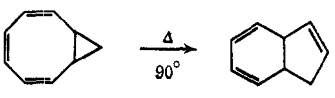
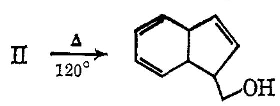


III IV

and Boekelheide[5]). Secondly, an assignment of the stereochemistry of I (as shown) on the basis of nuclear magnetic resonance (nmr) coupling constants by Bangert and Boekelheide[5] appeared to preclude, by reason of molecular geometry, the interaction postulated by Phillips. The present reinvestigation of the reduction of I (as the pure acid, R = H) justified the doubt and provided another example of the above valence-bond isomerization.

The pure acid I (R = H) was obtained by alkaline hydrolysis as described by Akiyoshi and Matsuda[1] (mp 162–163° uncor). This acid was reduced directly with lithium aluminum hydride in ethyl ether at room temperature to yield a single alcohol (by thin layer chromatography, tlc) which differed from that of Phillips by exhibiting $\lambda_{max}$ 246 m$\mu$ ($\epsilon$ 3400). The position of the ultraviolet absorption maximum, consistent with those of all reported bicyclo[6.1.0]nonatrienes,[1,2,4–6] and the simple, expected nmr spectrum identify the structure and stereochemistry[7] of this alcohol as II. The nmr spectrum in carbon tetrachloride (tetramethylsilane as internal standard) contained, in addition to one proton which exchanged upon $D_2O$ addition, a singlet at $\delta$ 5.94 (4 H), a broadened singlet at 5.81 (2 H), a doublet at 3.55 ($J$ = 6.5 cps) (2 H), a doublet at 1.33 ($J$ = 5.5 cps) (2H), and an unsymmetrical five-line multiplet centered at 0.65 (1 H). Heating of this alcohol either as a neat liquid or in a solution gave the alcohol characterized by Phillips, $\lambda_{max}$ 263 m$\mu$.

In one such thermolysis the [6.1.0] alcohol was prepared as an nmr sample in pentafluorobromobenzene,[8] degassed, and sealed under argon. The nmr spectrum, unchanged from that in carbon tetrachloride except for the observation of three distinct vinyl absorptions, was recorded and then the sample was heated at 120° in approximation of conditions of its isolation by Phillips. In 20 min >95% of the starting alcohol was observed to have rearranged.[9] The nmr spectral change, best expressed only qualitatively owing to lack of an internal reference, involved an increase in complexity and broadening of the vinyl absorption (6 H), a shift of one upfield proton to the region of those two on carbon bearing oxygen, and a shift of the two remaining upfield protons to the region $\delta$ 2.5–3.0. This spectrum is consistent with the rearrangement II → V, wherein the three cyclopropyl protons are converted to two allylic methine protons and one proton both doubly allylic and methine. Proof of the identity of this resulting alcohol (VI) with that obtained by Phillips was found in preparation, from this nmr sample, of the adduct with N-($p$-bromophenyl)maleimide,[10] mp 199–200° (lit. mp 198–201°). A mixture melting point with authentic material[11] was not depressed and the infrared spectra (KBr) were superimposable.



V

### Experimental Section

**Reduction of 9-Carboxybicyclo[6.1.0]nona-2,4,6-triene.**—To a magnetically stirred suspension of 100 mg (2 mmoles) of lithium aluminum hydride in 10 ml of sodium-dried ether at room temperature was added dropwise under nitrogen a solution of 50 mg (0.31 mmoles) of the acid I (R = H) in 5 ml of sodium-dried ether. The addition took ~15 min and the resulting suspension was stirred at room temperature for an additional 2 hr. At this time, the excess lithium aluminum hydride was decomposed cautiously and with ice cooling by adding 1 ml of a saturated aqueous solution of sodium potassium tartrate. An additional 10 ml of ether was added to permit easy stirring for 10 min more, at which time the mixture was filtered on sintered glass with light suction and concentrated under water vacuum at room temperature to provide 35 mg of 9-hydroxymethylbicyclo[6.1.0]nona-2,4,6-triene (II). An additional 11 mg of II could be obtained by acidification of the aluminum salts of the filter cake with 10% sulfuric acid and extraction with three 10-ml portions of ether and 5 ml of saturated sodium bicarbonate, brief drying over magnesium sulfate, filtration, and concentration. The combined product, 46 mg (100% theoretically) of a slightly yellow oil,[12] was dissolved in carbon tetrachloride and again concentrated to remove traces of ether. Samples thus prepared provided the physical data in the discussion. Thermal instability plus the anticipation of only isomeric impurities discouraged preparation of a sample for analysis.

**Acknowledgment.**—The author thanks Dr. E. E. van Tamelen for valuable discussions and Stanford University for a predoctoral research assistantship. This research was supported by U. S. Army Grant DA-31-124-ARO-D-285.

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(5) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

(6) A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **80**, 5505 (1958).

(7) See ref 5 above and especially ref 7 therein.

(8) Chosen for its high boiling point (137°), which facilitated degassing as well as the thermolysis experiment, and its availability (Imperial Smelting Corp. Ltd., London).

(9) It is noteworthy that, in an identical experiment in the case of the methyl ester I (R = $CH_3$), the time required to attain the same degree of rearrangement was ~13 hr. This amounts to a crude rate difference of a factor of 40 and explains isolation of the correct ester by early workers and isolation of only the rearranged alcohol without a clue to the rearrangement involved.

(10) To our knowledge this simple compound has not been reported in the literature. It was prepared without incident by the general method of M. Cava, *et al.*, *Org. Syn.*, **41**, 93 (1961). The product, pale yellow crystals, mp 122–123°, had as its major absorptions in the infrared 5.80, 6.70, 7.15 (s), 7.23, 8.7, and 12.0 $\mu$, that is, essentially the spectrum of the known N-phenylmaleimide. The nmr spectrum in chloroform-$d$ displayed an $A_2B_2$ pattern centered at $\delta$ 7.43 (4H) and a singlet at 6.83 (2 H).

(11) The author is grateful for a sample of the authentic N-(p-bromophenyl)maleimide adduct kindly provided by Dr. Phillips.

(12) This oil crystallized upon standing for several days at −20°. A sample was recrystallized from pentane to a constant melting point of 60–61°.

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## Catalytic Decomposition of Tetrachlorodiazocyclopentadiene. Formation of Spirocyclic Olefins

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West Lafayette, Indiana*

*Received July 22, 1966*

The reaction of 1,2,3,4-tetrachlorodiazocyclopentadiene (1) in several acetylenes has been examined as part of a continuing study on this extraordinarily

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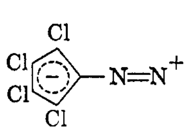
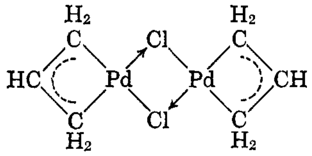
(1) Allied Chemical Corp. Research Fellow, 1963–1966.

stable diazo compound.[2] Copper or copper sulfate catalyzed decomposition of **1** in acetylenes gave quite different results from those obtained with di-$\mu$-chloro-di-$\pi$-allyldipalladium (**2**), a catalyst previously used to decompose ethyl diazoacetate under very mild conditions.[3]

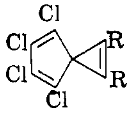
Decomposition of **1** at 75–82° in tolane or 3-hexyne using copper or cupric sulfate gave the expected substituted spiro[2.4]heptatriene (**3**). However, the reaction of **1** with dialkylacetylenes at 10–20°, induced by the palladium complex **2**, gave low yields of tetrachlorotetraalkylspiro[4.4]nonatetraenes (**4**), which are, to our knowledge, the first reported derivatives of the unknown parent compound, 1,3,6,8-spiro[4.4]nonatetraene.[4,5] No cyclopropene derivatives were found. The palladium catalyst also encouraged formation (50–60%) of tetrachlorocyclopentadienone azine (**5**), which was not formed at all under reaction conditions which afforded the spiro[2.4]heptatriene derivatives.



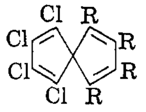
**1**



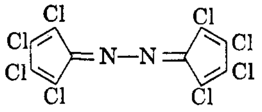
**2**



**3a**, R = $C_6H_5$
**b**, R = $CH_2CH_3$



**4a**, R = $CH_3$
**b**, R = $CH_2CH_3$

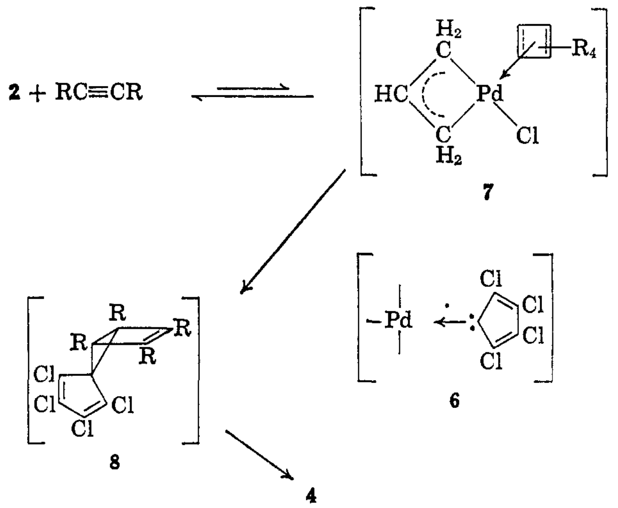


**5**

Compounds **3a** and **3b** both show the expected cyclopropene infrared absorption[6] at 5.40 and 5.26 $\mu$, respectively, and **3a** also displayed an ultraviolet absorption pattern reported by Breslow[7] to be characteristic of the 1,2-diphenylcyclopropene group.

Spectral data firmly support the assigned structures of both the spiro[4.4]nonatetraene derivatives. The nmr spectrum of **4a** contained two sharp methyl singlets of equal intensity at $\delta$ 1.47 and 1.89; **4b** showed two overlapping but distinct ethyl patterns with methyl resonances at $\delta$ 0.92 and 1.08 and methylene quadruplets centered at 1.90 and 2.31. Their ultraviolet spectra had relatively high extinction coefficients ($\epsilon$ 7500 to 8600) at $\lambda_{max}$ 270–280 m$\mu$, which may be the result of overlap of the absorption of each cyclopentadiene nucleus within **4a** or **4b**. Chlorinated[2] and alkylated[8] cyclopentadienes generally show extinction coefficients of about 2000–4000 in this region.

An insertion reaction of a highly selective tetrachlorocyclopentadienylidene carbene complex (**6**) on some form of a tetraalkylcyclobutadienepalladium $\pi$ complex (**7**), perhaps in equilibrium with **2**, might explain the formation of the spiro[4.4]nonatetraenes. This pathway suggests an intermediary substituted bicyclo[2.1.0]pent-2-ene (**8**) which could rearrange immediately, or during work-up, to its valence bond isomer **4**.[9,10]



Tetrachlorodiazocyclopentadiene (**1**) appears to act as a unique trapping agent in that its carbenoid intermediate fails to react with the acetylenic solvent[11] to form cyclopropenes but, rather, reacts with what is believed to be a cyclobutadiene $\pi$ complex. Although several stable cyclobutadiene metal $\pi$ complexes have been reported,[12] attempts to isolate or spectroscopically detect a similar complex in this work were unsuccessful. Evaporation of a slurry of **2** in 2-butyne gave a solid, whose nmr spectrum was identical with that of the starting complex. Moreover, **2** was too sparingly soluble in 2-butyne for direct observation in this solvent.

The spiro[4.4]nonatetraenes were thermally rearranged at 205–210° on a vapor phase chromatograph to isomeric indenes in yields of 63–65%. Surprisingly, only the 1,1,2,3-tetraalkyl-4,5,6,7-tetrachloroindene (**11a** or **11b**) was obtained in each case.[13,14] No analogous 1,1,2,3-tetrachloro isomers were isolated: either the latter derivatives were unstable under the reaction conditions or this rearrangement was less energetically favored. Most likely, indene formation occurred either by a concerted process or *via* the biradical **9**, both of which give initially an intermediary bicyclo[4.3.0]nonatetraene (**10**). The subsequent 1,2-alkyl migration of a type hitherto unnoted for a cyclo-

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[2] E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966).

[3] R. K. Armstrong, *ibid.*, **31**, 618 (1966). The author reported a 24% yield of a cyclopropene derivative from the decomposition of ethyl diazoacetate in 2-butyne with this catalyst.

[4] D. J. Cram and B. L. Van Duuren attempted the synthesis of this hydrocarbon: *J. Am. Chem. Soc.*, **77**, 3576 (1955).

[5] 1,2,3,4-Tetramethylspiro[4.4]nona-1,3,6-triene has been reported: R. Criegee, F. Förg, H.-A. Brune, and D. Schönleber, *Ber.*, **97**, 3461 (1964).

[6] W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

[7] R. Breslow and M. Battiste, *Chem. Ind.* (London), 1143 (1958).

[8] V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

[9] D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 123 (1965); see also J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966).

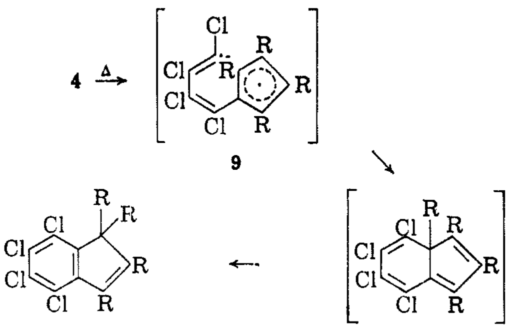
[10] The possibility that **8** is formed by an unlikely 1,2 addition of the acetylene to a cyclopropene derivatives has been considered. However, **3a** was recovered unchanged after treatment with 3-hexyne in the presence of **2**.

[11] The reaction of **1** in cyclohexene at room temperature in the presence of **2**, however, was facile and produced a 45% yield of the known compound,[2] norcarane-7-spiro-5′-(1′,2′,3′,4′-tetrachlorocyclopenta-1′,3′-diene).

[12] For a leading reference on cyclobutadiene metal complexes see: G. F. Emerson, L. Watts, and R. Petit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

[13] This fact makes structure **8** more attractive as it can only rearrange directly to the indenes (**11**); however, ultraviolet data favor the assignment of a spirononatetraene structure (**4**) for the initial product.

[14] The vinylcyclopropane group shows only end absorption beyond 210 m$\mu$: L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **88**, 2881 (1966); J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).


9

10

11a, R = $CH_3$
b, R = $CH_2CH_3$

pentadiene system[15] is presumably facilitated by the driving force to aromaticity.

Nmr and ultraviolet spectra[16] unequivocally support the proposed indene structures. Examination of the nmr spectrum of **11b** shows a well-shielded methyl triplet at $\delta$ 0.27 for the methyls of the allylic ethyl groups. Apparently these groups are sterically forced into and shielded by the anisotropic magnetic field due to the ring current.[17] The indene **11a** shows three methyl singlets, with the expected intensity (2:1:1), at $\delta$ 1.37, 1.88, and 2.29 in its nmr spectrum.

## Experimental Section[18]

Acetylenes were purchased from Farchan Research Laboratories and were used without further purification. The preparation of di-$\mu$-chloro-di-$\pi$-allyldipalladium[19] and tetrachlorodiazocyclopentadiene[2] have been reported previously.

**1,2-Diphenyl-4,5,6,7-tetrachlorospiro[2.4]hepta-1,4,6-triene (3a).**—Anhydrous cupric sulfate (2.7 g) was added to a magnetically stirred solution of 20 g (0.112 mole) of tolane, 4 g (0.0174 mole) of **1**, and 4 ml of cyclohexane. The internal temperature of the reaction flask was then raised to 75°; after an induction period of *ca.* 8 min, the theoretical equivalent of nitrogen was evolved in less than 3 min. The resulting black mass was cooled, dissolved in 100 ml of 1:1 (v/v) hexane–benzene, and eluted through a column (1.25 × 5 in.) of acid-washed alumina to remove catalyst and most tars. Evaporation of the eluate gave 23 g of a brown solid (largely tolane). Sublimation [55°(0.1 mm)] of this solid recovered excess tolane and left 3.02 g of a brown, crystalline residue. Hexane elution of the residue on acid-washed alumina (1 × 4 in.) gave 0.46 g of bis(pentachlorocyclopentadienyl),[20] identified by melting point and infrared comparison with an authentic sample;[21] further elution with benzene gave 2.5 g (38%) of **3a**. Sublimation of **3a** [129°(0.07 mm)] gave a white solid: mp 176–177° dec; $\lambda_{max}^{Nujol}$ 3.24 (w), 5.40 (w), 6.42 (s), and 14.70 (s) $\mu$; $\lambda_{max}^{EtOH}$ 222 m$\mu$ ($\epsilon$ 27,700), 230 (29,200), 287 (29,200) sh, 301 (38,600), and 318 (30,600). The nmr spectrum ($CDCl_3$) had a singlet at $\delta$ 7.44.

*Anal.* Calcd for $C_{19}H_{10}Cl_4$: C, 60.00; H, 2.63; Cl, 37.37; mol wt, 380. Found: C, 59.73; H, 2.79; Cl, 37.41; mol wt, 374.

**1,2-Diethyl-4,5,6,7-tetrachlorospiro[2.4]hepta-1,4,6-triene (3b).**—A solution of 4 g (0.0174 mole) of **1** in 60 ml of 3-hexyne containing 2 g of anhydrous cupric sulfate[22] was stirred at reflux (82°) for 8 hr.[23] After cooling, excess 3-hexyne was evaporated and recovered at reduced pressure and the dark, tarry residue was taken up in hexane and chromatographed on acid-washed alumina. An infrared spectrum of the eluted oil (2.2 g) showed absorptions characteristic of bis(pentachlorocyclopentadienyl) and the product **3b**. Distillation of this oil gave 0.5 g (*ca.* 10%) of **3b** as a light yellow oil, bp 76–80° (0.1 mm), which developed carbonyl and hydroxyl absorptions in its infrared spectrum after several days at room temperature in the atmosphere and darkened rapidly at temperatures over 100°. Spectral maxima appeared at $\lambda_{max}^{neat}$ 3.35 (s), 5.26 (m), 6.42 (s), 8.00 (s), 8.72 (s), and 14.35 (s) $\mu$; $\lambda_{max}^{EtOH}$ 239 m$\mu$ ($\epsilon$ 5700) and 284 m$\mu$ ($\epsilon$ 3400). The nmr ($CCl_4$) spectrum had a methyl triplet at $\delta$ 1.17 and a methylene quartet centered at 2.53 (area ratio 3:2).

*Anal.* Calcd for $C_{11}H_{10}Cl_4$: C, 46.48; H, 3.52; Cl, 50.00; mol wt, 284. Found: C, 44.87; H, 3.69; Cl, 49.53; mol wt, 279.

**1,2,3,4-Tetrachloro-6,7,8,9-tetramethylspiro[4.4]nona-1,3,6,8-tetraene (4a).**—Di-$\mu$-chloro-di-$\pi$-allyldipalladium (1 g) was stirred at room temperature for 12 hr in 80 ml of 2-butyne. The reaction flask was then cooled to and maintained at 10–15° while a solution of 7.75 g (0.034 mole) of **1** in 60 ml of 2-butyne was added dropwise (4 hr) to the well-stirred catalyst suspension. Afterwards the dark brown reaction mixture was stirred for 12 hr at room temperature. Excess 2-butyne was recovered and the dark residue was stirred with 100 ml of cold hexane and filtered to give 4.3 g (59%) of the major product, 1,2,3,4-tetrachlorocyclopentadienone azine (**5**). This material crystallized from hexane as deep red needles, mp 181–182°; spectral maxima were displayed at $\lambda_{max}^{Nujol}$ 6.42 (s), 8.20 (s), 12.10 (m), 13.04 (s), and 14.80 (m) $\mu$; $\lambda_{max}^{EtOH}$ 305 m$\mu$ ($\epsilon$ 39,000) and 316 m$\mu$ ($\epsilon$ 51,600).

*Anal.* Calcd for $C_{10}Cl_8N_2$: C, 27.78; Cl, 65.74; N, 6.48; mol wt, 432. Found: C, 28.01; Cl, 66.09; N, 6.39; mol wt, 440 ($CHCl_3$).

The filtrate was passed twice through 40-g portions of acid-washed alumina to remove last traces of **5**. Evaporation of the final filtrate afforded 3.8 g of a brown oil, from which crude **4a** (1.2 g, 16%) crystallized upon addition of a small amount of pentane (35–37°). A second product in the crude oil, a liquid, was not identified.[24] The product (**4a**) sublimed readily at 50° (0.1 mm) to give a white solid, mp 111–113°, having spectral maxima at $\lambda_{max}^{Nujol}$ 6.05 (w), 6.32 (s), 8.10 (s), 13.70 (s), and 15.03 (s) $\mu$; $\lambda_{max}^{EtOH}$ 272 m$\mu$ ($\epsilon$ 8600) and 320 m$\mu$ ($\epsilon$ 560). Nmr ($CDCl_3$) methyl singlets appeared at $\delta$ 1.47 and 1.89.

*Anal.* Calcd for $C_{13}H_{12}Cl_4$: C, 50.32; H, 3.87; Cl, 45.81; mol wt, 310. Found: C, 50.01; H, 3.52; Cl, 45.45; mol wt, 300.

**1,2,3,4-Tetrachloro-6,7,8,9-tetraethylspiro[4.4]nona-1,3,6,8-tetraene (4b).**—A solution of 8 g (0.0348 mole) of **1** in 40 ml of 3-hexyne was added dropwise (5 hr) to a stirred suspension of 0.5 g of di-$\mu$-chloro-di-$\pi$-allyldipalladium in 30 ml of 3-hexyne maintained at 15–20°. After addition, the reaction was stirred at room temperature overnight. Work-up, as described in the previous experiment, gave 3.65 g (49%) of **5** and 3.9 g of an amber oil containing **4b**, bis(pentachlorocyclopentadienyl), and resinous material. Repeated filtrations through alumina gave a light yellow oil which slowly darkened at room temperature. The oil was made to crystallize and sublimation [40°

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[15] For a lead reference on cyclopentadiene migrations see ref 2.

[16] P. Eaton, E. Carlson, P. Lombardo, and P. Yates [*J. Org. Chem.*, **25**, 1225 (1960)] report a similar ultraviolet absorption pattern for octachloroindene.

[17] An analogous shielding effect was observed in the nmr spectrum of 3-isopropyltetrachlorophthalide: G. C. Brumlik, R. L. Baumgarten, and A. I. Kosak, *Nature*, **201**, 388 (1964).

[18] All melting points are uncorrected. Analyses and molecular weights (osmometry in acetone unless otherwise stated) were determined by Dr. C. S. Yeh, Purdue University. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer, equipped with grating optics. Ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505 spectrometer. Nmr spectra were measured using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Chemical shifts are expressed as $\delta$ parts per million downfield from TMS. Vapor phase chromatography was performed on an Aerograph Model A-700 Autoprep. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6D.

[19] W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1585 (1964).

[20] This compound, never found in photolytic or thermolytic decompositions of **1**, was always formed in varying amounts in reactions involving copper, cupric sulfate, or palladium complex (**2**) catalyzed decompositions of **1**. It is believed that the catalyst is responsible for ligand transfer of a chlorine radical (tars may be the source of chlorine) into the carbenoid metal complex, forming a pentachlorocyclopentadienyl radical which then dimerizes.

[21] E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 4375 (1955).

[22] The use of copper bronze as catalyst was comparable to cupric sulfate in catalytic effectiveness but it produced higher yields of undesired bis(pentachlorocyclopentadienyl).

[23] This reaction time was necessary for complete decomposition. With tolane, however, the effectiveness of the copper catalysts is apparently increased.

[24] A small amount of bis(pentachlorocyclopentadienyl) was also detected in the infrared spectrum of the crude oil.

(0.1 mm)] of this material gave *ca.* 1.6 g (10%) of a waxy yellow solid, a second sublimation of which gave **4b**, as a white waxy solid, melting point range 65–71°, having spectral maxima at $\lambda_{max}^{Nujol}$ 6.34 (s), 8.10 (s), 13.42 (s), and 15.00 (m) $\mu$; $\lambda_{mxx}^{EtOH}$ 276 m$\mu$ ($\epsilon$ 7500) and 325 m$\mu$ ($\epsilon$ 500). The mass spectrum showed peaks corresponding to the isotopic parent molecular ions.

*Anal.* Calcd for $C_{17}H_{20}Cl_4$: C, 55.74; H, 5.46; Cl, 38.80. Found: C, 55.83; H, 5.18; Cl, 38.45.

**Thermal Rearrangements of 4a and 4b. 1,1,2,3-Tetraalkyl-4,5,6,7-tetrachloroindene** (11).—Both **4a** and **4b** were introduced to the vapor phase chromatograph in chloroform solution and isomerized to the corresponding 1,1,2,3-tetraalkylindene derivatives (**11a** and **11b**). The purity of each indene was confirmed by vpc on a 0.25 in. × 10 ft column of 20% Apiezon L on 60–80 mesh acid-washed firebrick (column temperature 240°, He flow rate 120 cc/min).

The indene **4a**, the sole peak in the chromatogram, was collected in 63% yield from a 0.25 in. × 5 ft column of 20% GE-SF96 on 60–80 mesh firebrick (column temperature 210°, injector temperature 270°, He flow rate 150 cc/min).

The indene **4b**, also the sole peak in the chromatogram, was obtained in 65% yield from a 0.5 in. × 10 ft column of 3% GE-SF96 on 60–80 mesh acid-washed Chromosorb P (column temperature 205°, injector temperature 285°, He flow rate 200 cc/min). Some decomposition of each spiro compound was evident as a carbonaceous deposit in the injector port. This accounts, at least in part, for the mass loss in these pyrolyses.

1,1,2,3-Tetramethyl-4,5,6,7-tetrachloroindene, a white solid after sublimation [80°(1.5 mm)], mp 91–92.5°, displayed spectral maxima at $\lambda_{max}^{CCl_4}$ 3.40 (m), 6.16 (m), 7.39 (s), 11.78 (s), and 14.05 (s) $\mu$; $\lambda_{max}^{EtOH}$ 222 m$\mu$ ($\epsilon$ 19,000), 228 (19,700), 234 (20,000), 242 (18,200), 277 (15,700), and 284 (15,500). The mass spectrum showed peaks corresponding to the parent ions.

*Anal.* Calcd for $C_{13}H_{12}Cl_4$: C, 50.32; H, 3.87; Cl, 45.87. Found: C, 50.29; H, 3.92; Cl, 45.85.

1,1,2,3-Tetraethyl-4,5,6,7-tetrachloroindene, a pale yellow, viscous oil displayed spectral maxima at $\lambda_{max}^{neat}$ 3.36–3.47 (s), 6.20 (w), 12.33 (s), and 13.88 (s) $\mu$; $\lambda_{max}^{EtOH}$ 224 m$\mu$ ($\epsilon$ 16,700), 231 (17,300), 237 (17,900), 246 (16,500), and a broad peak 279–289 (14,700). The nmr spectrum ($CCl_4$) had essentially three ethyl group patterns; methyl triplets were centered at $\delta$ 0.27, 1.15, and 1.18 (electronically integrated area of the upfield triplet was equal to the area sum of the overlapping downfield triplets). The methylene multiplets were in the range $\delta$ 1.50–2.95 and are not easily assignable; the methylenes of the allylic ethyl groups have magnetically nonequivalent protons[17] and produce a complex pattern, which overlaps with the remaining methylene quadruplets.

*Anal.* Calcd for $C_{17}H_{20}Cl_4$: C, 55.74; H, 5.46; Cl, 38.80; mol wt, 366. Found: C, 56.08; H, 5.29; Cl, 38.80; mol wt, 365.

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## 2-Cyclohexylethyltricyclohexylsilane. Formation of Cyclohexylethyllithium from the Cleavage of Ethyl Ether by Cyclohexyllithium

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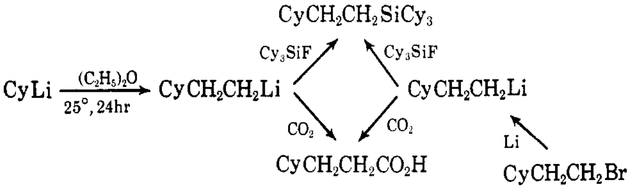
In the course of studying the condensation reaction between cyclohexyllithium and tricyclohexylfluorosilane to give tetracyclohexylsilane, (cyclo-$C_6H_{11})_4Si$,[1] a product was obtained, under certain conditions, which contained only carbon, hydrogen, and silicon, but whose analysis and molecular weight were just outside acceptable limits for the desired compound. Moreover, its melting point of 104° was abnormally low, while its retention time on a silicon-coated capillary vapor phase chromatographic column was greater than that of tetraphenylsilane which, in turn, was longer than that for tetracyclohexylsilane.

It was inferred that the new compound might be 2-cyclohexylethyltricyclohexylsilane, (cyclo-$C_6H_{11}$-$CH_2CH_2$)Si(cyclo-$C_6H_{11})_3$. Independent synthesis of this substance from 2-cyclohexylethyllithium and tricyclohexylfluorosilane confirmed the hypothesis.

These results suggested that cyclohexyllithium, under proper conditions, cleaved ethyl ether with the effective insertion of ethyl between the alkyl group and lithium, yielding 2-cyclohexylethyllithium. Indeed, a solution of cyclohexyllithium in ethyl ether at room temperature for 24 hr gave, after treatment with pulverized solid carbon dioxide, 3-cyclohexylpropionic acid, characterized as the amide, and identical with an authentic sample.

The above results are summarized in the following scheme where Cy = cyclo-$C_6H_{11}$.



Almost all previously reported reactions between ethyl ether and alkyllithiums have, aside from metallation side reactions, yielded, principally, lithium ethoxide and olefin–alkane mixtures.[2–5] The sole precedent for the present work is the reported cleavage of diethyl ether by isopropyllithium and *t*-butyllithium.[6] Although, as in these latter analogous cases, cyclohexyllithium also added to ethylene, to give 2-cyclohexyllithium, yields were poor and do not strongly support the concept of a reaction chain in which such addition is a link. The reaction mechanism for the present case in unknown.

Parallel examples wherein the ether solutions of cyclohexyllithium were kept below −10° until reaction work-up showed no anomalous behavior.[1]

These results suggest that this mode of cleavage may be more general than is suggested by the paucity of reported examples. It may be necessary to exercise caution when other secondary and tertiary organolithium derivatives are used in ether solution at room temperature.

### Experimental Section

All organolithium preparations and manipulations were performed under an argon atmosphere.

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[1] Part of a program to resolve the large disagreement between the paper by A. D. Petrov and T. I. Chernysheva, *Zh. Obshch. Khim.*, **24**, 1189 (1954), and M. Kanazashi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954). This will appear elsewhere.

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