomers, but we were not able to assign the stereochemistry. The monobromides are not always formed in detectable amounts; their formation seems to depend on the concentrations of reactants and how fast methyllithium is added.

With a methyl group at the *ortho* position to the ether function, as in compound *10c*, the generated cyclopropylidene may add at two locations on the aromatic ring; the more substituted bond would be favoured electronically but not sterically. The reaction of *10c* gave in almost equal amounts the allene *19c* and the tricyclic compound resulting from addition to the least hindered bond. The latter product was not isolated as such, but converted to the corresponding tropone *21* which was characterized spectroscopically. The reaction of *10d* with methyllithium gave the corresponding allene *19d* in almost quantitative yield; no cycloaddition product could be detected by either GLC or NMR. In compound *12*, the 5,6-related double bond bearing both substituents is nucleophilic due to the methoxy group; however, the reaction with methyllithium led exclusively to the allene *22*.

These results suggested that intermolecular addition of a cyclopropylidene to anisol might possibly take place provided the cyclopropylidene could not easily undergo ring opening. The cy-



23 24

27

26

28

29

Scheme 4.

Table 1. Reactions of *10b* with methyllithium at different temperatures.

Bath temp. (°C)	*17b*/%	*19b*/%
−100	no reaction	
− 78	67	33
− 30	53	47
0	47	53
20	40	60

clopropylidene derived from 7,7-dibromobicyclo-[4.1.0]heptane (*23*) and methyllithium seemed a good candidate for several reasons: i) ring opening to allene is severely restricted; ii) C−H insertion reactions are expected to have relatively high activation energies; and iii) additions to alkenes had been observed.[9] The reaction of *23* at −78 °C in the presence of a five-fold excess of anisol gave in addition to the expected volatile products[9] a higher boiling liquid in 25 % yield, which, according to GLC, consisted mainly of one compound. A pure sample was obtained by preparative GLC and characterized spectroscopically as the spirononatriene derivative *24*, the expected product from addition to the methoxy substituted double bond. (Scheme 4).

The ratio of addition to ring opening products is dependent on the reaction temperature. Under otherwise comparable conditions, the amount of allene increased as the temperature was raised from −78 °C to 20 °C. This is similar to previous observations from the reaction of compound *1* with methyllithium.[3] The results from reactions of *10b* at different temperatures are recorded in Table 1.

Discussion

1,1-Dibromocyclopropanes react with methyllithium by lithium-bromine exchange followed by elimination of lithium bromide to an intermediate with chemical properties characteristic of a carbene. Due to the electrophilic properties of the latter, a larger ratio of addition to ring opening products was expected from reactions of compund *8* with methyllithium than that observed from *1* under similar conditions.[3] Compounds which could arise from insertion of the carbene into the 1,3-related C−H bonds were not encountered. This is in accordance with the results obtained from similar ethers,[10] except for the observation by Hamond and Trenerry[11] that insertion may compete with ring opening. Moreover, the absence of any tricyclic compound in the product from the vinyl ether *9* suggests a significant degree of regioselectivity for the addition; it seems inherent that the double bond must be 5,6-related to the electrophilic carbon.

The tricyclic ethers *13* are surprisingly stable thermally. We have previously shown[12] that the allene *14a* rearranges thermally to 3-methylene-4-pentenal; hence, formation of only the 2-methylene isomers *15* from the corresponding tricyclic ethers *13* indicates that the latter do not rearrange thermally to the allenes *14*, in contrast to the behaviour of the related hydrocarbon *2a* under similar conditions.[13] The rearrangement may involve diradicals or be concerted, but our results do not allow a distinction between these alternatives.

Norcaradienes *25* must be the initial addition products from reactions of the aromatic ethers *10* and methyllithium; however, these compounds are not expected to survive even at −78 °C but undergo electrocyclic rearrangement to the tricyclic compounds *17*. The failure of compound *6* to undergo addition when treated with methyllithium strongly suggests that the electron donating properties of oxygen are responsible for the formation of addition products from the ethers *10* under similar conditions. The formation of the tricyclic compound *24* shows that the effect is sufficient to cause intermolcular addition of the cyclopropylidene generated from *23*, but not sufficient to compensate for the lower reactivity of the pyridine ring towards electrophilic reagents as indicated by the lack of addition product in the case of *10d*. As observed for the vinyl ethers, the reaction seems restricted to the double bond 5,6-related to the carbenyl carbon, but other configurational factors are important as well. This is demonstrated by the selective addition to the least substituted of the 5,6-related double bonds of compound *10c* and also by the absence of any addition product from reaction of the anisole derivative *12*. In the latter case, the 5,6 bond carrying the methoxy substituent is also disubstituted and apparently too crowded sterically for addition to become competitive with ring opening. Compounds that could derive from insertion into C−H bonds were not detected. The mono-

bromides *20* probably arise from the α-bromocyclopropyllithium intermediate and methyl bromide and not from the carbene.

The dependence of the product ratio on reaction temperature as recorded for compound *10b* in Table 1 is rationalized on steric grounds. The ring opening has only small steric demands and the entropy of activation is probably negligible. On the other hand, for the strongly oriented transition state of the addition reaction, a significant entropy contribution is expected and the ratio of tricyclic compounds *17* to allenes *19* should increase as the reaction temperature is lowered. Similar temperature effects have been recorded for other intramolecular cyclopropylidene reactions.[14]

Crow and McNab[15] have studied the intramolecular reactions of arylcarbenes *26* generated from the tosylhydrazone salts in the gas phase. The major products *27* resulted from addition to the 5,6-related double bonds, but small amounts of C–H insertion products *28* were identified as well (Scheme 4). The latter is in contrast to our results and, moreover, we have previously shown[16] that the thia analogue of *10a* reacted with methyllithium at −78 °C to give mainly the corresponding bicyclopropylidene *29* and no intramolecular addition product.

The electrocyclic rearrangement of compounds *17* to the alkenyltropones *18, 21* is a thermally allowed process as far as orbital symmetry is concerned, but we have no evidence for the concertedness of the reaction. The allenes *19* and other byproducts are easily separated from the tropones rendering the two-step reaction from *10* an addition to the wide variety of synthetic procedures for the preparation of this class of compounds.[17] The selectivity of the conversion enables the preparation of specifically substituted tropones which may turn out to be useful even with the moderate yields indicated by the present work.

Experimental

2,2-Dibromo-1-(2-phenylethyl)cyclopropane (6). Aqueous NaOH (50 ml, 50 %) was added dropwise to a cooled (0 °C) and stirred mixture of 4-phenyl-1-butene (13.2 g, 0.1 mol), bromoform (38 g, 0.15 mol) and TEBA (0.2 g) in CH_2Cl_2 (50 ml). The reaction mixture was stirred vigorously for 24 h at room temperature and worked up in the usual way. Distillation gave 21.2 g (70 %) of *6*, b.p. 76–80° (0.08 mmHg). ^{1}H NMR (60 MHz, CCl_4) δ 0.9–2.0 (5 H, compl. abs.) 2.75 (2 H, br.t), 7.12 (5 H s).

(2,2-Dibromocyclopropyl)methyl vinyl ether (8a). To a mixture of mercury(II) trifluoroacetate (0.40 g, 0.85 mol), 2,6-dimethylpyridine (0.30 g, 2.8 mmol) in 250 ml of ethyl vinyl ether was added 2,2-dibromocyclopropanemethanol[18] (17.5 g, 76 mmol). The reaction mixture was stirred for 3 h at room temperature, anh. K_2CO_3 added and excess ethyl vinyl ether distilled off. The residue was fractionally distilled through a column to yield 7.7 g (40 %) of *8a,* b.p. 87 °C (6 mmHg). Anal. $C_6H_8Br_2O$; C, H. IR (film): 1645, 1625, 1325, 1200, 1120, 1085, 835 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.70 (3H, m), 3.78 (2H, d, J = 4.0 Hz), 4.0 and 4.25 (2H, m) 6.41 (1H, dd, J = 7.0, 14.0 Hz).

(2,2-Dibromo-1-methylcyclopropyl)methyl vinyl ether. Compound *8b* was prepared from 2,2-dibromo-1-methylcyclopropanemethanol[19] in 48 % yield by the same procedure as for *8a*; b.p. 54–55 °C (1.0 mmHg). Anal. $C_7H_{10}Br_2O$: C, H. IR (film): 1635, 1615, 1320, 1200, 1080, 1040, 1010, 960, 820 cm^{-1}. ^{1}H NMR (60 MHz; CCl_4): δ 1.47 (3H, s), 1.53 (2H, dd, J = 7.5, 11.5 Hz) 3.74 (2H, s), 3985 and 4.22 (2H, m), 6.44 (1H, dd, J = 7.0, 14.0 Hz).

2-(2,2-Dibromocyclopropyl)ethanol (30). Aqueous NaOH (50 ml, 50 %) was added dropwise to a cooled (0 °C) and stirred mixture of 3-buten-1-ol dihydropyranyl ether (30.2 g, 0.194 mol), bromoform (101 g, 0.4 mol) and benzyltriethylammonium chloride (TEBA, 0.1 g) in CH_2Cl_2 (50 ml). The reaction mixture was stirred vigorously for 3 days and worked up in the usual way. The crude product was hydrolyzed with 4 M HCl in ethanol at room temperature overnight, and the product extracted with CH_2Cl_2, washed and dried ($MgSO_4$). Solvents were evaporated and the residue distilled to give 11.5 g (24 %) of *30*; b.p. 73–75 °C (0.2 mmHg). Anal. $C_5H_8Br_2O$: C, H. IR (film): 3300, 1060 cm^{-1}. ^{1}H NMR (60 MHz; CCl_4): δ 1.5 (5H, m) 3.43 (1H, s), 3.74 (2H, t, J = 6.0 Hz).

2-(2,2-Dibromocyclopropyl)ethyl vinyl ether. Compound *9* was prepared from *30* in 52 % yield

using the same procedure as for *8a*; b.p. 63–65 °C (1.0 mmHg). Anal. $C_7H_{10}Br_2O$: C,H. IR (film) 1640, 1620, 1325, 1205, 1115, 1090, 1010, 970, 830 cm^{-1}. ^1H NMR (60 Mz, CCl_4): δ 1.7 (5H, m), 3.77 (H, t, J = 6.5 Hz), 3.98 and 4.22 (2H, m), 6.37 (1H, dd J = 7.0, 14.0 Hz).

(2,2-Dibromocyclopropyl)methyl phenyl ether (10a). To a solution of phenol (3.85 g, 40 mmol) in dry methanol (40 ml) was added sodium methoxide (2.25 g, 41 mmol) and sodium iodide (200 mg). After stirring for 15 min, 1-bromomethyl-2,2-dibromocyclopropane[20] (10.25 g, 35 mmol) was added and the mixture refluxed under N_2 for 3 days. The methanol was distilled, and the residue diluted with ether, washed and dried ($MgSO_4$). The solvent was evaporated and the residue distilled to give 5.0 g (47 %) of *10a*; b.p. 95–97 °C (0.02 mmHg), m.p. 54 °C from pentane. Anal. $C_{10}H_{10}Br_2O$: C,H. IR (film): 1600, 1590, 1495, 1240, 1040, 760 cm^{-1}. ^1H NMR (60 MHz; CCl_4): δ1.8 (3H, m), 4.00 (2H, compl.t), 7.0 (5H, m).

(2,2-Dibromo-1-methylcyclopropyl)methyl phenyl ether (10b). To a solution of phenol (3.0 g, 32 mmol) in dry CH_3CN (60 ml) and dry DMSO (1.5 ml), was added sodium methoxide (1.68 g, 31 mmol) and sodium iodide (300 mg). After stirring for 15 min, 1-chloromethyl-1-methyl-2,2-dibromocyclopropane[21] (6 g, 23 mmol) was added and the mixture kept at 70 °C under N_2 for 6 days. The solvents were removed under reduced pressure, the residue diluted with Et_2O, washed with water, and dried ($MgSO_4$). The solvent was evaporated and the residue distilled to give 4.8 g (65 %) of *10b*; b.p. 102–105 °C (0.01 mmHg). Anal. $C_{11}H_{12}Br_2O$: C,H. IR (film): 1600, 1590, 1500, 1470, 1245, 1175, 1085, 1050, 765 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 1.53 (3H, s), 1.55 (2H, dd, J = 7.5, 13.0 Hz), 3.98 (2H, s), 7.04 (5H, m).

(2,2-Dibromo-1-methylcyclopropyl)methyl 2-tolyl ether (10c). The ether was prepared from β-methallyl 2-tolyl ether[22] (16.2 g, 0.10 mole), bromoform (50.6 g, 0.20 mole), TEBA (0.1 g), 50 % NaOH solution (40 ml), and CH_2Cl_2 (25 ml) using the procedure as described for the preparation of compound *30*. Distillation gave 7.8 g (23 %) of *10c*; b.p. 115–116 °C (0.15 mmHg). Anal. $C_{12}H_{12}Br_2O$: C,H. IR (film): 1600, 1590, 1495, 1465, 1435, 1390, 1290, 1245, 1195, 1050, 760 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 1.52 (2H, dd, J = 7.5, 13.5 Hz), 1.53 (3H, s), 2.21 (3H, s), 3.94 (2H, s), 6.85 (4H, m).

(2,2-Dibromo-1-methylcyclopropyl)methyl-3-pyridyl ether (10d). The ether was prepared from 3-hydroxypyridine (3.1 g, 33.0 mmol), sodium hydroxide (1.32 g, 33.0 mmol), 1-bromomethyl-2,2-dibromo-1-methylcyclopropane[21] (10.0 g, 32.6 mmol), dry DMF (50 ml) and methanol (30 ml) following the procedure for the preparation of *10a*. Short path distillation at 87 °C (0.01 mmHg) gave 2.7 g (26 %) of *10d*. A small portion was distilled, b.p. 98–100 °C (0.015 mmHg). Anal. $C_{10}H_{11}Br_2NO$: C,H. IR (film): 1600, 1585, 1500, 1490, 1470, 1440, 1400, 1280, 1240, 1200, 1065, 1050, 1030, 810 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 1.57 (3H, s), 1.67 (2H, dd, J = 7.5, 12.0 Hz), 4.12 (2H, s), 7.25 and 8.3 (4H, m).

4-(2-Methoxyphenyl)-2-methyl-1-butene (31). A Grignard reagent was prepared from 2-methoxybenzyl chloride (33.0 g, 0.21 mol) and magnesium turnings (5.1 g, 0.21 mole) in ether (100 ml). To the cooled (0 °C) reagent, β-methallyl chloride (18.1 g, 0.20 mol) was added followed by 3 drops of 0.1 M Li_2CuCl_4 in THF. The mixture was allowed to attain room temperature, then refluxed for 1 h. The mixture was worked up in the usual way. Distillation gave 21.5 g, (61 %) of *31*; b.p. 104–108 °C (10 mmHg). IR (film): 1650, 1610, 1595, 1500, 1470, 1250, 1185, 1120, 1060, 1050, 895, 765 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 1.73 (3H, s), 2.30 (2H, m), 2.75 (2H, m), 3.74 (3H, s), 4.66 (2H, s), 6.95 (4H, m).

2,2-Dibromo-1,(2-(2-methoxyphenyl)ethyl)-1-methylcyclopropane (12). The compound was prepared from the olefin *31* (17.6 g, 0.10 mol), bromoform (50.6 g, 0.2 mol), tributylamine (0.4 ml), 50 % NaOH solution (40 ml), and CH_2Cl_2 (25 ml) using the same procedure as for compound *30* with 18 h reaction time. Distillation gave unreacted olefin (7.4 g). The residue was purified by short path distillation at 126 °C (0.01 mmHg), yielding 12.5 g (62 % based on recovered olefin) of *12*. Anal. $C_{13}H_{16}Br_2O$: C,H. IR (film): 1600, 1585, 1490, 1460, 1435, 1290, 1240, 1175, 1115, 1050, 1030, 760 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 1.15–1.8 (2H, m), 1.51 (3H, s), 2.21 (3H, s), 3.94 (2H, s), 6.85 (4H, m).

Reactions of gem-*dibromocyclopropane derivatives with methyllithium – general procedure.* A 1.5–1.8 M methyllithium solution in ether was added dropwise to a stirred solution of the gem-dibromocyclopropane in ether cooled to −78 °C (bath temperature). The mixture was stirred for 30 min at the bath temperature, allowed to warm to room temperature, and hydrolyzed with water. The aqueous portion was extracted with ether. The combined ether solutions were washed with saturated aq. NaCl solution and dried ($MgSO_4$). Evaporation of ether left the crude product which was analyzed by NMR and by GC on a 2 m 10 % SP 2100 column. Preparative GC was carried out on a 2 m 15 % QF-1 column at 100–150 °C.

5-Phenyl-1,2-pentadiene (7). A solution of compound *6* (3.15 g, 5 mmol) in ether (5 ml) was treated with 1.7 M ethereal methyllithium (3.5 ml, 6 mmol) according to the general procedure. Evaporation of solvent gave 0.8 g of crude product which contained one component. Separation by prep. GLC gave a pure sample of *7*. Anal. $C_{11}H_{12}$: C,H. IR (film): 1965 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 2.30 (2H, m), 2.70 (2H, m), 4.58 (2H, m), 5.05 (1H, p), 7.08 (5H, s).

Reaction of 8a *with methyllithium.* Compound *8a* (2.5 g, 10.1 mmol) in ether (10 ml) was treated with 1.5 M ethereal methyllithium (7.6 ml, 11.3 mmol) according to the general procedure. The solvent was evaporated through a column leaving 0.9 g of crude product which was shown to consist of *13a* (88 %) and *14a* (12 %). The compounds were separated by prep. GLC. The allene *14a* was identical with an authentic sample.[12] 2-Oxatricyclo[4.1.0.$0^{4,6}$]heptane (*13a*): IR (film): 2980, 2920, 2840, 1245, 1100, 1065, 980, 930, 890, 870 cm^{-1}. ^1H NMR (98 MHz, CCl_4): δ 1.63 (1H, d, J = 8.0 Hz), 1.84 (1H, dd, J = 3.0, 8.0 Hz), 3.26 (1H, m), 3.66 (2H, s) 4.46 (1H, s), 4.55 (2H, m). ^{13}C NMR (25.14 MHz, CCl_4): δ 37.08 (C-5), 46.56 (C-4), 65.97 (C-7), 79.67 (C-1), 91.88 (C-3). The spiro carbon (C-6) was not visible.

Less than 5 % of compound *13a* was converted thermally on GLC (15 % QF-1 at 130 °C, injector temp. 300 °C) to 2-methylene-4-pentenal (*15a*) ^1H NMR (60 MHz, CCl_4): δ 2.94 (2H, d, J = 6.0 Hz), 4.8–5.2 (2H, m), 5.2–5.8 (1H, m), 6.06 (2H, d, J = 13.0 Hz), 9.50 (1H, s).

Reaction of 8b *with methyllithium.* Compound *8b* (2.7 g, 10 mmol) in ether (10 ml) was treated with 1.7 M ethereal methyllithium (6.5 ml, 11 mmol) according to the general procedure. The solvent was evaporated through a column leaving 1.1 g of crude product which was shown to consist of *13b* (87 %) and *14b* (13 %). The compounds were separated by prep. GLC, which caused *13b* to rearrange in part to the aldehyde *15b*.

4-Methyl-2-oxatricyclo[4.1.0.$0^{4,6}$]heptane (*13b*): ^1H NMR (98 MHz, CCl_4): δ 1.28 (3H, s), 1.62 (2H, dd, J = 3.0, 9.0 Hz), 3.47 (2H, dd, J = 3.0, 5.5 Hz), 4.39 (1H, s), 4.50 (2H, s).

2-Methyl-2,3-butadienyl vinyl ether (*14b*): IR (film): 1960 cm^{-1} ^1H NMR (60 MHz, CCl_4): δ 170 (3H, t), J = 3.0 Hz), 3.9 and 4.23 (2H, m), 4.10 (2H, t, J = 2.0 Hz), 4.65 (2H, m), 6.33 (1H, dd, J = 7.0, 14.0 Hz).

4-Methyl-2-methylene-4-pentenal (*15b*): IR (film): 1690, 1655, 960, 900 cm^{-1}. ^1H NMR (98 MHz, CCl_4): δ 1.67 (3H, s), 2.96 (2H, s), 4.83 (2H, d, J = 4.5 Hz), 6.20 (2H, d, J = 9.0 Hz), 10.70 (1H, s).

3,4-Pentadienyl vinyl ether (16). Reaction of compound *9* (3.1 g, 11.5 mmol) in ether (10 ml) with 1.5 M ethereal methyllithium (8.6 ml, 13 mmol) according to the general procedure, gave crude *16* (1.3 g). A pure sample was obtained by prep. GLC. IR (film): 1960 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 2.30 (2H, m), 3.65 (2H, t, J = 6.5 Hz), 4.15 (1H, d, J = 2.0 Hz), 4.60 (2H, m), 5.00 (1H, m), 6.32 (1H, dd, J = 7.0, 14.0 Hz).

Reaction of 10a *with methyllithium.* The ether *10a* (1.0 g, 3.2 mmol) in ether (25 ml) was treated with 1.5 M ethereal methyllithium (2.5 ml, 3.7 mmol) according to the general procedure. The crude product (0.5 g) was shown by GLC to consist of the compounds *19a, 17a* and *20* in 29, 59 and 12 %, respectively. The compounds were separated by prep. GLC.

4-Phenoxy-1,2-butadiene (*19a*): ^1H NMR (400 MHz, $CDCl_3$): δ 4.86 (2H, m), 5.40 (1H, p, J = 0.65 Hz), 6.95–7.28 (5H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 65.92 (C-4), 76.36 (C-1), 87.26 (C-3), 115.10, 121.00, 129.42, 158.52 (Ar.C), 209.50 (C-2).

11-Oxatricyclo[5.4.0.$0^{7,9}$]undeca-1,3,5-triene (*17a*): ^{13}C NMR (100.6 HMz, $CDCl_3$): δ 27.04 (C-8), 28.73 (C-9), 34.55 (C-7), 71.07 (C-10), 96.84

(C-2), 121.79, 125.02, 127.72, 129.31 (C-3, 4, 5, 6) ~ 160 (C-1, uncertain).

(2-bromo-2-methylcyclopropyl)methyl phenyl ether (*20*) as 85: 15 mixture of stereoisomers: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.15 (3H, m), 1.81 and 1.83 (3H, s), 4.15 (2H, d, J = 0.7 Hz), 6.81–7.32 (5H, m).

2-(2-Propenyl)-2,4,6-cycloheptatrienone. Compound *18a* was formed from *17a* when the injector temperature of the GLC was 195 °C or higher. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.42 (2H, d, J = 0.7 Hz), 5.15 (2H, m), 5.95 (1H, m), 6.82–7.32 (5H, m).

Reaction of 10b *with methyllithium.* The ether *10b* (1.0 g, 3.1 mmol) in ether (20 ml) was treated with 1.5 M ethereal methyllithium (2.4 ml, 3.6 mmol) according to the general procedure. The crude product (0.5 g) was shown by GLC to consist of *19b* and *17b* in 33 and 67 %, respectively, which were separated by prep. GLC. The proportion of the two compounds in the mixture was dependent on the reaction temperature (see Table 1).

3-Methyl-4-phenoxy-1,2-butadiene (*19b*): IR (film): 1960 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.77 (3H, t, J = 3.0 Hz), 4.44 (2H, t, J = 2.0 Hz), 4.73 (2H, m), 7.0 (5H, m).

9-Methyl-11-oxatricyclo[5.4.0.0^{7,9}]undeca-1,3,5-triene (*17b*): IR (film): 1650, 1620, 1595, 1570, 1390, 1290, 1240, 1210, 1140, 1105, 1040, 990, 960, 860, 765 cm^{-1}. UV [EtOH(ε)]: 250/sh. (2400), 342 (1040) nm. ^{1}H NMR (98 MHz, CCl_4): δ 0.62 (1H, d, J = 5.0 Hz), 1.03 (1H, d, J = 5.0 Hz), 1.28 (3H, s), 2.39 (2H, dd, J = 8.5, 16.0 Hz), 4.70 (1H, d, J = 11.5 Hz), 5.12 (1H, d, J = 7.0 Hz), 5.6 (3H, m). ^{13}C NMR (25.14 MHz, CCl_4): δ 14.5 (CH_3), 31.7 (C-9), 33.0 (C-8), 74.7 (C-10), 97.1 (C-2), 120.2, 121.3, 127.7, 129.4 (C-3, 4, 5, 6), 160.6 (C-1). The resonance due to C-7 was not visible.

2-(2-Methyl-2-propenyl)-2,4,6-cycloheptatrienone (19b). This compound was formed from *18b* when the injection temperature of GLC was 175 °C or higher. IR (film): 1650, 1630, 1590, 1510, 1470, 900, 795 cm^{-1}; UV [EtOH(ε)]: 318 (3840) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (3H, s), 3.37 (2H, s), 4.81 (2H, d, J = 5.6 Hz), 6.96 (2H, m), 7.10 (2H, m), 7.26 (1H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 22.4 (CH_3), 42.0 (CH_2), 113.0 (olef. CH_2), 133.5 (olef. C), 132.6, 135.0, 135.0, 140.3, 143.4 (olef. CH), 153.0 (olef. C), 186.8 (C=O).

Reaction of 10c *with methyllithium.* The ether *10c* (3.3 g, 10 mmol) in ether (10 ml) was treated with 1.7 M ethereal methyllithium (6.5 ml, 11 mmol) according to the general procedure. The crude product (1.8 g) was shown by GLC to consist of *19c* (45 %) and *17c* (55 %). The former was separated on prep. GLC, but the latter rearranged to the tropone *21,* (see below).

3-Methyl-4-(2-methylphenoxy)-1,2-butadiene (*19c*): IR (film): 1970 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.71 (3H, t, J = 3.0 Hz), 2.13 (3H, s), 4.35 (2H, t, J = 2.0 Hz), 4.60 (2H, m), 6.8 (4H, m).

7-Methyl-2-(2-methyl-2-propenyl)-2,4,6-cycloheptatrienone (21). Under prep. GLC conditions with an injector temperature of 200 °C, *21* was formed from *17c*. IR (film): 1650, 1625, 1580, 1380, 900, 790 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.75 (3H, d, J = 2.0 Hz), 2.23 (3H, d, J = 2.0 Hz), 3.24 (2H, s), 4.5 (1H, br. s), 4.78 (1H, br. d., : = 5.0 Hz), 7.0 (4H, m).

3-Methyl-4-(3-pyridyloxy)-1,2-butadiene (19d). Reaction of the ether *10d* (0.6 g, 1.9 mmol) in ether (5 ml) with 1.7 M ethereal methyllithium (1.2 ml, 2.0 mmol) according to the general procedure gave a crude product (0.3 g) which consisted of the allene *19d.* It decomposed on attempted purification by prep. GLC. IR (film): 1960 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.75 (3H, t, J = 3.0 Hz), 4.52 (2H, t, J = 2.0 Hz), 4.72 (2H, m), 7.17 (2H, m), 8.25 (2H, m).

5-(2-Methoxyphenyl)-3-methyl-1,2-pentadiene (22). Reaction of compound *12* (3.5 g, 10 mmoles) in ether (25 ml) with 1.7 M ethereal methyllithium (6.5 ml, 11 mmol) according to the general procedure gave crude allene *22* (1.9 g). A pure sample was obtained by prep. GLC. IR (film): 1960 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 1.68 (3H, t, J = 3.0 Hz), 2.10 (2H, m), 2.65 (2H, m), 3.73 (3H, s), 4.51 (2H, m), 6.85 (4H, m).

2-Methoxy-2,4,6-cycloheptatrienespiro-7'-bicyclo[4.1.0]heptane (24). An ethereal 1.7 M solution of methyllithium (65 ml, 0.11 mol) was

added dropwise to a stirred solution of anisole (54.1 g, 0.5 mol) and 7,7-dibromobicyclo-[4.1.0]heptane (*23*) (25.4 g, 0.10 mol) in ether (5 ml) kept at −78 °C. After the usual work-up solvents, excess anisole and volatile products were evaporated under vacuum, and the residue short path distilled at 98 °C (0.05 mmHg) giving 7.2 g (25 %) of *24*. IR (film): 1620, 1605, 1535, 1060 cm^{-1}. UV [EtOH(ε)]: 298 (3400) nm. ^1H NMR (98 MHz, CS_2): δ 1.0–2.3 (10H, m), 3.44 (3H, s), 4.94 (1H, d, J = 10 Hz), 5.04 (1H, d, J = 6.5 Hz), 6.15 (3H, m). ^{13}C NMR (25.14 MHz, CS_2): δ 19.8, 20.1 (CH_2), 21.4, 22.5 (CH), 55.4 (OCH_3), 97.1, 118.8, 124.4, 128.5, 129.2 (olef. CH), 154.5 (olef. C). The spiro carbon was not visible.

References

1. Kirmse, W. *Carbene Chemistry,* 2nd ed. Academic Press, New York 1971.
2. Moore, W. R. and Ward, H. R. *J. Org. Chem. 25* (1960) 2073; Jones, W. M., Grasley, M. H. and Brey, W. S., Jr. *J. Am. Chem. Soc. 85.* (1963) 2754; Jones, M. J., Jr. and Petrillo, E. W., Jr. *Tetrahedron Lett.* (1969) 3953; Rostek, C. J. and Jones, W. M. *Tetrahedron Lett.* (1969) 3957; Bee, L. K., Everett, J. W. and Garratt, P. J. *Tetrahedron 33* (1977) 2143.
3. Skattebøl, L. *J. Org. Chem. 31* (1966) 2789.
4. Baird, M. *Chem. Commun.* (1974) 197; Brinker, U. H. and Streu, J. *Angew. Chem. 92* (1980) 641; Brinker, U. H., Gomann, K. and Zorn, R. *Angew. Chem. 95* (1983) 893; *Angew. Chem. Suppl.* (1983) 1241.
5. Watanabe, W. H. and Conlon, L. E. *J. Am. Chem. Soc. 79* (1957) 2828.
6. Makosza, M. and Fedorynski, *Synth. Commun. 3* (1973) 305; Skattebøl, L., Abskharoun, G. A. and Greibrokk, T. *Tetrahedron Lett.* (1973) 1367.
7. Toda, T., Saito, K. and Mukai, T. *Bull. Chem. Soc. Jpn. 52* (1979) 151.
8. Bagli, J. F. and St-Jacques, M. *Can. J. Chem. 56* (1978) 578.
9. Moore, W. R. and Ward, H. R. *J. Org. Chem. 25* (1960) 2073.
10. Baird, M. S. *Chem. Commun.* (1971) 1145.
11. Hamon, D. P. G. and Trenerry, V. C. *Aust. J. Chem. 33* (1980) 809.
12. Karlsen, S., Frøyen, P. and Skattebøl, L. *Acta. Chem. Scand. B 30* (1976) 664.
13. Frey, H. M., Hopkins, R. G. and Skattebøl, L. *J. Chem. Soc. B* (1971) 539.
14. Brinker, U. H. and Ritzer, J. *J. Am. Chem. Soc. 103* (1981) 2116.
15. Crow, W. D. and McNab, H. *Aust. J. Chem. 34* (1981) 1037.
16. Arct, J. and Skattebøl, L. *Acta Chem. Scand. B 36* (1982) 593.
17. Pietra, F. *Chem. Rev. 73* (1973) 293; Takaya, H., Hayakawa, Y., Makino, S. and Noyori, R. *J. Am. Chem. Soc. 100* (1978) 1778; Banwell, M. G. *Chem. Commun.* (1982) 847; Feldman, K. S., Come, J. H., Freyer, A. J., Kosmiche, B. J. and Smith, C. M. *J. Am. Chem. Soc. 108* (1986) 1327.
18. Holm, K. H., Lee, D. G. and Skattebøl, L. *Acta Chem. Scand. B 32* (1978) 693.
19. Kleveland, K., Skattebøl, L. and Sydnes, L. K. *Acta Chem. Scand. B 31* (1977) 463.
20. Labeish, N. N., Kharicheva, E. M., Mandelshtam, T. V. and Kostikov, R. R. *Zh. Org. Khim. 14* (1978) 878.
21. Baird, M. C., Baxter, A. G. W., Devlin, B. R. J. and Searle, R. J. G. *Chem. Commun.* (1979) 210.
22. Bartz, Q. R., Miller, R. F. and Adams, R. *J. Am. Chem. Soc. 57* (1935) 371.

Received April 16, 1986.