N-methylbenzylamine. The amine itself was shown to be stable under these reaction conditions.

Cleavage of N-Methyl-N-*p*-chlorophenyl-*p*-toluenesulfonamide (XV). Treatment of 1 mmole of XV with *ca.* 4 mmoles of sodium anthracenide in the usual manner (10 min reaction time, 25°) resulted in formation of N-methyl-*p*-chloroaniline (95% yield, gc analysis), but no detectable N-methylaniline.

Analysis of Salts from Cleavage Reactions. Salts were isolated either by filtration from air-quenched reaction mixtures or by extraction into aqueous solution, washing with ether, and concentration under reduced pressure. Sodium toluenesulfinate was identified by the Smiles test[23] and its concentration determined by comparison of the absorption of the Smiles test solution at 515 nm with a standard curve prepared from known concentrations of sulfinate ion. The ir (KBr) of the salts from an air-quenched reaction exhibited bands at 1140 (s), 665 (m), and 550 cm^{-1} (w) due to thiosulfate, and at 970 (s), 630 (m), and 490 cm^{-1} (m) due to sulfite, as well as bands due to adventitious carbonate. (The ir spectrum could be almost exactly duplicated using a mixture of sodium thiosulfate, sodium sulfite, and the ether insoluble residue of air-quenched sodium naphthalenide.) The characteristic bands at 510 and 420 cm^{-1} of dithionite ion do not appear in the ir spectrum of the salts. The identity of thiosulfate ion was confirmed through a positive test with Zwikker's reagent,[24] that of sulfide through lead acetate paper (and nose) test, and that of sulfite through formation and characterization of barium sulfite.

A semiquantitative measurement of the yield of sulfide, sulfite, and thiosulfate was performed as follows: the salt products from reaction of 1.2 mmoles of II were dissolved in 75 ml of water and acidified with hydrochloric acid to the phenolphthalein end point. A 1.0 *M* zinc acetate solution was then added till no more precipitate formed, and the zinc sulfide separated and washed with water by centrifugation. The zinc sulfide was then mixed with an excess of standard cupric sulfate solution, warmed to convert the sulfide to cupric sulfide (which was separated by centrifugation), and the excess cupric ion determined iodometrically. The original filtrate, containing sulfite and thiosulfate, was divided into two parts. One part was titrated with standard iodine solution to determine the sum of sulfite and thiosulfate present; the other part was mixed with 6 ml of 37% aqueous formaldehyde to complex the sulfite and the remaining thiosulfate determined iodometrically.

Gas Chromatographic Analyses. The determination of amines by gas chromatography is notoriously difficult. Two techniques were used to improve reproducibility and overall accuracy. One was to precondition the column at the temperature used by injecting large samples of the amine to be determined until the peak area for a given amount of the amine remained constant. This would have to be repeated after a few hours use of the column. The other technique was to convert the amines to the corresponding amides by treating the reaction mixtures with a large excess of either acetic or propionic anhydride. The amides gave more reproducible results (±3% average reproducibility) as compared to the amines (±5% average reproducibility) but were a little more difficult to separate from other components of the reaction mixtures. A Varian A-90 P instrument, equipped with thermal conductivity detector, was used for most of the analyses. Quantitative measurements were made using the internal standard technique and comparison with known mixtures. Peak areas were determined by cutting and weighing. Most of the analyses were performed on 5-8 ft × 0.25 in. columns of SE-30 or Carbowax 20M on 60-80 mesh Chromosorb W.

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[23] A. I. Vogel, "Elementary Practical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1961, p 528.

[24] F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., New York, N. Y., 1947, p 386.

The Addition of Dihalocarbenes to 1-Germacyclopent-3-enes and to 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene

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Pierre Mazerolles, Georges Manuel, and Françoise Thoumas

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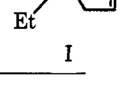
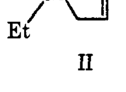
des Organogermanes du C. N. R. S., Faculté des Sciences,
Toulouse, France. *Received July 2, 1969*

Abstract: The reaction of dichlorocarbene (generated *via* $CHCl_3$ + Me_3COK or $PhHgCCl_2Br$) with the 1,1-diethyl-1-germacyclopent-3-enes I, II, and III gave the expected 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexanes IV, V, and VI, but these were not very stable thermally. Only 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexane (IV) itself could be isolated as a pure substance. Methyl substituents on the germacyclopentene C=C bond (as in II and III) tended to decrease the stability of the CCl_2 adduct. The decomposition of these dichlorogermabicyclohexanes most likely proceeds *via* concerted C-Cl ionization and electrocyclic, disrotatory cyclopropane ring opening with concomitant ***reversible*** loss of HCl to give a 1,1-diethyl-4-chloro-1-germacyclohexa-2,4-diene or irreversible Ge-C cleavage to give a diethylchlorogermyl-substituted pentadiene ($Et_2ClGeCH_2CH{=}CCl{-}CH{=}CH_2$ in the case of IV). The 3,3-diethyl-6,6-difluoro-3-germabicyclo[3.1.0]hexane structure is much more stable than the analogous chloro system. 1,3,3,5-Tetramethyl-6,6-dichloro-3-silabicyclo[3.1.0]hexane was found to be unstable at room temperature.

The reaction of germanium(II) iodide with the appropriate 1,3-dienes, followed by treatment of the products with ethyl Grignard reagent, gave the novel 1,1-diethyl-1-germacyclopent-3-enes I, II, and III.[2a,b]


I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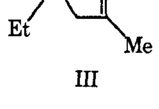
III

During a study of the action of various reagents on these compounds, two types of behavior were observed:

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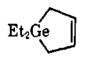
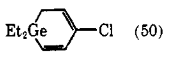
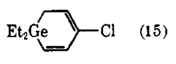
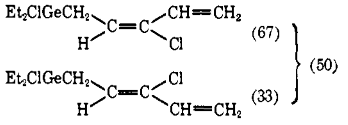
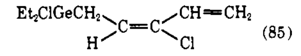
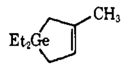
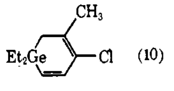
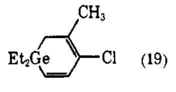
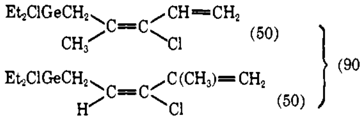
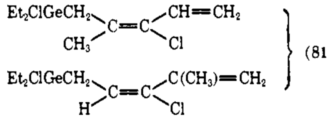
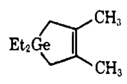
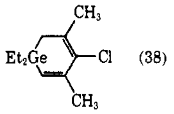
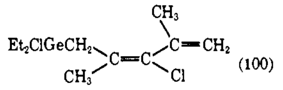
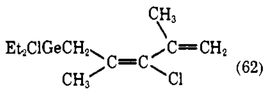
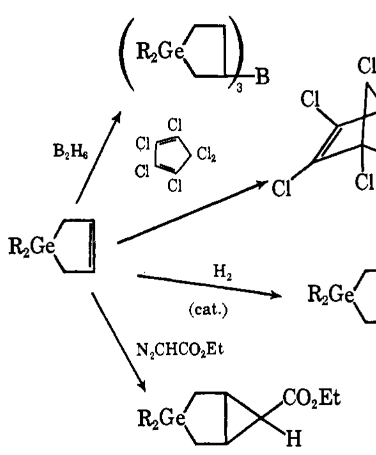
[1] (a) Fellow of the John Simon Guggenheim Memorial Foundation, 1968; (b) Postdoctoral Research Associate at M.I.T., 1967-1968; (c) National Science Foundation Graduate Fellow at M.I.T., 1967-1969.

[2] (a) P. Mazerolles and G. Manuel, *Bull. Soc. Chim. Fr.*, 327 (1966); (b) P. Mazerolles, G. Manuel, and F. Thoumas, *Compt. Rend.*, C, 267, 619 (1968).

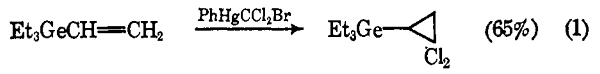
Table I. Products of 1-Germacyclopent-3-ene–Dichlorocarbene Reactions

Germacyclopentene	Products (% of total products) Doering–Hoffmann method	Products (% of total products) PhHgCCl₂Br procedure
	 (50)	 (15)
	 (67) (33) (50)	 (85)
	 (10)	 (19)
	 (50) (50) (90)	 (81)
	 (38)	 (100)
	 (62)	

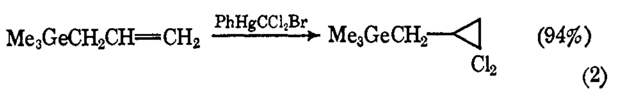
(a) reactions accompanied by ring opening, *e.g.*, the low-temperature bromination and iodination of these compounds, and (b) additions to the C=C bonds of I, II, and III with preservation of the GeC_4 ring system.



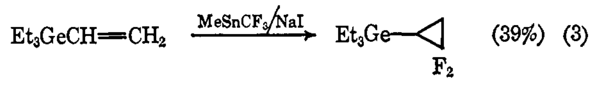
In view of these successful additions to the C=C bonds of these germacyclopentenes, it was of interest to examine the addition of dihalocarbenes to I, II, and III. Acyclic, unsaturated organogermanes are known to react readily with dihalocarbenes,[3,4] *e.g.*



$$\mathrm{Et_3GeCH{=}CH_2 \xrightarrow{PhHgCCl_2Br} Et_3Ge\!-\!\underset{Cl_2}{\triangleleft}}\qquad (65\%)\qquad (1)$$



$$\mathrm{Me_3GeCH_2CH{=}CH_2 \xrightarrow{PhHgCCl_2Br} Me_3GeCH_2\!-\!\underset{Cl_2}{\triangleleft}}\qquad (94\%)\qquad (2)$$

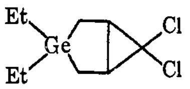


$$\mathrm{Et_3GeCH{=}CH_2 \xrightarrow{MeSnCF_3/NaI} Et_3Ge\!-\!\underset{F_2}{\triangleleft}}\qquad (39\%)\qquad (3)$$

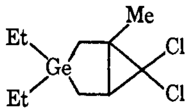
and thus one would expect CX_2 addition to I, II, and III to occur readily to give the respective 3-germabicyclo[3.1.0]hexanes. We report here concerning the reactions of I, II, and III with dichlorocarbene generated by the Doering–Hoffmann procedure,[5] as well as by the $PhHgCCl_2Br$ route,[6] and of III with difluorocarbene generated by the Me_3SnCF_3–NaI reagent.[4] Dichlorocarbene addition (*via* $CHCl_3$ + Me_3COK) to 1,1-dimethyl-1-germacyclopent-3-ene in 70% yield had been claimed previously by Russian workers,[7] but neither the structure nor the physical and spectroscopic properties of their product(s) were reported.

Results and Discussion

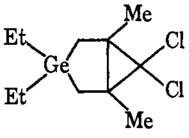
The first set of essentially "preparative" experiments in which dichlorocarbene reactions with I, II, and III were studied did not result in the isolation of the expected 6,6-dichloro-3-germabicyclo[3.1.0]hexanes, IV, V, and VI. Instead, on the "usual" work-up (filtration, trap-to-trap vacuum distillation of the filtrate followed by gas–liquid partition chromatography (glpc) of the filtrate, or, alternatively, direct vacuum fractional distillation of the filtrate), two different types of products, VII and VIII, both derivable from the expected 6,6-dichloro-3-germabicyclo[3.1.0]hexanes, were obtained. Table I presents the results in more detail.



IV



V



VI

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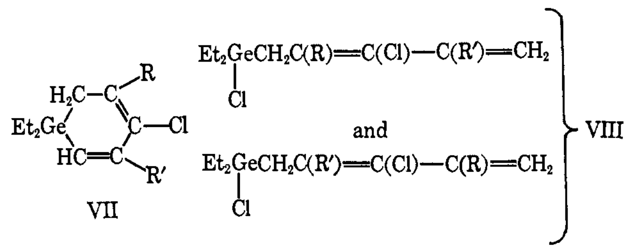
(3) D. Seyferth, T. F. Jula, H. Dertouzos, and M. Pereyre, *J. Organometal. Chem.*, 11, 63 (1968).

(4) D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, 32, 2980 (1967).

(5) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 76, 6162 (1954).

(6) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *ibid.*, 87, 4259 (1965).

(7) O. M. Nefedov, S. P. Kolesnikov, A. S. Khachaturov, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, 154, 1389 (1964).



VII

$$\mathrm{Et_2GeCH_2C(R){=}C(Cl){-}C(R'){=}CH_2}\ (\text{Cl on Ge})\quad \text{and}\quad \mathrm{Et_2GeCH_2C(R'){=}C(Cl){-}C(R){=}CH_2}\ (\text{Cl on Ge})$$

VIII

At this point, before a discussion of how these products were formed, it is worthwhile to inquire at what stage of these experiments they were produced. In the case of the reactions where dichlorocarbene was generated by the Doering–Hoffmann procedure, the reaction was carried out at *ca.* −4 to 0°; the reaction mixture then was hydrolyzed and the organic phase was distilled at reduced pressure, with head temperatures reaching 75–92°. Analysis by glpc of the distillates required temperatures of *ca.* 200°. Thus it was entirely possible that the conversions of IV, V, and VI to products of type VII and VIII could have taken place during work-up or glpc analysis. In the experiments in which $PhHgCCl_2Br$ was used as the dichlorocarbene source, the initial experiments with I, II, and III were carried out at 80° in benzene solution. Work-up of the reaction mixtures by high-vacuum distillation and examination of the distillates obtained by nmr spectroscopy prior to glpc separation failed to provide evidence for the presence of detectable amounts of IV, V, or VI. It was the products shown in Table I which nmr analysis showed to be present.

The reaction of phenyl(bromodichloromethyl)mercury with olefins is known to proceed even at room temperature, albeit slowly,[8a] and therefore this mercurial and I and II were allowed to react at room temperature in carbon tetrachloride solution for 17 days.[8b] Examination of the reaction mixtures at the end of this time by nmr spectroscopy provided excellent evidence that germabicyclo[3.1.0]hexanes of type IV–VI are indeed the first products formed.

Figure 1 illustrates the case of 1,1-diethyl-1-germacyclopent-3-ene (I). In Figure 1a the nmr spectrum of this olefin is shown. In Figure 1b is depicted the nmr spectrum of the initial reaction mixture, which had never been subjected to temperatures above 25°. The resonances for the olefinic and ring methylene protons of I had largely disappeared[9] and the multiplet at δ 1.00 assigned to the Et_2Ge moiety was broadened and had become significantly more complex. A symmetrical multiplet also was present at δ 2.13 ppm which could be assigned to the bridgehead protons of the proposed intermediate IV. A small impurity peak just to the left of the central line of the multiplet distorts the symmetry slightly. However, in a 100-MHz spectrum (Figure 2), the impurity is moved further downfield and the presence of a symmetrically coupled pattern is confirmed. In support of this assignment of the δ 2.13 resonance to the cyclopropyl protons of IV, we note the following as-

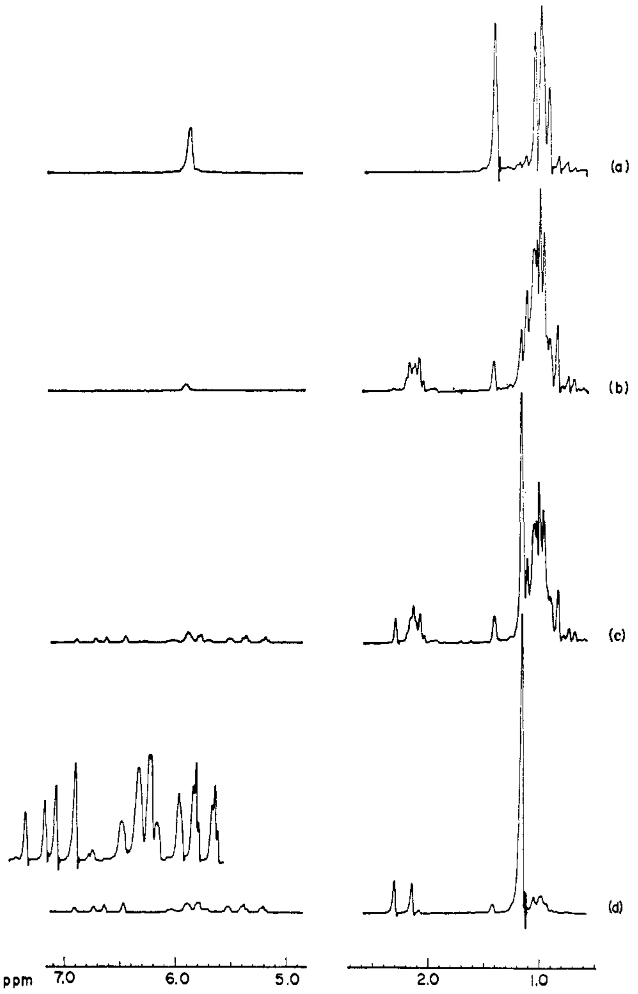


Figure 1. The 1,1-diethyl-1-germacyclopent-3-ene–phenyl(bromodichloromethyl)mercury system. Nmr spectra in CCl_4 *vs.* internal $BrCH_2CH_2Br$: (a) nmr spectrum of 1,1-diethyl-1-germacyclopent-3-ene; (b) the 1,1-diethyl-1-germacyclopent-3-ene–$PhHgCCl_2Br$ reaction mixture after 17 days at room temperature; (c) the reaction mixture in b after being heated for 45 min at 80°; (d) the reaction mixture in b after being heated for 3.25 hr at 80°; the spectrum is essentially that of the diene IX; insert, the vinyl region × 10. Note series b–d is attenuated to accommodate the δ 1.16 peak.

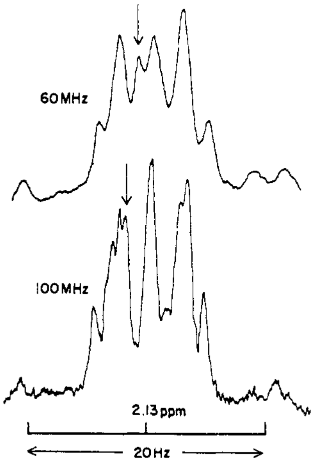


Figure 2. The cyclopropyl protons in the 1,1-diethyl-1-germacyclopent-3-ene–$PhHgCCl_2Br$ reaction mixture after 17 days at room temperature at 60 and 100 MHz. Arrow indicates resonance due to impurity.

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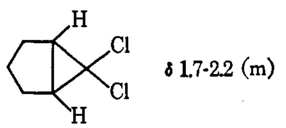
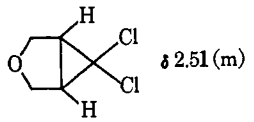
[8] (a) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 4953 (1967) (footnote 7). (b) Carbon tetrachloride may be used as solvent in mercurial-derived CCl_2 reactions, as previous work has shown.[8a,c] (c) M. E. Gordon, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.

[9] Integration of the ring methylene protons of I and the cyclopropyl protons of the product IV in the spectrum shown in Figure 1b indicated a 1:5.7 I:IV ratio was present.

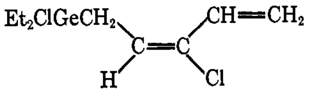
signments in previous literature (ref 10 and 11, respectively).





The integrated ratio of the δ 2.13 and 1.00 resonances (corrected for the presence of *ca.* 15% of I) was 2.0:14.3, in good agreement with the expected 2.0:14.0 ratio. No additional lines were observed in the vinyl region of the spectrum, and thus at this point no detectable decomposition of IV had as yet taken place. The infrared spectrum of the reaction mixture was unlike those of the final reaction products of the previous experiments. A sharp shoulder at 3005 cm^{-1} may be attributed to cyclopropyl C–H absorption.

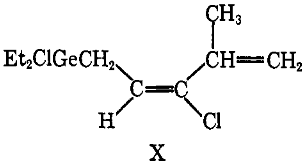
The changes caused by heating at 80° in the sealed nmr tube the carbon tetrachloride solution of the initial (room temperature) $PhHgCCl_2Br$–I reaction product were of great interest and some significance (*cf.* Figure 1c and 1d). After 3.25 hr of heating, the following were observed: (a) the multiplet at δ 1.00 had sharpened to a singlet at δ 1.16; (b) the multiplet at δ 2.13 had collapsed and had been replaced by a doublet at δ 2.23; and (c) a highly complex but interpretable pattern had appeared in the vinyl region. The new nmr spectrum was essentially that of the ring-opened product, IX.



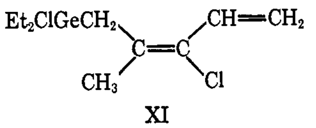
IX

Although the other geometric isomer had been obtained in the Doering–Hoffmann reaction experiments, *only* this single isomer was detectable in the nmr spectrum.

A similar set of nmr spectra was obtained when the room temperature reaction of $PhHgCCl_2Br$ with II was studied. The initial reaction solution showed resonances in the vinyl region and in the aliphatic C–H region which were attributable to two of the previously identified ring-opened dienic products, X and XI. The X:



X



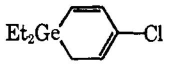
XI

XI ratio was ~1:1.3 as determined by integration of the Et_2GeCH_2 resonances of the two compounds. Also present in the nmr spectrum were multiplets at δ 1.02 and 1.73 and a singlet at δ 1.50, attributable to the $Et_2Ge(CH_2\text{–})_2$, bridgehead C–H and CH_3 protons, respectively, of the proposed intermediate, V. Heating of the reaction solution for 2.5 hr at 80° caused collapse of the latter three lines, giving a sharp, clear spectrum of X and XI.

It should be emphasized that in neither of these cases were ring-expanded type VII products observed. The heated reaction mixtures did not give off hydrogen chloride fumes. Moist litmus paper was not affected until it came in direct contact with the liquid phase.

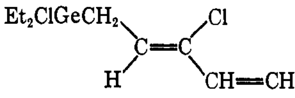
It would thus appear that the decompositions of IV and V are clean and stereospecific processes.

The nmr experiments described above suggested that the isolation and characterization of 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexane(IV) should be possible, provided suitable precautions were taken. This was the case when the reaction of I with $CHCl_3$–Me_3COK was carried out in such a manner that the temperature was maintained as low as possible during all steps of the work-up. Isolation of IV in pure form was achieved by means of a molecular distillation at 0.0001 mm. The availability of pure IV allowed a more controlled investigation of its thermolysis under various different conditions. (1) Distillation at 110° (0.02 mm) gave a 70% recovery of IV. The remaining material was converted to the germacyclohexadiene XII (15% yield) and the open-chain pentadiene IX (15%). (2)



XII

Distillation of IV at 200–220° (30 mm) resulted in its complete destruction and in the formation of a 1:1 mixture of IX and XII. (3) Upon gas chromatography (injection at 250° onto an SE-30 analytical column at 180°) the same result was observed; an equimolar mixture of IX and XII was eluted. (4) However, gas chromatography at more strenuous conditions (injection at 260° onto an SE-30 preparative column at 220°) gave not only XII (50%) and IX (33%), but also the latter's geometric isomer, XIII, in 17% yield. It is thus shown that XIII is not a primary degration product, but that the germacyclohexadiene, XII, is. The initially puzzling feature of these experiments is that the latter product is observed only in some experiments; for instance, no evidence for its formation was obtained in the nmr experiments described above. Very revealing is the fact that XII was formed only in those experiments where the thermolysis was carried out under experimental conditions where volatile materials would be rapidly removed from the reaction zone; in the nmr experiments a closed system was involved. These observations suggest that the dehydrochlorination of IV to give XII is a reversible process.



XIII

Further evidence for the reversibility of the HCl elimination from the bicyclic germane IV was obtained in a study of the reaction of XII with deuterium chloride. In this reaction deuterated IX was indeed obtained, and the distribution of deuterium provided useful information concerning the XII + HCl → IX conversion. The nmr spectrum of the IX produced indicated that deu-

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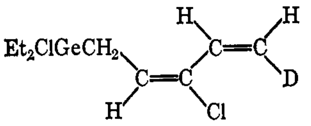
(10) W. R. Moser, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

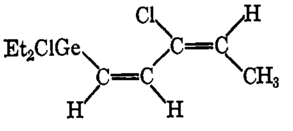
(11) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 4874 (1964).

terium had been introduced both at the terminal vinyl proton and at the methylene group adjacent to the germanium atom. Furthermore, the introduction of deuterium into the vinyl group was highly stereospecific, isomer XIV being the major (and possibly the only) one



XIV

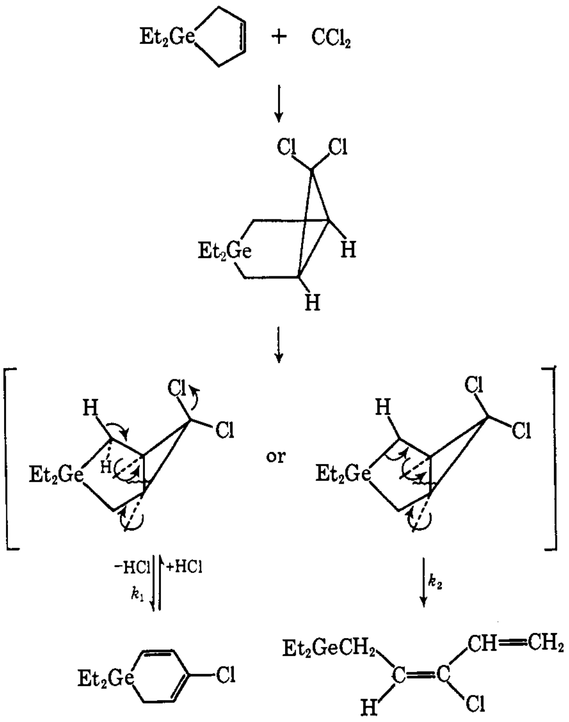
present. The observation that deuterium had been introduced into the $Ge-CH_2$ moiety excluded simple HCl cleavage of the $Ge-CH{=}CH$ bond as the unique mode of formation of IX from XII. It may be noted that vinylgermanes have been shown to undergo HX addition to the $C{=}C$ bond rather than Ge–C cleavage under comparable conditions.[12] Thus the $Ge-CH{=}CH$ cleavage route seems unlikely. Cleavage of the other, allylic Ge–C bond of XII would, in principle, be a more likely possibility, since cleavage of the allyl–Ge bond by hydrogen halides is a facile process,[12] but such a reaction would not lead to the product observed, rather to the pentadiene XIVa. This diene was, however, not among the observed products.



XIVa

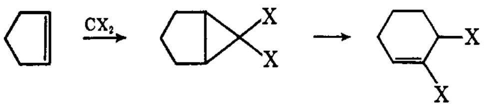
The results described thus far allow us to propose a plausible reaction scheme for the formation of all observed products (Scheme I).

Scheme I[a]

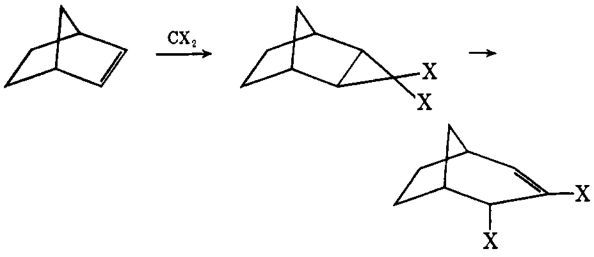


[a] Not indicated but quite possible is intra- or intermolecular attack by the chloride leaving group at germanium occurring in concert with the other events indicated.

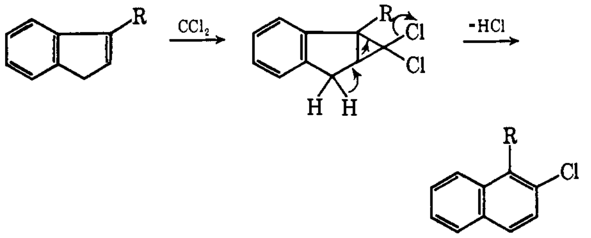
Ample precedent exists for much of the general chemistry in this scheme. The instability of the bicyclo[3.1.0]hexane system is well documented[13,14]



(4)

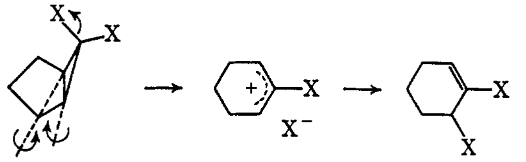


(5)



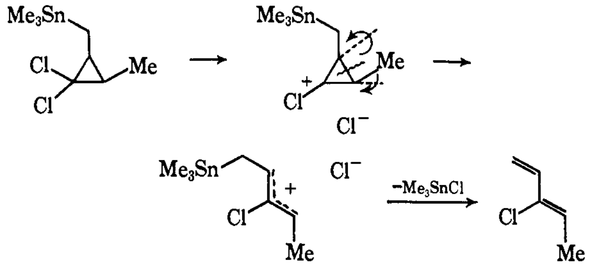
(6)

A process such as that shown in eq 4, on the basis of theory[15] and experiment,[16,17] would proceed *via* concerted ionization of the *endo*-halogen atom and a disrotatory cyclopropane ring opening as shown below. The resulting cyclic allylic carbonium–chloride ion pair would collapse to give the final covalent product.



(7)

The thermal decomposition of 1,1-dihalo-2-trimethylsilylmethylcyclopropanes and 1,1-dihalo-2-trimethyltinmethylcyclopropanes (eq 8) which we have studied previously[18] would appear to be related to the present decomposition of IV to IX in which also a cyclopropane ring is opened and a metal–carbon bond is cleaved. In the process shown in eq 8, however, outward, rather than inward, rotation of the cyclopropane ring substituents occurs because the constraint of a bicyclic system is absent.



(8)

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(12) P. Mazerolles and M. Lesbre, *Compt. Rend.*, **248**, 2018 (1959).

(13) (a) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962); (b) W. R. Moore, W. R. Moser, and J. E. La Prade, *ibid.*, **28**, 2200 (1963).

(14) (a) W. E. Parham and H. E. Reiff, *J. Amer. Chem. Soc.*, **77**, 1177 (1955); (b) W. E. Parham, H. E. Reiff, and P. Schartzentruber, *ibid.*, **78**, 1437 (1956).

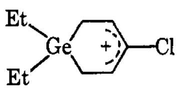
(15) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(16) C. H. De Puy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

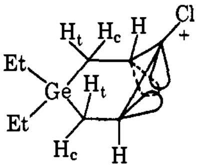
(17) (a) M. S. Baird, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc., C*, 1173 (1969); (b) D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969).

(18) D. Seyferth and T. F. Jula, *J. Amer. Chem. Soc.*, **90**, 2938 (1968).

The decomposition of IV is more complicated than that shown in eq 7. First of all, it does not stop at a stable 4,5-dihalo-1-germacyclohex-3-ene stage; secondly, further decomposition involves both irreversible cleavage of the Ge–C bond to give the Et_2ClGe-substituted pentadiene IX and reversible elimination of HCl to give the germacyclohexadiene XII. Scheme I as shown would lead to the prediction that only a single isomeric Et_2ClGe-substituted pentadiene would be formed and that this would have the stereochemistry shown. (We note that our structure assignment to IX is based on this prediction; ir and nmr spectral data were of no help in determining the structure of IX.) Scheme I must also accommodate the fact that HCl adds to XII in a stereospecific manner and that the introduction of deuterium into the vinylic position of IX gives isomer XIV; on the basis of the principle of microscopic reversibility it will be required that HCl elimination from IV (or rather from the intermediate which lies on the pathway between IX and XII) also is stereospecific. This observed stereospecificity is not easily rationalized in terms of an intermediate cyclic allylic carbonium ion, XV, and for this reason we prefer to suggest a fully concerted process in Scheme I. If one would wish to write a stepwise process rather than this concerted process, then the cyclopropenium ion intermediate XVI, which is not symmetrical with respect to the CH_2 environment, would be preferable to XV.[19]



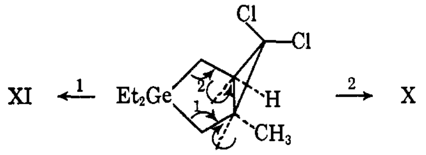
XV



XVI

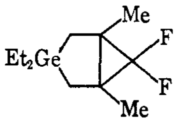
Thermolysis of 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexane in the presence of an excess of ethylmagnesium bromide at 110° in di-*n*-butyl ether (no reaction in refluxing diethyl ether) provided a rough measure of the relative rates of the two competing decomposition processes. In this experiment *both* processes are irreversible, the HCl released in step k_1 being quantitatively destroyed by the Grignard reagent. The relative amounts of the products formed, the germacyclohexadiene XII, and $Et_3GeCH_2CH{=}CCl{-}CH{=}CH_2$ (XVII, the ethylation product of IX) then would serve as a measure of the ratio $k_1{:}k_2$. It was found that the ratio of XII to XVII was 0.25; hence the elimination of Ge–Cl is *ca.* four times faster than the elimination of HCl.

The formation of two methyl positional isomers in the decomposition of the germabicyclohexane V is readily understandable in terms of Scheme I. Germanium–carbon bond rupture could occur in either way shown. In agreement with the nmr experiments which indicated that V is less stable than IV was the fact that attempts to isolate pure V were unsuccessful. Even very mild heating (45° at 0.1 mm) resulted in partial decomposition to X and XI.



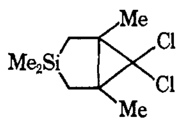
The finding that the 6,6-dichloro-3-germabicyclo[3.1.0]hexane system is not very stable led us to consider other related ring systems whose stability might be greater. One might expect that the ring opening process would be more difficult to achieve if ionization of a C–F bond were required. Accordingly, we examined the reaction of difluorocarbene with the germacyclopentene III, the olefin whose derived dichlorocarbene adduct VI was the least stable.

The reaction of III with the Me_3SnCF_3–NaI reagent in 1,2-dimethoxyethane (DME)[4] at reflux gave, after the usual work-up (vacuum distillation and glpc separation of products), two isomeric products in *ca.* 34% and 18% yields. Examination of the infrared and nmr spectra of the product formed in lesser yield clearly showed it to have the 1,3-pentadiene structure, $Et_2\,FGeCH_2C(Me){=}C(F){-}C(Me){=}CH_2$. The proton resonance spectrum of the major product was consistent with that expected for the 3-germabicyclo[3.1.0]hexane XVIII; however, the complexity of the resonance pattern does not allow analysis using first-order approximations. It would thus appear that the 6,6-difluoro-3-germabicyclo[3.1.0]hexane system is significantly more stable than the analogous chloro system.



XVIII

In view of these interesting results obtained in organogermanium systems, a brief study of an analogous organosilicon system was carried out. 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene was prepared and allowed to react with phenyl(bromodichloromethyl)mercury in benzene at 80°. However, the initially formed cyclopropane derivative, XIX, did not survive the reaction and work-up conditions, and the only product obtained (in 74% yield) was $Me_2ClSiCH_2C(Me){=}C(Cl){-}C(Me){=}CH_2$. A room temperature experiment in which this silacyclopentene and phenyl(bromodichloromethyl)mercury in carbon tetrachloride were allowed to react during 17 days gave the same result. The nmr spec-



XIX

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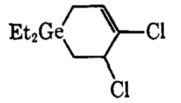
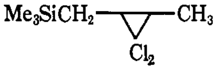
(19) A referee has suggested that although 1,1-diethyl-4,5-dichloro-1-germacyclohex-3-ene (XVIa) was not isolated, it may indeed be an



XVIa

intermediate in reversible, stereospecific equilibrium with XII. Ring opening of XVIa certainly would lead to the products observed. The apparent instability of such an intermediate, were it to exist at all, would indicate a very loosely bonded structure, approaching perhaps an associated ion pair, XVI^+Cl^-. (It is quite possible that the site of the chloride counterion could play an important role in determining the observed stereospecificity.) Attempts to obtain evidence for the intermediacy of XVIa by means of low-temperature nmr studies of the reaction of XII with HCl were unsuccessful. Only the nmr spectrum of IX was apparent, even at −50°.

trum of the reaction solution (which never had been heated above room temperature) was that of a mixture of the ring-opened diene and a small amount of the starting olefin. Clearly, XIX is not stable even at room temperature. Comparison of the instability of XIX with the high stability of XX[18] suggests that some structural property of the silabicyclo[3.1.0]hexane system in XIX is a decisive factor. If the decomposition of the latter involves concerted ionization of a C–Cl bond and electrocyclic opening, then this structural factor would be the ring strain associated with this bicyclic system. Equally striking is the comparison between the allyltrimethylgermane–CCl_2 adduct (*cf.* eq 2) and IV. The former is very stable, surviving distillation and glpc at high temperatures undecomposed; the latter, as has been discussed, decomposes moderately rapidly at 80°.



XX

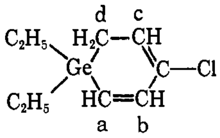
In conclusion, the results of this study have shown clearly that the addition of dihalocarbenes to the C=C bond of the germacyclopentenes examined gives the expected 6,6-dihalo-3-germabicyclo[3.1.0]hexanes, but that these have only limited thermal stability. Their stability appears to fall off IV > V > VI, which is in line with expectations.[20]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Infrared spectra were recorded using Perkin-Elmer 237B or 337 spectrophotometers, nmr spectra using Varian Associates A-60 or T-60 spectrometers. Chemical shifts are reported in δ units in parts per million downfield from tetramethylsilane.

Reactions Using the Doering–Hoffmann Procedure. (a) 1,1-Diethyl-1-germacyclopent-3-ene. A mixture of potassium *t*-butoxide prepared from 6.8 g (0.173 g-atom) of potassium and 200 ml of anhydrous *t*-butyl alcohol and 9.25 g of the germacyclopentene (0.05 mol) in 50 ml of dry pentane in a 1-l. two-necked flask was cooled to −4° under nitrogen. To this magnetically stirred mixture was added 7.0 g of chloroform in 30 ml of pentane at such a rate that the reaction temperature did not exceed 0°. After the addition had been completed the reaction mixture was allowed to warm to 20° and then was hydrolyzed. The aqueous phase was extracted with petroleum ether and the organic phase was washed with water to remove *t*-butyl alcohol. Following drying over calcium chloride, the organic phase was fractionally distilled to give 6.7 g of unconverted starting olefin (bp 65°, 17 mm) and 2.3 g of a fraction boiling at 76° (0.5 mm). Glpc analysis (Aerograph Model 705, 30% SE 30 on Chromosorb W, at 200°) showed the presence of a 50:50 mixture of 1,1-diethyl-1-germa-4-chlorocyclohexa-2,4-diene (XII) and 1-diethylchlorogermyl-3-chloropenta-2,4-diene (IX + XIII). Glpc separation gave samples for characterization as follows.

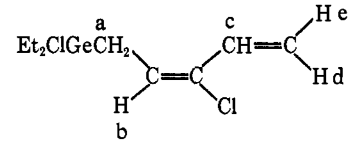
1,1-Diethyl-1-germa-4-chlorocyclohexa-2,4-diene: bp 115° (15 mm); $n^{20}D$ 1.5194; nmr (in CCl_4) δ 0.75–1.45 (m, 10 H, Et_2Ge),



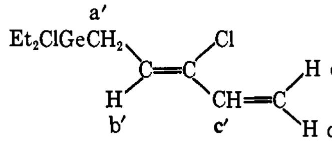
XII

1.78 (d, 2 H_d, J = 6 Hz), 6.0 (t, 1 H_c, J = 6 Hz), this resonance partially overlapping, 6.2 (d, H_a, J = 14 Hz), 6.60 ppm (d, H_b, J = 14 Hz, with fine splitting); ir (liquid film, KBr) 3100 w, 3020 m, 2960 s, 2940 m, 2920 m, 2880 m, 2840 w, 1680 m, 1600 w, 1550 m, 1455 m, 1420 w, 1370 m, 1350 m, 1260 m, 1225 w, 1195 w, 1125 w, 1040 m, 945 m, 855 m, 805 m, 730 m, 710 m, 675, 620, 595, and 575 cm^{-1}. *Anal.* Calcd for $C_9H_{15}ClGe$: C, 46.74; H, 6.54; Cl, 15.33. Found: C, 46.47; H, 6.42; Cl, 15.12.

1-Diethylchlorogermyl-3-chloropenta-2,4-diene: $n^{20}D$ 1.5257; d_4^{20} 1.2528. *Anal.* Calcd for $C_9H_{16}Cl_2Ge$: C, 40.37; H, 6.03; Cl, 26.49. Found: C, 39.96; H, 6.19; Cl, 25.75. The nmr spectrum (in CCl_4) of this compound indicated the presence of two geometric isomers, IX and XIII. Beside a single peak at 1.15 ppm (10 H, Et_2Ge) there were centered at 2.20 and 2.30 ppm two doublets characteristic, respectively, of the two protons a and a′, with J_{ab} = 10 Hz and $J_{a'b'}$ = 9 Hz. Between 5.0 and 6.1 ppm there was a complex resonance assignable to protons b, d, and e, and b′, d′, and e′), between 6.1 and 7.0 ppm, 6 observable peaks due to H_c and $H_{c'}$, with J_{ce} = $J_{c'e'}$ = 10 Hz and J_{cd} = $J_{c'd'}$ = 17 Hz; this system is formed by two superimposed AM*X* quartets. Integration of the doublets due to a and a′ showed IX and XIII to be present in a 2:1 ratio. Infrared data (liquid film) for combined isomers IX and XIII are: 3110 m, 3020 w, 2970 s, 2940 s, 2920 s, 2880 s, 2840 w, 2750 w, 1820 w, 1720 w, 1625 s, 1600 w, 1580 w, 1450 s, 1410 s, 1400 w, 1390 m, 1320 m, 1300 w, 1272 w, 1260 w, 1225 m, 1197 m, 1180 m, 1135 m, 1100 m, 1040 m, 1020 s, 970 s, 935 s, 910 s, 860 s, 810 w, 775 s, 695 s, 640 w, and 590 s cm^{-1}.



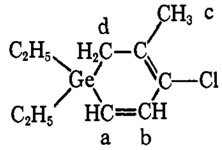
IX



XIII

(b) 1,1-Diethyl-3-methyl-1-germacyclopent-3-ene. Essentially the same procedure was used in the reaction of 0.173 mol of potassium *t*-butoxide and 6.0 g of chloroform in the presence of 10 g (0.05 mol) of the germacyclopentene (200 ml of *t*-butyl alcohol and 30 ml of pentane). Vacuum distillation of the dried organic phase gave 5.7 g of distillate at 88–92° (0.4 mm). Glpc analysis of the latter showed it to consist of 10% of 1,1-diethyl-5-methyl-4-chloro-1-germacyclohexa-2,4-diene (XXI) and 90% of a 1:1 mixture of 1-diethylchlorogermyl-4-methyl-3-chloropenta-2,4-diene (X) and 1-diethylchlorogermyl-2-methyl-3-chloropenta-2,4-diene (XI).

1,1-Diethyl-5-methyl-4-chloro-1-germacyclohexa-2,4-diene was not formed and isolated in quantities sufficient to permit other than its spectral characterization: nmr (in CCl_4) δ 1.1 (m, 10 H, Et_2Ge),



XXI

1.66 (s, 2 H_d), 2.0 (s, 3 H_c), 5.9 and 6.7 ppm (d, H_a and H_b, J_{ab} = 14 Hz); ir (in CCl_4) 3090 sh, 2990 sh, 2945 s, 2920 sh, 2900 s, 2880 s, 2820 sh, 2720 w, 2300 w, 1670 w, 1605 sh, 1550 m, 1450 m, 1430 sh, 1375 m, 1345 sh, 1225 w, 1180 w, 1140 sh, 1015 m, 975 m, 925 s, 915 s, 860 w, 790–690 (solvent), 700 sh, 675 sh, 645 w, 585 s, and 550 sh cm^{-1}.

1-Diethylchlorogermyl-2-methyl-3-chloropenta-2,4-diene and 1-diethylchlorogermyl-4-methyl-3-chloropenta-2,4-diene (1:1 mixture, by nmr): $n^{20}D$ 1.5242; d_4^{20} 1.2344. *Anal.* Calcd for $C_{10}H_{18}Cl_2Ge$: C, 42.63; H, 6.44; Cl, 25.17. Found: C, 42.73; H, 6.41; Cl, 24.78. In the mixture nmr spectrum (in CCl_4) the individual spectra of XI and X could be recognized: XI, δ 1.15 (m, 10 H, Et_2Ge) (the only part of the spectrum which XI and X had in common), 2.0 (s, 3 H_b), 2.32 (s, 2 H_a), 5.0–5.8 (2 H, H_d, and H_e) overlapping complex pattern, 6.6 (AMX, q, H_c, J_{cd} = 10 Hz, J_{ce} = 14 Hz); X, 1.15 (m, 10 H, Et_2Ge), 1.90 (q, 3 $H_{c'}$, allylic coupling with d′ and e′, $J \sim 1$ Hz), 2.15 (d, 2 $H_{a'}$, $J_{b'a'}$ = 8 Hz), 5.0–5.1 ($H_{d'}$ and $H_{e'}$, two broadened single resonances showing fine splitting), 5.62 ppm (t, $H_{b'}$, $J_{b'a'}$ = 8 Hz); ir of mixture (liquid film): 3090 w, 2960 s, 2930 s, 2910 s, 2875 s, 1625 s, 1585 w, 1460 s,

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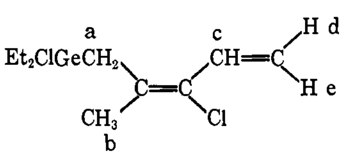
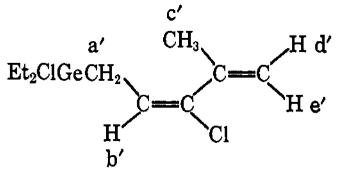
(20) G. C. Robinson, *J. Org. Chem.*, 33, 607 (1968).



XI

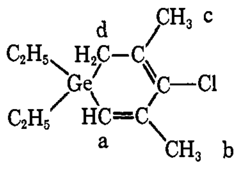


X

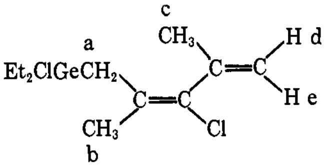
1420 m, 1400 m, 1380 m, 1240 w, 1225 w, 1140 m, 1120 m, 1020 m, 965 m, 905 m, 880 m, 760 m, and 690 m cm^{-1}.

(c) **1,1-Diethyl-3,4-dimethyl-1-germacyclopent-3-ene.** The same procedure was used in conducting the reaction of 0.173 mol of potassium *t*-butoxide and 0.058 mol of chloroform in the presence of 0.05 mol of this germacyclopentene in *t*-butyl alcohol–pentane medium. Distillation of the organic phase gave 9.2 g of a fraction boiling between 87 and 91° at 0.7 mm. Glpc analysis indicated that the latter was composed of 38% of 1,1-diethyl-3,5-dimethyl-4-chloro-1-germacyclohexa-2,4-diene and 62% of 1-diethylchlorogermyl-2,4-dimethyl-3-chloropenta-2,4-diene (XXII).

1,1-Diethyl-3,5-dimethyl-4-chlorocyclohexa-2,4-diene: $n^{20}\text{D}$ 1.5211, d_4^{20} 1.1878. *Anal.* Calcd for $C_{11}H_{19}ClGe$: C, 50.95; H, 7.39; Cl, 13.67. Found: C, 51.42; H, 7.43; Cl, 13.76. The compound showed: nmr (in CCl_4) δ 1.0 (m, 10 H, Et_2Ge), 1.67 (s, 2 H_d), 2.04–2.09 (3 H_b, d, J_{ba} ~ 1 Hz, 3 H_c, s, at 2.09), 5.83 ppm (q, H_a, J_{ab} ~ 1 Hz); ir (liquid film) 2960–2900 s, 2870 m, 1770 w, 1710 w, 1670 w, 1650 w, 1600 m, 1555 m, 1455 m, 1435 m, 1370 m, 1325 w, 1290 w, 1220 m, 1120 m, 1015 m, 940 s, 885 m, 850 w, 780 s, 750 m, 725 m, 695 m, 600 w, 570 m, 555 m, 480 w, 460 w, and 420 w cm^{-1}; mass spectrum, molecular ion (^{74}Ge, ^{35}Cl) M^+ = 260 and fragments *m/e* 231 (M–Et), 195, 167, 139, 93... (carried out at the Varian Laboratory in Zürich using a Type M 66 spectrograph by Dr. H. Budzikiewicz).



1-Diethylchlorogermyl-2,4-dimethyl-3-chloropenta-2,4-diene: $n^{20}\text{D}$ 1.5112, d_4^{20} 1.2098. *Anal.* Calcd for $C_{11}H_{20}Cl_2Ge$: C, 44.67; H, 6.82; Cl, 23.97. Found: C, 45.05; H, 6.88; Cl, 23.90. Nmr (in CCl_4) δ 1.18 (s, 10 H, Et_2Ge), 1.88 (s, 6 H, 3 H_b, and 3 H_c), 2.30 (s, 2 H_a), 4.9 m, and 5.1 m, ppm (H_e and H_d); ir (liquid film, KBr) 3080 w, 2960 w, 2930 m, 2910 m, 2875 m, 2730 w, 2380 w, 1815 w, 1765 w, 1700 w, 1680 w, 1620 m, 1600 w, 1445 s, 1430 w, 1370 m, 1280 m, 1225 m, 1165 m, 1075 w, 1020 m, 980 m, 915–900 m, 880 m, 765 m, 695 m, 585 m, 545 m, 410 m, and 365 s cm^{-1}; mass spectrum, molecular ion (^{74}Ge, ^{35}Cl) M^+ = 296, fragments *m/e* 267 (M–Et), 167, 139, 109....



XXII

Reactions Using Phenyl(bromodichloromethyl)mercury. (a) 1,1-Diethyl-1-germacyclopent-3-ene. Phenyl(bromodichloromethyl)mercury[21] (4.42 g, 10.0 mmol) and the germacyclopentene (2.13 g, 11.5 mmol) were added under nitrogen to 20 ml of dry benzene in a 50-ml, three-necked flask equipped with a reflux condenser, magnetic stirring unit, and nitrogen inlet tube. The reaction flask was immersed in an oil bath maintained at 80–81° and the mixture was stirred for 2 hr. The reaction mixture was allowed to cool to room temperature and then was filtered to remove 3.55 g (99%) of phenylmercuric bromide, mp 276–279°. Benzene was removed from the filtrate by distillation at atmospheric pressure and the clear yellow residue was analyzed by glpc (MIT isothermal unit, glass column packed with 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb W, 185°, 15 psi of helium, preheater 210°, postheater 200°). In addition to benzene and a small amount of starting material, only two other components were eluted at 11.8 and 20.4 min in an area ratio of *ca.* 1:5, respectively. Ir and nmr spectral data showed the minor component to be the germacyclohexadiene XII, the major component the diethylchlorogermylpentadiene IX. The nmr spectrum (in CCl_4) of IX showed the following resonances: δ 1.15 (s, 10 H, Et_2Ge), 2.15 (d, 2 H_a, J_{ab} = 9 Hz), 5.79 (t, H_b, showing fine splitting, J_{ba} = 9 Hz), 6.65 (q, H_c, AM*X*, J_{cd} = 10 Hz, J_{ce} = 17 Hz), 5.2 (d, H_d, showing fine splitting, J_{cd} = 10 Hz), 5.57 ppm (d, H_e, partially overlapping the triplet at 5.79, J_{ce} = 17 Hz). The yield of IX was 56%, of XII, *ca.* 10% (by glpc, external standard method).

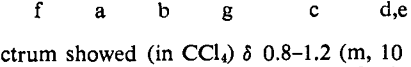
(b) **1,1-Diethyl-3-methyl-1-germacyclopent-3-ene.** The same procedure was used in the reaction of 10 mmol of the mercurial with 10.4 mmol of this germacyclopentene. Phenylmercuric bromide was recovered in 97% yield. Analysis by glpc (at 175°) showed a minor component at 6.5 min and a broad major peak at 12 min. Samples of each component were collected by preparative glpc. The major product was identified as XI (76% yield) (free of isomer X), the minor product as the germacyclohexadiene XXI (18%).

In another similar experiment carried out on the same scale, the initial filtrate was trap-to-trap distilled in two fractions: (1) at 0.05 mm to a pot temperature of 25° and (2) at 0.01 mm to a pot temperature of 80°. Analysis of fraction 2 by glpc indicated essentially the same product composition as in the previous experiment, but examination of the chromatogram showed that the peak due to the major product had a pronounced leading edge. Accordingly, the nmr spectrum of fraction 2 was examined prior to glpc separation. In addition to the resonances due to XI and XXI, additional resonances due to the isomeric pentadiene X were observed.

(c) **1,1-Diethyl-3,4-dimethyl-1-germacyclopent-3-ene.** The same procedure was used in the reaction (8 hr) of 10 mmol of the mercurial with 10.8 mmol of this germacyclopentene. Phenylmercuric bromide was isolated in 98% yield. The filtrate was analyzed by glpc (column at 185°). Two trace components at 3.4 and 4.2 min, a minor component at 6.5 min, and a major component at 10.3 min were present. The latter was identified by means of its ir and nmr spectra as the diethylchlorogermylpentadiene XXII, and its yield (by glpc) was 94%.

Reaction of 1,1-Diethyl-3,4-dimethyl-1-germacyclopent-3-ene with Me_3SnCF_3–NaI Reagent. Approximately 20 ml of DME was distilled from potassium onto 1.94 g (13.0 mmol) of anhydrous sodium iodide under nitrogen in a 50-ml, three-necked flask equipped with a reflux condenser, a magnetic stirring unit, and a nitrogen inlet tube. Trimethyl(trifluoromethyl)tin[22] (2.34 g, 10.0 mmol) and 9.6 mmol of the germacyclopentene were added to the initially clear, colorless solution. The reaction flask was immersed in an oil bath at 85–88° and the reaction mixture was stirred for 18 hr. During this period the reaction mixture became yellow. Upon cooling to room temperature, a white, powdery precipitate formed. Volatiles were removed in a trap-to-trap distillation at 0.03 mm (pot temperature to 85°). The clear, pale yellow distillate was analyzed by glpc (at 150°) and found to contain, in order of elution times, a major component (5 min), a trace component (7.5 min), and a minor component (9.0 min), in addition to DME and trimethyltin iodide. Samples of the products were collected by preparative glpc.

A collected sample containing the 5-min and 9.0-min components (*ca.* 2:1 mixture) suggested that they were isomers of the expected product. *Anal.* Calcd for $C_{11}H_{20}F_2Ge$: C, 50.27; H, 7.67; F, 14.46. Found: C, 49.92; H, 7.05; F, 14.43. The minor isomer, obtained in 18% yield (by glpc), was identified as



$$\underset{f}{Et_2FGe}\underset{a}{CH_2}\underset{b}{C(Me)}{=}\underset{g}{C(F)}{-}\underset{c}{C(Me)}{=}\underset{d,e}{CH_2}$$

The nmr spectrum showed (in CCl_4) δ 0.8–1.2 (m, 10 H, Et_2Ge), 1.75 (d, 3 H_b, J_{bg} = 4 Hz), 1.88 (s, 3 H_c, showing further fine splitting), 2.05 (d, 2 H_a, J_{af} = 7 Hz), 5.12 ppm (m, 2 $H_{d,e}$). Spectral data obtained for the major product suggested (but did not rigorously prove) that it was the expected 3-germabicyclo[3.1.0]hexane XVIII: nmr (in CCl_4, microcell) δ 0.8–1.3 (12 H, Et_2Ge and 2 H_a

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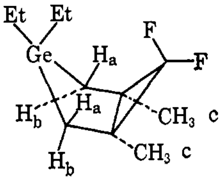
or H_b), 1.55 (d, 2 H_a or H_b, showing fine splitting, J = 7 Hz), 1.7–2.0 (m, 6 H_c, unsymmetrical four-line pattern showing fine splitting), no resonances in the olefinic region; ir (liquid film) 2980 sh, 2950 s, 2925 s, 2905 s, 2870 s, 2825 sh, 2725 w, 1655 w, 1575 m, 1460 sh, 1445 s, 1390 sh, 1375 m, 1320 m, 1245 w, 1225 w, 1170 sh, 1135 s, 1095 s, 1060 sh, 1030 sh, 1010 m, 955 w, 900 w, 782 m, 735 m, 725 m, 692 m, 670 sh, and 650 w cm^{-1}.



XVIII

An additional component was observed with a retention time of 30 min. This was collected with considerable difficulty due to its extreme air sensitivity. Its nmr spectrum was very similar to that of the diethylfluorogermylpentadiene with one notable exception, the $GeCH_2$ resonance appeared as a singlet shifted to somewhat lower field, which suggests replacement of Ge–F by Ge–I and that this compound is the halogen exchange product, $Et_2IGeCH_2C(Me){=}C(F){-}C(Me){=}CH_2$: nmr (in CCl_4) δ 1.0–1.4 (m, Et_2Ge), 1.75 (d, 3 H, J = 4 Hz), 1.87 (s, 3 H, showing further fine splitting), 2.40 (s, 2 H, $GeCH_2$), and 5.0–5.3 ppm (m, 2 H).

Nmr Experiments. (a) With 1,1-Diethyl-1-germacyclopent-3-ene. In a flame-dried 100-ml three-necked flask was placed under nitrogen 5.10 g (11.6 mmol) of $PhHgCCl_2Br$, 2.25 g (12.2 mmol) of the germacyclopentene, and 45 ml of dry carbon tetrachloride. The flask was agitated briefly to effect solution of the mercurial, sealed and stored at room temperature in the dark for 10 days. At this time filtration under nitrogen gave 2.73 g (66% yield) of phenylmercuric bromide. The filtrate was sealed under nitrogen and stored at room temperature for another 7 days. The phenylmercuric bromide which formed was filtered to give a total yield of 79%. Volatiles were removed from the filtrate by trap-to-trap distillation at 0.08 mm (pot temperature to 25°), leaving a thin white coating (presumably arylmercury compounds) on the sides of the distillation flask and a light yellow liquid containing a small amount of white solid in the bottom. The liquid was diluted with 2 ml of carbon tetrachloride and transferred by syringe to a dried centrifuge tube capped with a no-air rubber septum. The tube was cooled to −5° in order to precipitate additional solids and then centrifuged while cold. Aliquots of the supernatant liquid were used in subsequent spectral studies. The pertinent nmr data (*cf.* Figures 1a, 1b, and 1d)) are as follows.

1a. Pure 1,1-diethyl-1-germacyclopent-3-ene: δ 1.00 (m, 10 H, Et_2Ge), 1.42 (m, CH_2, 4 H), 5.88 (m, 2 H, vinyl hydrogens).

1b. Reaction mixture, after 17 days at room temperature: δ 1.42, 5.88 (starting germacyclopentene); 7.28 (trace of phenylmercury compound); 1.00 (Et_2Ge protons of the remaining germacyclopentene and of the 3-germabicyclo[3.1.0]hexane and the CH_2 protons of the latter, a multiplet considerably more complex than the δ 1.00 multiplet of the germacyclopentene), and 2.13 (symmetrical multiplet) cyclopropane hydrogens of the 3-germabicyclo[3.1.0]hexane).

1d. Reaction mixture, after further 12.5 hr at 80°: δ 1.42 (starting germacyclopentene); 7.28 (trace of phenylmercury compound); resonances due to $Et_2ClGeCH_2CH{=}C(Cl){-}CH{=}CH_2$ (IX): δ 1.16 s, 2.23 d (J = 9.5 Hz), 5.20 d (J = 10.0 Hz) with secondary fine splitting, 5.66 d (J = 16.5 Hz) with secondary fine splitting, 5.88 t (J = 9.5 Hz) with secondary fine splitting, 6.68 q (AM*X*) (J = 10.0, 16.5 Hz); (chemical shifts *vs.* internal 1,2-dibromoethane, δ = 3.62 ppm). The reaction mixture after 17 days at room temperature, after filtration and concentration, showed the following bands in the infrared spectrum (in CCl_4): 3005 sh, 2950 s, 2915 m, 2870 m, 2822 sh, 1604 w, 1460 m, 1422 m, 1402 m, 1375 w, 1340 w, 1261 m, 1203 m, 1140 m, 1098 m, 1028 s, 1014 sh, 944 m, 880 w, 704 m, and 623 w cm^{-1}.

(b) With 1,1-Diethyl-3-methyl-1-germacyclopent-3-ene. The same procedure was used in the reaction of 4.70 g (10.7 mmol) of $PhHgCCl_2Br$ and 2.15 g (10.8 mmol) of the germacyclopentene in 45 ml of carbon tetrachloride. The reactant solution was stored at room temperature under nitrogen in the dark for 17 days. The phenylmercuric bromide yield was 83%. The pertinent nmr data are as follows.

(1) Pure 1,1-diethyl-3-methyl-1-germacyclopent-3-ene: δ 1.01 (m, Et_2Ge), 1.68 (s, 3 H, CH_3), 1.41 (m, 4 H, CH_2), 5.47 (m, 1 H, vinyl).

(2) Reaction mixture, after 17 days at room temperature (starting germacyclopentene not detected): δ 7.28 (trace of phenylmercury compound); 1.02 m, 1.50 s, 1.73 m (intermediate 3-germabicyclo[3.1.0]hexane); resonances due to diethylchlorogermylpentadienes (see below).

(3) Reaction mixture, after further 2.5 hr at 80°. $Et_2ClGeCH_2C(Me){=}C(Cl){-}CH{=}CH_2$: δ 1.15 s, 2.00 s, 2.35 s, 5.14 d (J = 10 Hz) with secondary fine splitting, 5.50 d (J = 16 Hz) with secondary fine splitting, 6.62 q (AM*X*) (J = 10, 16 Hz). $Et_2ClGeCH_2CH{=}C(Cl){-}C(Me){=}CH_2$: δ 1.15 s, 1.90 s with secondary fine splitting, 2.17 d (J = 9 Hz), 5.0–5.1 m (2 peaks with secondary fine splitting), 5.68 t (J = 9 Hz) (chemical shifts *vs.* 1,2-dibromoethane, δ = 3.62 ppm).

Isolation and Characterization of 3,3-Diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexane. To a mixture of potassium *t*-butoxide prepared from 0.25 g-atom of potassium and 0.063 mmol of 1,1-diethyl-1-germacyclopent-3-ene in 250 ml of *n*-hexane at −30° under nitrogen was added slowly, with magnetic stirring, 0.17 mol of chloroform in 50 ml of hexane. During the addition the temperature rose to −5°; upon completion of the addition, the reaction mixture was stirred at 20° for 3 hr and then was hydrolyzed. The dried organic layer was concentrated at reduced pressure (20° bath temperature). Subsequent distillation (48° bath temperature at 0.005 mm) served to remove unconverted germacyclopentene (3.04 g). A liquid residue of 8.65 g (70% based on unrecovered starting material) remained. A 2.8-g aliquot of this residue was subjected to molecular distillation using a Leybold M 07 apparatus, bath temperature to 49°, at 0.0001 mm. Pure IV (1.70 g), $n^{20}D$ 1.5136, d_4^{20} 1.3168, was thus obtained. *Anal.* Calcd for $C_9H_{16}Cl_2Ge$: C, 40.37; H, 6.02; Cl, 26.48. Found: C, 40.76; H, 6.14; Cl, 26.11.

The nmr spectrum (in CCl_4) showed a multiplet centered at δ 1.00 ppm due to the $Et_2Ge(CH_2)_2$ protons and a symmetrical multiplet centered at 2.13 ppm due to the cyclopropane hydrogens. Ir (liquid film, KBr plates) showed: 3020 sh, 2955 s, 2880 s, 2825 sh, 1457 m, 1420 m, 1400 m, 1372 m, 1338 w, 1293 w, 1227 w, 1203 m, 1140 m, 1065 sh, 1028 s, 945 s, 883 m, 820 s, 768 s, 738 s, 702 m, 625 m, 576 m, 552 m, 540 m, 498 m, and 430 w cm^{-1}.

When IV was heated at 200–220° (30 mm), a mixture of the germacyclohexadiene XII and the Et_2ClGe-substituted pentadiene IX was formed. As indicated above, these may be separated by glpc, but chemical procedures also may be used. Alkaline hydrolysis of the mixture converts the latter to the high-boiling germoxane, $O(Et_2GeCH_2CH{=}CCl{-}CH{=}CH_2)_2$ from which XII may be easily separated by fractional distillation. On the other hand, the action of anhydrous hydrogen chloride on the mixture converts XII to IX quantitatively, and thus pure IX may be isolated; $n^{20}D$ 1.5295; $d^{20}{}_4$ 1.2598. *Anal.* Calcd for $C_9H_{16}Cl_2Ge$: C, 40.37; H, 6.03. Found: C, 40.39; H, 6.05.

Action of Deuterium Chloride on 1,1-Diethyl-4-chloro-1-germacyclohexa-2,4-diene (XII). Deuterium chloride was generated by reaction of D_2O with PCl_5. In a dried 50-ml, three-necked flask fitted with no-air stoppers and a gas inlet tube was placed 2.5 g of PCl_5. An eyedropper filled with anhydrous calcium chloride pierced one of the stoppers and was attached *via* a small length of Tygon tubing to a stainless steel needle. Dry nitrogen was passed through the system for several minutes before adding D_2O (99.5%) *dropwise* with a syringe to generate DCl.

The germacyclohexadiene (85–90 μl) in 200 μl of carbon tetrachloride was placed in a small, dry centrifuge tube capped with a no-air stopper. DCl was bubbled into this solution in a slow stream for *ca.* 20 min. Samples then were transferred using dry syringes to nmr tubes for spectral study.

Table II summarizes the nmr spectrum of undeuterated IX, the product of the reaction of XII with HCl, and the expectations for 100% D_1 incorporation at H_a, H_d, and H_e.

The nmr spectrum of the IX obtained from the XII–DCl reaction showed evidence of deuterium incorporation at both H_a and H_e. The doublet at 2.15 ppm (H_a) was broadened (deuterium coupling) and reduced in intensity; the 5.79-ppm triplet showed a multiplet structure, as did the 6.65-ppm quartet; the 5.57-ppm doublet was reduced in intensity. Only the 5.2-ppm doublet (H_d) remained undiminished in intensity. Although incorporation of *any* deuterium at H_d cannot be rigorously eliminated, incorporation at H_e certainly is highly preferred.

Reaction of 1,1,3,4,-Tetramethyl-1-silapent-3-ene with Phenyl(bromodichloromethyl)mercury. The silacyclopentene was pre-

Table II

Nmr spectrum of IX (undeuterated)	Expected changes for incorporation of one deuterium atom at H_a	H_d	H_e
H_a 2.15 d (J = 9 Hz)	1/2 intensity		
H_b 5.79 t (J = 9 Hz)	d (J = 9 Hz)		
H_c 6.65 q (AMX, J_c = 10 Hz, J_t = 17 Hz)		d (J = 17 Hz)	d (J = 10 Hz)
H_d 5.2 d (J_c = 10 Hz)		Not present	
H_e 5.57 d (J_t = 17 Hz)			Not present

pared according to the procedure of Weyenberg, *et al.*,[23] bp 64–66° (44 mm), $n^{25}D$ 1.4570 (lit.[23] $n^{25}D$ 1.4574). Nmr (in CCl$_4$): δ 0.15 (s, 6 H, Me$_2$Si), 1.30 (s, 4 H, SiCH_2) (somewhat broadened), 1.68 (s, 6 H C–CH$_3$).

A solution of 1.65 g (11.8 mmol) of this silacyclopentene and 4.51 g (11.0 mmol) of PhHgCCl$_2$Br in 30 ml of dry benzene was stirred under nitrogen at 80–82° for 3 hr. Filtration gave phenylmercuric bromide in 88% yield. The filtrate was trap-to-trap distilled at 0.01 mm (pot temperature to 80°). Glpc analysis of the distillate showed the presence of only a single product (74% yield) which was identified as $Me_2ClSiCH_2C(Me){=}C(Cl){-}C(Me){=}CH_2$. *Anal.* Calcd for $C_9H_{16}Cl_2Si$: C, 48.44; H, 7.23. Found: C, 49.16; H, 7.60. Nmr (in CCl$_4$): δ 0.43 (s, 6 H, Me$_2$Si), 1.86 (s with shoulder at *ca.* 1.84, 8 H, SiCH_2 + CH$_3$–C), 4.95 and 5.05 ppm, (2 H, =CH$_2$) two single resonances showing further fine splitting.

Reaction of 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene with Me$_3$SnCF$_3$–NaI. A solution of 1.50 g (10.2 mmol) of anhydrous sodium iodide, 2.62 g (11.2 mmol) of trimethyl(trifluoromethyl)tin, and 1.41 g (10.0 mmol) of the silacyclopentene in 30 ml of DME (freshly distilled from potassium) was stirred under nitrogen at reflux for 10 hr. Trap-to-trap distillation of volatiles at 0.03 mm (pot temperature to 80°) was followed by glpc analysis of the distillate (at 130°). In addition to starting materials and trimethyltin iodide there were present one major product (46% yield) and two minor products with slightly longer retention times. The major product was identified as

$$\mathrm{Me_2FSi}\underset{a}{\mathrm{CH_2}}\underset{b}{\mathrm{C(Me)}}{=}\mathrm{C(F)}{-}\underset{c}{\mathrm{C(Me)}}{=}\underset{d,e}{\mathrm{CH_2}}$$

Anal. Calcd for $C_9H_{16}F_2Si$: C, 56.80; H, 8.47; F, 19.97. Found: C, 56.28; H, 8.30; F, 20.04. Nmr (in CCl$_4$): δ 0.25 (d, 6 H, Me$_2$Si, J = 7.5 Hz), 1.72 (d, 3 H$_b$, J = 4 Hz), 1.86 (s, 3 H$_c$) (showing further fine splitting), 5.07 (s, H$_c$ + H$_d$, broad). The H$_a$ proton resonance appears to coincide with those of the CH$_3$ groups. Ir (liquid film): 3090 w, 2965 m, 2930 m, 2870 sh, 1640 w, 1460 m, 1410 sh, 1380 w, 1305 w, 1260 s, 1220 w, 1190 m, 1155 w, 1095 s, 1035 w, 1005 w, 950 w, 910 sh, 895 sh, 880 s, 845 s, 808 s, 765 w, 750 w, and 660 w cm^{-1}.

Acknowledgments. The authors are grateful to the National Science Foundation (Grant 6466X) for generous support of that portion of this work which was carried out at Massachusetts Institute of Technology and to the John Simon Guggenheim Memorial Foundation for the award of a fellowship to D. S. which made possible useful discussions of this joint project at the University of Toulouse in May 1968.

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Binding of Cyclic Polyethers to Ion Pairs of Carbanion Alkali Salts

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Abstract: Complexation of cyclic polyethers of the "crown" type to ion pairs of fluorenyl alkali salts was studied in ethereal solvents and pyridine by nmr and by uv–visible spectroscopy. The absorption spectra of these complexes are identical with the spectra of the solvent-separated ion pairs of the fluorenyl alkali salts. The complexing with the ion pairs leads to strong upfield shifts in the nmr spectrum of the polyether ring protons. The binding of fluorenylsodium with dimethyldibenzo-18-crown-6 is so strong that a slow exchange process with free cyclic polyether is observed, with an activation energy of 12.5 kcal/mole. The selectivity of this particular cyclic polyether with respect to alkali ions in THF was found to be $Na^+ \gg K^+ > Cs^+ > Li^+$, but this sequence is dependent on the solvent medium. In oxetane, the cyclic polyether prefers the fluorenylpotassium above the sodium salt. The complexing with some other cyclic polyethers was also investigated.

Various spectroscopic methods have recently been used to study structures of ion pairs and their solvates in aprotic solvents.[1,2] The ion pairs of carbanion salts have been of special interest to us for some time, since specific cation solvent interactions in a variety of aprotic media give rise to the formation of both contact- and solvent-separated ion pairs, and for certain types of carbanions, *e.g.*, fluorenyl alkali salts; the fractions of the two kinds of ion pairs can be quantitatively determined from their characteristic optical absorption spectra.[1] In addition, nmr spectroscopy has proven to be a valuable tool in the study of specific solvation phenomena and the fluorenyl alkali salts again provide us with a convenient probe to study structures of ion pairs in which certain agents are complexed to the cation.

In the study presented here we have investigated the complexes of fluorenyl alkali salts with cyclic polyethers

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