

POLYCHLORONORBORNADIENYLLITHIUM REAGENTS*

DIETMAR SEYFERTH, ANTHONY B. EVNIN** AND DAVID R. BLANK

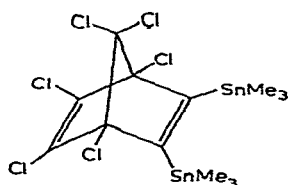
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., 02139 (U.S.A.)

(Received January 2nd, 1968)

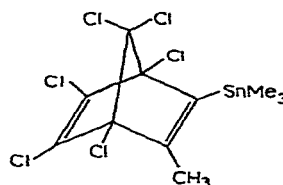
SUMMARY

2-Lithio-3-bromo-, 2-lithio-3-methyl- and 2-lithio-3-chloro-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene have been prepared by bromine-lithium exchange between the respective bromides and *n*-butyllithium in diethyl ether at -75° . Reactions with trimethylchlorosilane, trimethyltin chloride, mercuric halide, carbon dioxide and water or ethanol served to demonstrate their synthetic utility. It was determined that 2-lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene has a half-life of about 3 h in diethyl ether at $27-29^{\circ}$, but the nature of its decomposition was not ascertained.

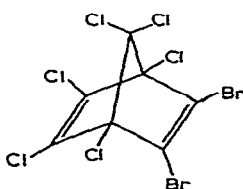
A recent study of the Diels-Alder reactions of hexachlorocyclopentadiene with organotin-substituted acetylenes included the preparation of the mono- and bis(trimethylstannyl)polychloronorbornadienes (I) and (II)². Cleavage of the Sn-C bonds of these compounds with bromine gave 2,3-dibromo-1,4,5,6,7,7-hexachloro-



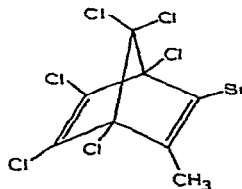
(I)



(II)



(III)

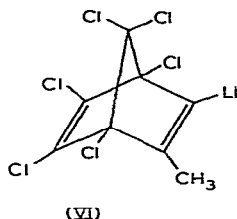
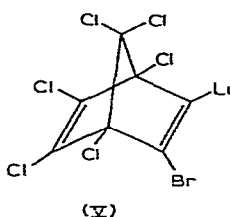


(IV)

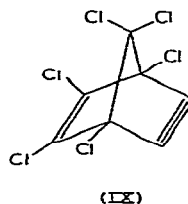
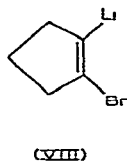
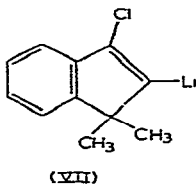
* Preliminary communication: ref. 1.

** National Institutes of Health Predoctoral Fellow, 1963-1966

bicyclo[2.2.1]hepta-2,5-diene (III) and 2-bromo-3-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (IV). The chemistry of these bromides was of interest to us, especially the possibility that their bromine substituents might be exchangeable for lithium via the standard RBr/R'Li exchange reaction. If such exchange did occur, then the question of the stability of the highly halogenated lithium reagents (V) and (VI) would be of some interest.



Usually β -chloroalkyl- and β -chlorovinyl lithium reagents are only stable at very low temperatures, since their decomposition via β -elimination of lithium chloride is quite facile^{3,4}. However, Wittig and his coworkers^{5,6} have shown that cyclic β -halovinyl lithium reagents of type (VII) and (VIII) are much more stable, presumably



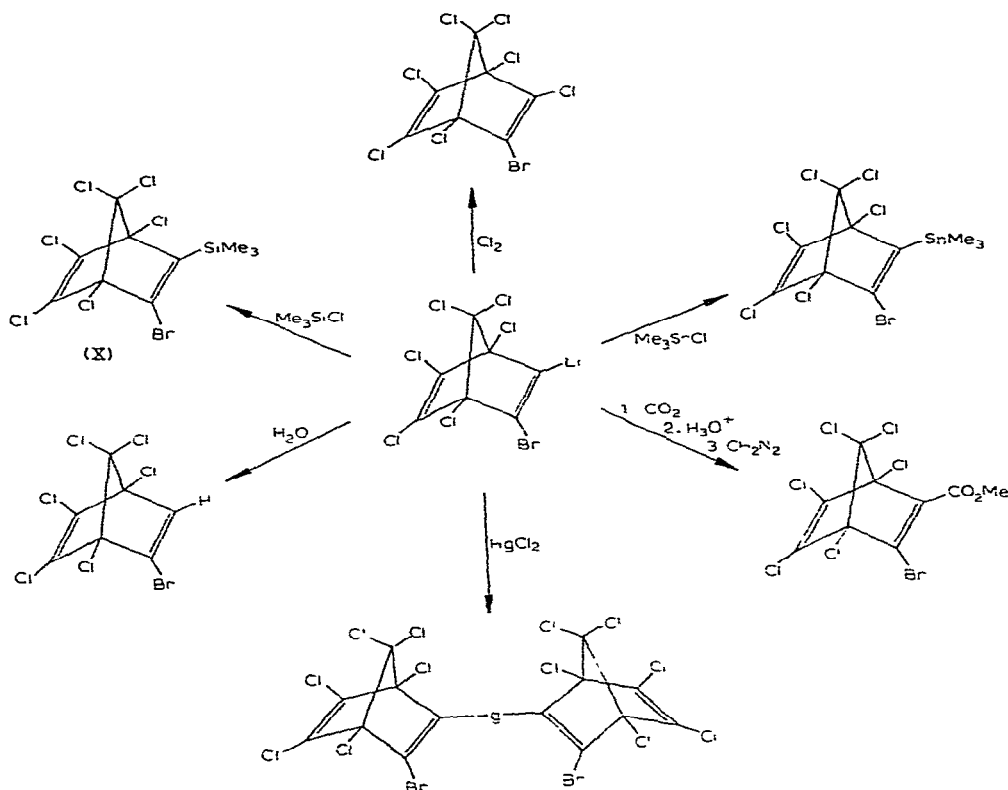
because of the high strain energy which would have to be overcome in forming the cyclic, acetylenic β -elimination product, *e.g.* cyclopentyne in the case of (VIII). The lithium reagent (VIII) had a half-life of about 3 h in diethyl ether solution at 21°, and the formation of lithium bromide as a result of its decomposition followed first order kinetics. The short-lived cyclopentyne formed by decomposition of (VIII) could be trapped (in low yield) by means of its Diels–Alder reaction with 2,5-diphenylisobenzofuran.

Lithium reagent (VII) was even more stable. We would expect (V) and (VI) to be comparable in stability to (VIII). In the case of (V), the formation of hexachlorobicyclo[2.2.1]hept-2-ene-5-yne, (IX), via loss of lithium bromide should be quite unfavorable energetically due to the high strain energy of (IX), and the alternative elimination of lithium chloride to give an *anti*-Bredt olefin should be even less favorable. This second alternative is the only one open to (VI) in its decomposition via β -elimination. Accordingly, it was expected that the synthesis of (V) and (VI) should be possible and that these should be useful reagents for the synthesis of various substituted polychloronorbornadienes.

Lithium reagent (V) was prepared by reaction of the dibromohexachloronorbornadiene (III) with one molar equivalent of *n*-butyllithium in diethyl ether at -75° under an atmosphere of nitrogen. The reaction mixture became first light brown and then deep green and was stirred at -75° for an additional 3 h. Addition of trimethylchlorosilane (in excess) was followed by warming to room temperature,

a vacuum distillation and gas-liquid partition chromatographic (GLC) analysis. It was shown that 2-bromo-3-(trimethylsilyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hepta-2,5-diene (X) had been formed in 95 % yield; a *ca.* 5 % recovery of the starting bromide was indicated. The other product of the exchange reaction, *n*-butyl bromide, was produced in 94 % yield. Further reactions of lithium reagent (V) with trimethyltin chloride, mercuric chloride, carbon dioxide, chlorine and water were carried out and are summarized in Chart 1. The yields of products were variable and no attempts were made to optimize reaction and work-up conditions.

CHART 1



A similar reaction of the bromide (IV) with *n*-butyllithium in ether at -75° gave the lithium reagent (VI) in high yield. Chart 2 summarizes the conversions of (VI) which were studied.

The availability of 2-bromo-1,3,4,5,6,7,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene from chlorination of lithium reagent (V) prompted a brief study of its reaction with *n*-butyllithium under the conditions used with the other polychloronorborenadienyl bromides. The chlorination of (V) proved not to be readily adaptable to larger scale preparations, thus placing a practical limit on this study. However, as Chart 3 shows, 2-lithio-1,3,4,5,6,7,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene can be prepared and it undergoes the usual reactions with protonic reagents and with trimethylchlorosilane. Also available for study was octachlorobicyclo[2.2.1]hepta-2,5-

CHART 2

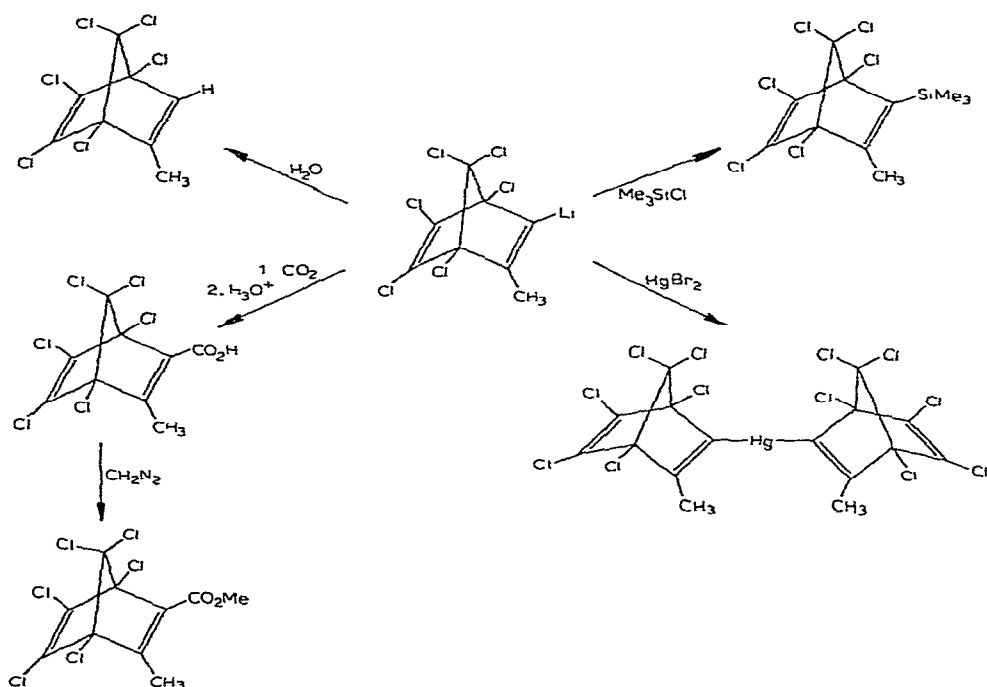
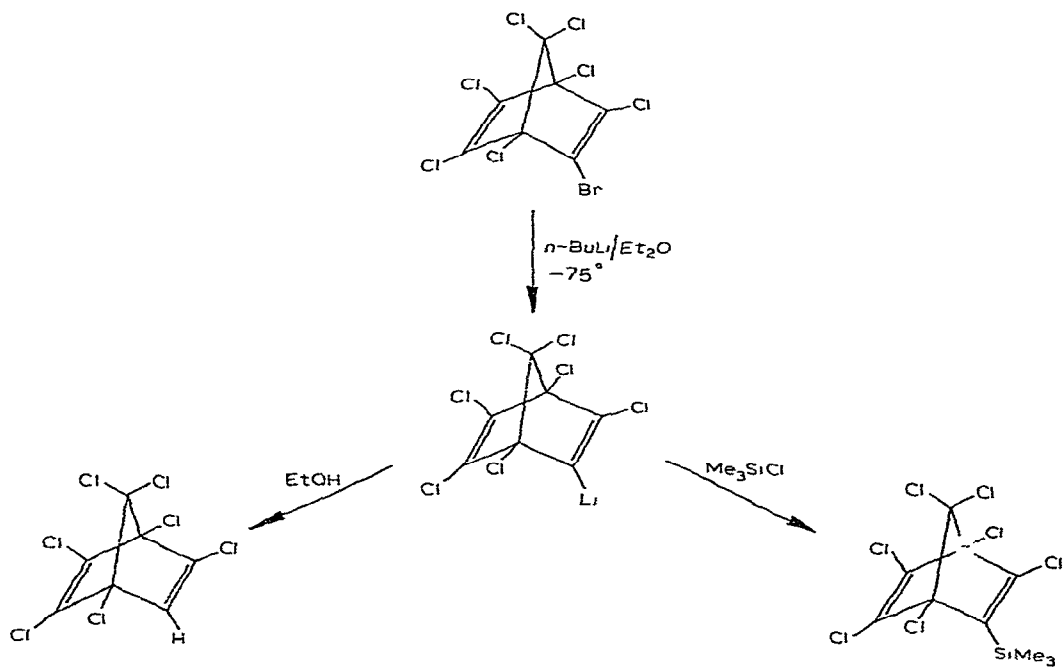
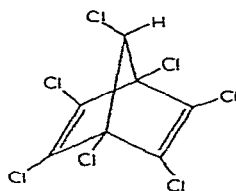


CHART 3



diene². The course of its reaction with *n*-butyllithium was quite different. A considerable amount of starting material (> 30 %) was recovered and the major product (when the reaction mixture was quenched with ethanol) was 1,2,3,4,5,6,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene (XI). Other, higher boiling products appeared to contain the



(XI)

same bicyclic skeleton, but their IR and NMR spectra suggested the presence of a 7-*n*-butyl substituent as well. Unfortunately, insufficient amounts of these products were available for complete structural characterization. The recent observation⁷ that 7,7-dichloronorcarane reacts with *n*-butyllithium at low temperature to give the 7-chloro-7-norcaranyl radical by one-electron transfer may be of relevance in this connection.

Treatment of the dibromohexachloronorbornadiene (III) with two equivalents of *n*-butyllithium at -75° did not appear to give 2,3-dilithio-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. When the reaction mixture was quenched with trimethylchlorosilane, only 2-bromo-3-(trimethylsilyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (49 % crude yield) could be isolated. Examination of the volatile products of the reaction by quantitative GLC indicated the presence of *n*-butyl bromide (61 %) and *n*-butyl chloride (23 %). The formation of the latter (not observed in the 1 : 1 reaction) suggests that attack of a second equivalent of *n*-butyllithium on the bromine atom bonded to the charged, solvated 2,3 double bond of (V) is not favorable and that attack at one of the chlorines occurs at an at least comparable rate. The formation of greater than 50 % of the theoretical amount of *n*-butyl bromide does, however, provide a suggestion that some of the dilithio compound may have been formed, at least transiently. Attempts to synthesize the 2,3-dilithio derivative by metal-metal exchange between the 2,3-bis(trimethyltin) compound (I) and two equivalents of *n*-butyllithium were entirely unsuccessful; tars were obtained from which only starting material could be isolated. This aspect of the investigation was not pursued further.

As Charts 1-3 indicate, the polychloronorbornadienyllithium reagents which are the subject of this study are useful preparative reagents at -75° in diethyl ether. Their stability in ether at room temperature also was of interest. A series of experiments was carried out in which 2-lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V) was prepared by the reaction of *n*-butyllithium with (III) in ether at -75° and then was allowed to warm to room temperature during 35-40 min. In separate experiments, these lithium reagent solutions were quenched with trimethylchlorosilane immediately upon reaching room temperature, one, 2.5 and 5 h afterwards, and in each case the yield of *n*-butyl bromide and of the silylated product, (X), was determined by GLC. The results of these experiments are given in Table 1. A plot of the log [yield of (X)] *vs.* time gave a straight line from which a

TABLE 1

DECOMPOSITION OF 2-LITHIO-3-BROMO-1,4,5,6,7,7-HEXACHLOROBICYCLO[2.2.1]HEPTA-2,5-DIENE IN ETHER AT 27-29°

Time (h)	Yield of n-BuBr (%)	Yield of (X) (%)
0 ^a	99.1 (95.0)	65.8 (65.3)
1.0	97.7	48.9
2.5	97.3	34.0
5.0	96.8 (91.3)	19.2 (22.8)

^a Zero time: reagent solution was quenched immediately upon reaching room temperature.

reagent half-life of about 3 h could be estimated. Thus lithium reagent (V) is as stable at room temperature as 1-lithio-2-bromo-1-cyclopentene (VIII), a result which is in line with expectations. However, all attempts to trap the presumed cycloalkyne product of the decomposition of lithium reagent (V) were unsuccessful. When the decomposition of (V) was allowed to take place in the presence of furan or 2,5-diphenylisobenzofuran, no adduct of (IX) with these dienes could be isolated, nor was there any evidence for their formation from NMR or TLC examination of the crude reaction mixtures. An attempt to trap (IX) by allowing (III) to decompose in the presence of an excess of phenyllithium also was not successful. At present we have no experimental evidence concerning the nature of the decomposition of lithium reagent (V) at room temperature.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Thin layer chromatography utilized Eastman Silica Gel Chromagram Sheet K 301R, with pentane as eluent and iodine vapor as the developer. GLC analyses were carried out using an F&M 700 gas chromatograph with columns containing General Electric Co. SE-30 silicone rubber gum on Chromosorb P. IR spectra were recorded using Perkin-Elmer 237B or 337 grating IR Spectrometers, NMR spectra with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal tetramethylsilane. Elemental analyses were performed by Dr. S. M. Nagy (MIT) or the Galbraith Laboratories (Knoxville, Tenn.). In the early stages of this research n-butyllithium was prepared by reaction of lithium with n-butyl chloride in pentane; in later stages it was purchased from Foote Mineral Co. as a solution in hexane. The active organolithium content of these solutions was determined by the double titration procedure using 1,2-dibromoethane as the organic halide. The polychloronorbornadienes used in this study were prepared by the procedures reported by us previously².

Preparation of 2-bromo-3-(trimethylsilyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (X)

A solution of 1.141 g (2.5 mmoles) of (III) in 50 ml of diethyl ether (distilled from calcium hydride) in a 100 ml three-necked round-bottomed flask equipped with

a magnetic stirring assembly, reflux condenser topped with a gas inlet tube and addition funnel was cooled to -75° . n-Butyllithium (2.07 ml of 1.20 N in pentane), diluted to 20 ml with ether, was added dropwise during 1 h. The reaction mixture became light brown and then deep green. Stirring was continued at -75° for another 3 h. To the reaction mixture was added 1.9 ml (15.0 mmoles) of freshly distilled trimethylchlorosilane (Dow Corning Corp.), and after 30 min at -75° , the reaction mixture was allowed to warm to room temperature. The solvent and volatile products were separated by trap-to-trap distillation (0.45 mm, pot temperature to 45°). Analysis of the distillate by GLC at 71.5° (25% SE-30 on Chromosorb P) using toluene as internal standard indicated the presence of 2.34 mmoles (93.5%) of n-butyl bromide (identification by IR and retention time). The residue from the distillation (black solids and an oil) was sublimed ($25-65^{\circ}/0.03$ mm) onto a cold finger inserted directly into the reaction vessel via a vacuum adapter. The cold finger was washed carefully with carbon tetrachloride (50 ml) and the resulting CCl_4 solution was analyzed by GLC (7.5% SE-30 on Chromosorb P. $150-222^{\circ}$ at 10° per min) using 1-chloronaphthalene as internal standard. The presence of (X) (2.36 mmoles, 94%) and (III) (0.12 mmole, 4.8%) was established.

A pure sample of (X) was obtained in a similar reaction in which the distillation residue was worked up by column chromatography (Silica Gel-G/pentane) and crystallization from ether/methanol mixtures (yield 66%). The sample, m.p. $97-98.5^{\circ}$, had a singlet in the NMR spectrum (in CCl_4) at 0.34 ppm and absorbed in the ultra-violet at λ_{sh} 225 μ (ϵ 4250), λ_{max} 237 μ (ϵ 4250) and λ_{sh} 275 μ (ϵ 310). The IR spectrum (CCl_4) showed bands at 2985 w, 2965 m, 2905 w, 1610 s [$\text{C}(\text{Cl})=\text{C}(\text{Cl})$], 1540 s [$\text{C}(\text{Br})=\text{C}(\text{SiMe}_3)$], 1415 m, 1265 m, 1258 s (Me_3Si), 1110 s, 1068 s, 1025 m, 975 m, 905 m, 890 s, 877 s, 845 s, 700 s, 690 s, 667 m, 662 m, 645 m, 615 m and 595 cm^{-1} . (Found: C, 26.78; H, 2.11; Br, 17.95. $\text{C}_{10}\text{H}_9\text{BrCl}_6\text{Si}$ calcd.: C, 26.92; H, 2.02; Br, 17.76%.)

Preparation of 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene

To lithium reagent (V) prepared from 7.60 mmoles of (III) as described above at -75° was added 15 ml of saturated aqueous ammonium chloride and the reaction mixture was allowed to warm to room temperature. The dried ether layer was concentrated and the residue chromatographed on alumina (Woelm, neutral, activity 1) using pentane as eluent. The chromatography residue was 2.534 g (90% crude yield) of light yellow oil which was homogeneous by TLC. Short path distillation yielded a colorless liquid, b.p. $\sim 60^{\circ}/0.05$ mm, which discolored on exposure to air. (Found: C, 22.42; H, 0.42; Cl, 56.09; Br, 20.74. $\text{C}_7\text{HCl}_6\text{Br}$ calcd.: C, 22.26; H, 0.27; Cl, 56.32; Br, 21.15%.) The NMR spectrum (CCl_4) showed a single peak at 6.80 ppm. The IR spectrum (liquid film) showed absorptions at 3125 w, 3090 w, 1605 s [$\text{C}(\text{Cl})=\text{C}(\text{Cl})$], 1565 s [$\text{CH}=\text{C}(\text{Br})$], 1225 s, 1155 s, 1097 s, 1043 m, 1023 m, 1002 s, 908 s, 900 s, 892 s, 823 s, 792 s, 669 m, 658 m and 597 cm^{-1} .

Preparation of 2-bromo-3-(trimethylstannyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene

To lithium reagent (V) prepared from 5.0 mmoles of (III) in ether at -75° was added 1.67 g (8.38 mmoles) of trimethyltin chloride in ether. The reaction mixture was stirred and slowly allowed to warm to room temperature and subsequently was

stirred for 2 h more. Removal of solvent at reduced pressure left a black residue which was chromatographed on a Silica Gel G column using pentane as eluent. IR spectroscopy showed the chromatography residue (2.121 g) to contain a small amount of (III) as well as a new compound. Crystallization from pentane/methanol gave three crops of crystals: 0.323 g (m.p. 84.3–86.3°); 0.480 g (m.p. 82–85°); 0.290 g (m.p. 81–86°). Recrystallization of the last two crops gave 0.650 g (m.p. 83–86°). Total yield of product: 0.973 g (36%). Another recrystallization gave an analytical sample, m.p. 85–86.5°. (Found: C, 21.97; H, 1.73; Cl + Br, 54.06. $C_{10}H_9Cl_6BrSn$ calcd.: C, 22.22; H, 1.68; Cl + Br, 54.13%.) The IR spectrum (CCl_4 -KBr pellet composite) showed bands at 2980 w, 2915 w, 1605 m [$C(Cl)=C(Cl)$], 1535 m [$C(Br)=C(SnMe_3)$], 1400 w, 1300 w, 1211 w, 1190 w, 1145 m, 1090 m, 1060 s, 1020 m, 900 w, 885 m, 845 m, 775 s, 700 m, 685 m, 660 m, 612 m and 530 cm^{-1} .

Preparation of 2-bromoheptachlorobicyclo [2.2.1] hepta-2,5-diene

Gaseous chlorine was passed into a solution of lithium reagent (V) at -75° [prepared from 1.06 mmoles of (III)] for 10 min. Removal of volatiles at reduced pressure left an oily, yellow residue. Sublimation at 30–50°/0.03 mm was followed by crystallization of the sublimate from ether/methanol to give 0.334 g of solid. GLC analysis (7.5% SE-30 on Chromosorb P at 218°) indicated the presence of three components: a minor amount of the hydro compound, some (III) and another (major) component of intermediate retention time whose yield was estimated as ca. 60%. Collection of the latter by GLC gave colorless crystals, m.p. 92.5–95°. (Found: C, 20.52; Br, 19.62; Cl, 60.10. C_7BrCl_7 calcd.: C, 20.40; Br, 19.39; Cl, 60.21%.) The IR spectrum (CCl_4) showed bands at 1605 s [$C(Cl)=C(Cl)$]; 1585 s [$C(Br)=C(Cl)$], 1265 w, 1175 w, 1150 s, 1130 s, 1100 s, 1055 s, 1010 s, 925 m, 910 s, 905 s, 880 m, 700 s, 685 s, 660 s, 635 s, and 550 $w\ cm^{-1}$.

Ten-mmole scale reactions also were carried out, but in all cases such mixtures were obtained. Only GLC served in their separation and hence only small amounts of this material became available for further study.

Preparation of bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo [2.2.1] hepta-2,5-dien-3-yl)-mercury

To a solution of lithium reagent (V) in ether prepared from 3.5 mmoles of (III) at -75° was added 1.74 mmoles of mercuric bromide. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Removal of volatiles at reduced pressure was followed by chromatography of the green-black residue on silica gel. A total of 1.226 g (72%) of product was obtained. Several recrystallizations from ether/pentane gave 1.084 g (65%) of material with m.p. 185–195° (dec). An analytical sample had m.p. 195–198° (dec).^{*} (Found: C, 17.25; Br + Cl, 61.26; Br, 16.47. $C_{14}Br_2Cl_{12}Hg$: calcd.: C, 17.62; Br + Cl, 61.35; Br, 16.75%.) The UV spectrum (EtOH) showed the following absorptions: λ_{max} 238 $m\mu$ (ϵ 11,400) and λ_{max} 285 $m\mu$ (ϵ 930). The maxima are typical of the compounds in this series and the

^{*} The m.p. seemed to depend on the rate of heating. Analytical data were obtained with a sample for which this m.p. was recorded, but samples with m.p. (dec.) as high as 204° were obtained during this study.

extinction coefficients are roughly double those of the others, as expected for the presence of two perhalonorbornadienyl moieties. The IR spectrum (CCl_4) showed bands at 1605 m, 1550 m [$\text{C}(\text{Br})=\text{C}(\text{Hg})$], 1260 s, 1150 m, 1105 m, 1080 s, 1035 w, 1005 m, 895 s, 885 w, 700 s, 665 m, and 630 cm^{-1} .

Preparation of 2-bromo-3-carbomethoxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene

The lithium reagent (V) prepared from 2.52 mmoles of (III) was poured via glass and Tygon connecting tubes onto an excess of crushed Dry Ice in a flask equipped with a magnetic stirring assembly. The reaction mixture was allowed to warm to room temperature. After it had been stirred for 1 h, the reaction mixture was hydrolyzed with 50 ml of distilled water. Removal of solvent from the organic layer left a black oil. Treatment with carbon tetrachloride gave 0.60 g of brown solid. A suspension of the latter (0.20 g) was treated with ethereal diazomethane until the yellow color of diazomethane persisted. Removal of volatiles left a brown oil which could be crystallized from ether/methanol to give 0.105 g of colorless crystals, m.p. $83\text{--}87^\circ$. Sublimation at $45^\circ/0.05 \text{ mm}$ gave an analytical sample. (Found: C, 25.09; H, 1.08. $\text{C}_9\text{H}_3\text{O}_2\text{BrCl}_6$ calcd.: C, 24.84; H, 0.70%). The NMR spectrum (CCl_4) showed a singlet at 3.85 ppm. The IR spectrum (CCl_4) showed absorptions at 2950 w, 1735 s ($\text{C}=\text{O}$), 1605 m, 1590 m [$\text{C}(\text{Br})=\text{C}(\text{CO}_2\text{Me})$], 1550 (sh), 1440 m, 1305 s, 1270 s, 1195 w, 1150 s, 1130 s, 1100 s, 1045 w, 1010 m, 975 w, 905 m, 700 s, and 670 cm^{-1} .

Preparation of other compounds

Reactions of 2-lithio-3-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and 2-lithio-heptachlorobicyclo[2.2.1]hepta-2,5-diene (prepared at -75° by reaction of one molar equivalent of n-butyllithium with the respective bromide in ether) were carried out in much the same way. The following compounds were prepared.

2-(Trimethylsilyl)-3-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. M.p. $78\text{--}80.5^\circ$; 43% yield. (Found: C, 34.29; H, 2.97. $\text{C}_{11}\text{H}_{12}\text{Cl}_6\text{Si}$ calcd.: C, 34.31; H, 3.14%). IR spectrum (CCl_4): 2950 m, 2890 m, 2840 w, 1605 s, 1580 m, 1425 m, 1400 m, 1365 m, 1254 s, 1224 m, 1151 s, 1134 s, 1096 s, 1043 s, 1013 s, 939 s, 872 s, 840 s, 716 m, 682 s, 655 w, 630 m, and 584 cm^{-1} .

2-Methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. Obtained in 92% yield (by GLC); its IR spectrum agreed with that of an authentic sample².

2-Carboxy-3-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. M.p. $198\text{--}200^\circ$ (dec.); 75% yield. (Found: C, 30.68; H, 1.25; Cl, 59.56. $\text{C}_9\text{H}_4\text{Cl}_6\text{O}_2$ calcd.: C, 30.29; H, 1.13; Cl, 59.61%). In the IR spectrum (nujol mull) the $\text{C}=\text{O}$ band was observed at 1690 cm^{-1} , the absorptions due to $\text{C}(\text{Cl})=\text{C}(\text{Cl})$ and $\text{C}(\text{Me})=\text{C}(\text{CO}_2\text{H})$ at 1603 and 1630 cm^{-1} , respectively.

Treatment of this acid with ethereal diazomethane gave 2-carbomethoxy-3-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, m.p. $73\text{--}74.5^\circ$, in 74% yield. (Found: C, 32.63; H, 1.93; Cl, 57.12. $\text{C}_{10}\text{H}_6\text{Cl}_6\text{O}_2$ calcd.: C, 32.38; H, 1.63; Cl, 57.36%). The IR spectrum (CCl_4) showed the carbonyl group at 1723 cm^{-1} , the double bond frequencies, $\text{C}(\text{Cl})=\text{C}(\text{Cl})$ and $\text{C}(\text{Me})=\text{C}(\text{CO}_2\text{Me})$, at 1603 and 1627 cm^{-1} , respectively. In the NMR spectrum (CCl_4) the vinylic methyl and the carboxymethyl groups appeared at 2.24 and 3.82 ppm, respectively.

Bis(2-methyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dien-3-yl)mercury. M.p. 176–178°; 65% yield. The NMR spectrum (CDCl_3) showed a sharp singlet at 2.10 ppm. The UV spectrum (EtOH) showed λ_{max} 230 $\text{m}\mu$ (ϵ 13,820) and λ_{max} 279 $\text{m}\mu$ (ϵ 1044). In the IR spectrum (CCl_4) there were observed bands at 2950 w, 2900 w, 2825 w, 1610 s, 1592 s, 1430 s, 1375 m, 1148 s, 1127 s, 1090 s, 1045 m, 995 s, 942 s, 900 s, 862 s, 685 s, and 650 cm^{-1} . (Found: C, 23.29; H, 0.94. $\text{C}_{16}\text{H}_6\text{Cl}_{12}\text{Hg}$ calcd.: C, 23.31; H, 0.73%.)

2-(Trimethylsilyl)heptachlorobicyclo[2.2.1]hepta-2,5-diene. 25% yield. (Found: C, 29.73; H, 2.20; Cl, 61.30. $\text{C}_{10}\text{H}_7\text{ClSi}$ calcd.: C, 29.62; H, 2.24; Cl, 61.21%.) The IR spectrum (liquid film) showed bands at 2950 m, 2880 w, 1615 m [$\text{C}(\text{Cl})=\text{C}(\text{SiMe}_3)$], 1603 m [$\text{C}(\text{Cl})=\text{C}(\text{Cl})$], 1425 w, 1360 w, 1258 s, 1192 w, 1152 s, 1128 s, 1095 s, 1067 w, 1030 m, 1017 w, 973 m, 922 m, 905 m, 855 (sh), 845 s, 735 w, 703 s, and 680 cm^{-1} .

1,2,4,5,6,7,7-Heptachlorobicyclo[2.2.1]hepta-2,5-diene. 64%. (Found: C, 25.26; H, 0.47; Cl, 74.31. C_7HCl_7 calcd.: C, 25.23; H, 0.30; Cl, 74.47%.) The IR spectrum (liquid film) showed absorptions at 3110 w, 1605 s, [$\text{C}(\text{Cl})=\text{C}(\text{Cl})$], 1575 [$\text{CH}=\text{C}(\text{Cl})$], 1210 s, 1145 s, 1098 s, 1045 w, 1020 s, 995 s, 920 s, 900 s, 830 s, 785 s, 702 s, 673 s, and 655 cm^{-1} .

Reaction of octachlorobicyclo[2.2.1]hepta-2,5-diene with one equivalent of n-butyllithium

A solution of 0.915 g (2.49 mmoles) of the diene in 50 ml of diethyl ether at -75° was treated with 2.53 mmoles of n-butyllithium in 15 ml of 10/1 ether/hexane. The solution became bright green during the course of the addition. After the mixture had been stirred at -75° for 3.5 h, it was quenched with 1 ml of absolute ethanol. Trap-to-trap distillation of the mixture at 0.3 mm (pot temperature to 30°) served to remove solvent and further distillation ($80^\circ/0.07$ mm) into a trap at -78° gave 0.203 g of solid material and an oil. The former was washed with cold methanol to give solid, m.p. $75\text{--}78^\circ$, which GLC (at 200°) showed to be starting material of better than 95% purity; m.p. of pure starting material: $87.5\text{--}88.5^\circ$ (ref. 2). The oil and the residue from the last distillation were combined and examined by GLC at 200° (7.5% SE-30 on Chromosorb P). The major component was starting material (GLC retention time and IR spectrum). The major product had a shorter GLC retention time than the starting material and was identified as 1,2,3,4,5,6,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene. Its IR spectrum was nearly identical to that of the starting material and showed absorptions at 1605 s, 1585 m, 1280 m, 1265 s, 1145 s, 1100 w, 1055 s, 1015 m, 920 m, 860 s, 695 s, 660 w, and 595 cm^{-1} (in CCl_4). A singlet at 4.85 ppm was observed in the NMR spectrum (CCl_4). [The 7H in 7-chlorobicyclo[2.2.1]hepta-2,5-diene occurs at 4.22 ppm⁸.] The mass spectrum had a fairly weak molecular ion, M^+ 332 ($\text{C}_7^{35}\text{Cl}_6^{37}\text{ClH}$) and then, a very strong ion at $^+\text{C}_7\text{Cl}_6\text{H}$, corresponding to loss of a chlorine and formation of the stable quadricyclic (or tropylium) ion. (This behavior is analogous to that observed in the case of norbornadiene itself⁹.) Other favorable ions were $^+\text{C}_7\text{Cl}_5\text{H}$, $^+\text{C}_5\text{Cl}_5$ and $^+\text{C}_5\text{Cl}_4$.

Two minor products, which had longer GLC retention times than the starting material, were present in insufficient amounts to identify and their very similar retention times did not permit their GLC separation. A collected sample of the two had NMR and IR spectra which indicated the presence of a butyl substituent. The

NMR spectrum (CCl_4) showed complex absorption between 0.8–1.8 ppm and the IR spectrum (CCl_4) had bands at 3030 w, 2965 s, 2940 s, 2880 m, 1610 s, and 1585 s cm^{-1} , among others.

Reaction of 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene with two equivalents of n-butyllithium

To a solution of 2.50 mmoles of (III) in 60 ml of diethyl ether at -75° was added under nitrogen with stirring 5.20 mmoles of n-butyllithium in hexane during 1.8 h. The reaction mixture was stirred at -75° for 4 h after completion of the addition and then was quenched with 14.2 mmoles of trimethylchlorosilane. The volatiles were removed by trap-to-trap distillation at 0.1 mm and room temperature and were analyzed by GLC for n-butyl bromide (61.3%) and n-butyl chloride (22.8%). The distillation residue was sublimed (25–60°/0.05 mm) to give 0.551 g (49% crude yield) of tan crystals, m.p. 92–97°, whose IR spectrum showed them to be slightly impure 2-bromo-3-(trimethylsilyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. Twice sublimed material had the correct analysis for this compound. No pure compounds could be isolated by column chromatography or crystallization from the brown sublimation residue.

The stability of lithium reagent (V) at room temperature

In a series of experiments the lithium reagent (V) was prepared from 2.19 mmoles of (III) and 2.26 mmoles of n-butyllithium in 60 ml of diethyl ether at -75° as described in the first experiment. The reagent solution was stirred at -75° for 3 h, then was allowed to warm to room temperature (27–29°) slowly without external heating. The warm-up period generally required 35–40 min. The reagent solution was then quenched with 0.8 ml of trimethylchlorosilane after it had been allowed to stir for various times at room temperature. The yields of 2-bromo-3-(trimethylsilyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and of n-butyl bromide were determined by GLC using the procedure outlined in the first experiment. The results are summarized in Table 1.

The possibility that the exothermic reaction of reagent (V) with trimethylchlorosilane at room temperature might result in thermal destruction of some of the lithium reagent was examined. After the reagent mixture had been warmed to room temperature it was cooled immediately to -75° and quenched with trimethylchlorosilane. The yields of n-butyl bromide and the silylated derivative were 90.0% and 69.9%, respectively. Thus no large-scale destruction of reagent (V) during the room temperature reaction with trimethylchlorosilane is indicated.

ACKNOWLEDGEMENTS

The authors are grateful to National Science Foundation (Grant GP 6466X) and the National Lead Foundation for generous support of this work, and to M&T Chemicals, Inc. for gifts of chemicals. This investigation was supported in part by Public Health Service Fellowship 5-F1-GM-20,099-03 (to A.B.E.).

REFERENCES

- 1 D. SEYFERTH, A. B. EVNIN AND D. R. BLANK, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 181.
- 2 D. SEYFERTH AND A. B. EVNIN, *J. Amer. Chem. Soc.*, 89 (1967) 1468.
- 3 M. SCHLOSSER AND V. LADENBERGER, *Angew. Chem.*, 78 (1966) 547.
- 4 G. KÖBRICH AND K. FLORY, *Chem. Ber.*, 99 (1966) 1773.
- 5 G. WITTIG AND H. HEYN, *Chem. Ber.*, 97 (1964) 1609.
- 6 G. WITTIG, J. WEINLICH AND E. R. WILSON, *Chem. Ber.*, 98 (1965) 458.
- 7 D. B. LEDLIE, Ph.D. Thesis, Mass. Inst. of Technology, 1966.
- 8 E. I. SNYDER AND B. FRANZUS, *J. Amer. Chem. Soc.*, 86 (1964) 1166.
- 9 Z. DOLEISEK, V. HANUS AND H. PRINZBACH, *Angew. Chem.*, 74 (1962) 902.

J. Organometal. Chem., 13 (1968) 25-36