(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 λ_{max}^{Nujol} 6.34 (s), 8.10 (s), 13.42 (s), and 15.00 (m) μ; λ_{max}^{EtOH} 276 mμ (ε 7500) and 325 mμ (ε 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) μ; λ_{max}^{EtOH} 222 mμ (ε 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 λ_{max}^{neat} 3.36–3.47 (s), 6.20 (w), 12.33 (s), and 13.88 (s) μ; λ_{max}^{EtOH} 224 mμ (ε 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 δ 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 δ 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.

Acknowledgment.—The authors are indebted to the Allied Chemical and Dye Corporation for financial support of this work.

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

LEONARD SPIALTER AND CHARLES W. HARRIS

Chemistry Research Laboratory, Aerospace Research Laboratories,
Office of Aerospace Research,
Wright-Patterson Air Force Base, Ohio

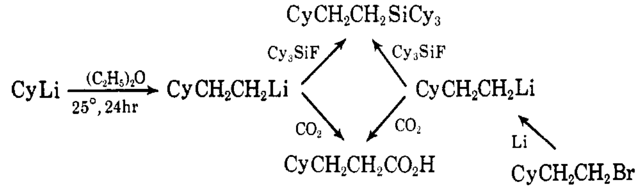
Received June 13, 1966

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.

---

(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.

(2) H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954).

(3) R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6079 (1956).

(4) K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950).

(5) R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

(6) P. D. Bartlett, S. Friedman, and R. M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953).

3-Cyclohexylpropionic Acid (from Cyclohexyllithium and Ether).—To 6.3 g (0.90 g-atom) of lithium shot of high (0.8%) sodium content in 10 ml of diethyl ether was added 53.6 g (0.41 mole) of cyclohexyl chloride in 200 ml of ether. After reaction had begun, the system was cooled to and kept at −24°. After addition was complete, the mixture was stirred at room temperature for 48 hr. It was then poured onto Dry Ice, hydrolyzed, and neutralized with acid. Extraction with ether in the usual manner and separation by solubility in 10% aqueous sodium carbonate gave 12 g of nonacidic material (not investigated further) and 4.3 g of a liquid acid. Whereas cyclohexanecarboxylic acid is a solid, mp 30°,[7] 3-cyclohexylpropionic acid melts at 16°.[7] The infrared spectrum of the product agreed with that of authentic 3-cyclohexylpropionic acid prepared directly from the appropriate lithium compound and carbon dioxide. The liquid acid was converted, *via* thionyl chloride and ammonia, to the amide, mp 117–119°, after recrystallization from ether–ethanol (lit.[8] mp 120°; cyclohexanecarboxamide mp 185–186°[9]).

3-Cyclohexylpropionic Acid (from Cyclohexyllithium and Ethylene).—To 6.2 g (0.89 g-atom) of lithium shot of high (0.8%) sodium content in 10 ml of freshly purified tetrahydrofuran was added, over a 2-hr period, 47.4 g (0.40 mole) of cyclohexyl chloride in 190 ml of tetrahydrofuran. After reaction had begun at room temperature, the rest of the addition was conducted at −70° (Dry Ice bath). After overnight stirring at −25°, the dark gray mixture was saturated with ethylene bubbled in continuously for 16 hr. It was then poured onto pulverized dry ice and hydrolyzed and the solvent evaporated. By the usual ether extractive procedure there was isolated 3.7 g of a liquid acidic fraction. Its infrared absorption spectrum agreed with that of authentic 3-cyclohexanepropionic acid, and its amide derivative melted at 117°.

2-Cyclohexylethyltricyclohexylsilane (from Cyclohexyllithium in Ether).—To 2.1 g (0.30 g-atom) of lithium wire of high (0.8%) sodium content in 100 ml of anhydrous diethyl ether was gradually added, over a 4-hr period, 16.2 g (0.14 mole) of cyclohexyl chloride in 150 ml of ether. After initiation of the endothermic reaction at room temperature, the rest of the addition occurred at −30°. Then, to the mixture warmed to room temperature, 10 g (0.034 mole) of tricyclohexylfluorosilane was added. The reaction system was stirred for 30 hr, hydrolyzed, neutralized, and extracted with ether. After drying, evaporation, and recrystallization from pentane–ethanol, there was obtained 5.9 g (48%) of 2-cyclohexylethyltricyclohexylsilane, mp 103–104°.

Anal. Calcd for $C_{26}H_{48}Si$: C, 80.34; H, 12.45; Si, 7.21; mol wt, 388.7. Found: C, 80.02; H, 12.29; Si, 7.78; mol wt (vapor osmometric), 386.

The identity of the product was confirmed by comparison with an authentic sample, described below, *via* mixture melting point, infrared absorption spectrum, and vapor phase chromatographic retention time on a DC-550 silicone-coated capillary column in a Barber-Colman Model 61-C chromatograph.

2-Cyclohexylethyltricyclohexylsilane (from 2-Cyclohexylethyl Bromide).—To a mixture of 3.0 g (0.01 mole) of tricyclohexylfluorosilane and 0.76 g (0.11 g-atom) of lithium wire of high (0.8%) sodium content in 3 ml of anhydrous diethyl ether was gradually added 9.56 g (0.05 mole) of 2-cyclohexylethyl bromide[10] in 15 ml of ether. After the first few drops of halide had initiated reaction, as evidenced by cloudiness and activity at the metal surface, the system was cooled to −25° and maintained at that temperature during the rest of the addition for a total of 3 hr. After further stirring at room temperature for 37 hr, the reaction mixture was hydrolyzed with excess water and neutralized with 3 *N* hydrochloric acid. The ether phase and ether washings of the water phase were collected, dried, and evaporated. The residue was recrystallized from pentane–ethanol mixture to give 2.3 g (59%) of 2-cyclohexylethyltricyclohexylsilane, mp 102–103°.

Anal. Calcd for $C_{26}H_{48}Si$: C, 80.34; H, 12.45; Si, 7.21; mol wt, 388.7. Found: C, 80.27; H, 12.24; Si, 7.23; mol wt (vapor osmometric), 382.

---

[7] G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 2385 (1926).

[8] N. Zelinsky, *Ber.*, **41**, 2676 (1908).

[9] W. Markownikoff, *ibid.*, **25**, 3355 (1892).

[10] Prepared by the method of G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **48**, 1089 (1926).

---

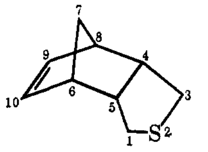
exo,cis-2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol *via* an Interannular Interaction[1]

PELHAM WILDER, JR., AND LUIS A. FELIU-OTERO[2]

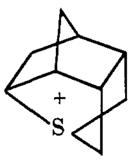
Department of Chemistry, Duke University,
Durham, North Carolina 27706

Received June 28, 1966

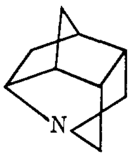
In a recent paper[3] the preparation of 2-thia-1,2-dihydro-*endo*-dicyclopentadiene (I) was described along with its facile cyclization to the sulfonium salt II, similar to the previously reported tertiary amine[4] III. Now we wish to report an example of a remarkable interannular interaction in which the bromosulfonium salt IV in a mildly alkaline solution specifically gives *exo,cis*-2-thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol (V).



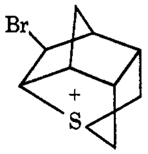
I



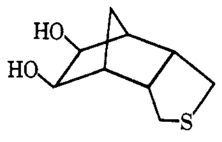
II



III

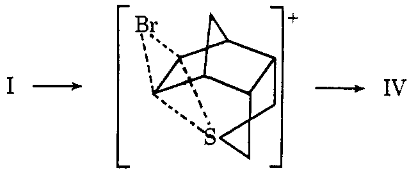


IV



V

Bromination of sulfide I in chloroform under mild conditions afforded the bromosulfonium salt (IV) in excellent yield. It is significant that no material having the *exo*-ring skeleton was observed among the reaction products. Most certainly reaction occurs through the bromonium intermediate VI which collapses to give the product IV.



VI

In lithium carbonate solution the salt IV was transformed smoothly into *cis*-glycol V. The structure of V was assigned on the basis of (1) a doublet at 3626 and 3689 cm^{-1} in the infrared corresponding to a $\Delta\nu$ of 63 cm^{-1} characteristic of strongly bonded *cis* glycols,[5]

---

[1] (a) Taken from a dissertation submitted by L. A. Feliu-Otero to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, 1965. (b) The support of this research by Research Grant CA-4298 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, and, in part, by funds from an American Cancer Society Institutional Grant to Duke University is gratefully acknowledged.

[2] Department of Chemistry, University of Puerto Rico at Mayaguez.

[3] P. Wilder, Jr., and L. A. Feliu-Otero, *J. Org. Chem.*, **30**, 2560 (1965).

[4] P. Wilder, Jr., and C. F. Culberson, *J. Am. Chem. Soc.*, **81**, 2027 (1959); C. F. Culberson and P. Wilder, Jr., *ibid.*, **82**, 4939 (1960).

[5] L. P. Kuhn, *ibid.*, **74**, 2492 (1952).