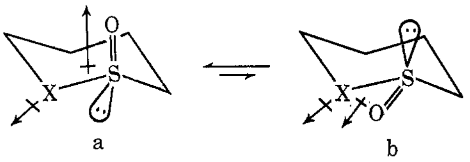
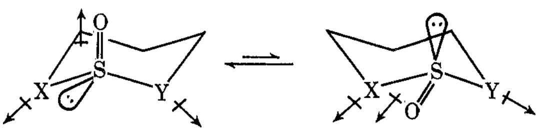
Since the nmr spectra of both **3a** and **4** are unchanged over a wide temperature range (−90 to +150°), it may be concluded that both these compounds are conformationally pure. Thus **3** (and presumably **4**) adopt the same axial sulfoxide conformation as do the sulfites. Since only one isomer is observed at room temperature for sulfite **1a**, the oxides of oxathiane **3**, oxathiazine **1b**, and dithiane **4** under conditions where less than 5% of the minor isomer would be detectable, a conformational barrier in excess of 2000 cal exists for these compounds. This is more than 1800 cal greater than the barrier observed for sulfoxide **1c** (X = Y = CH_2).

We suggest that this strong preference for an axial S=O configuration results from a dipolar interaction analogous to the anomeric effect observed in carbohydrate systems.[16] The conformation in which the S=O bond is in an equatorial position possesses an unfavorable dipolar arrangement, since the net dipole resulting from the nonbonded lone-pair electrons of oxygen is nearly parallel to that of the S=O bond. This unfavorable arrangement is relieved with the S=O bond adopting an axial configuration. Such a dipolar effect has been used to explain the conformational preference (500 cal) of the trans-diaxial conformation of *trans*-1,2-dibromocyclohexane over the corresponding diequatorial isomer.[17] For methyl glycosides, the dipolar or anomeric effect is approximately 1.5 kcal;[18] for a highly polar group as a sulfoxide, this effect should be even greater.



3, X = O
4, X = S

A similar argument may be advanced for the conformational preference of an axial S=O bond in sulfite **1a** and the oxathiazine oxide **1b**. Thus, in all of these cases **1a**, **1b**, **3**, and **4**, the sulfoxide bond is adjacent to at least one heteroatom bearing lone-pair electrons and therefore should experience an electrostatic dipole repulsion when the S=O bond is in an equatorial conformation.[19]



1a, X = Y = O
b, X = O; Y = NH

Experimental Section

1,2-Dithiane, 1,1-Dioxide (2).—This compound was prepared as previously described,[20] mp 54–56°.

1,2-Oxathiane 2-Oxide (3).—Substance **3** was formed by desulfurization with tris(diethylamino)phosphine[21] as described in an earlier publication,[20] bp 60–61° (0.5 mm).

1,2-Oxathiane 2,2-Dioxide (5).—To a solution of 100 mg (0.84 mmol) of 1,2-oxathiane 2-oxide (**3**) in 5 ml of water was added an aqueous potassium permanganate solution until the permanganate color persisted. The solution was filtered and acidified with concentrated hydrochloric acid, and the solvent removed under vacuum; the residue was dissolved in ether and dried, and the ether removed under vacuum to provide a clear oil identical in its ir and nmr spectrum with an authentic sample.

1,2-Dithiane 1-Oxide (4).—A solution of 10.0 g (82 mmol) of 1,4-butanedithiol in 200 ml of acetic acid was cooled to 10° and 17 ml (175 mmol) of a 35% hydrogen peroxide solution was slowly added. To maintain solution, 25–40 ml of methylene chloride was added as necessary. After this stirred for 24 hr, the solvent was removed under vacuum, the residue diluted with water, extracted with ether, washed with water, and dried, and the solvent removed under vacuum to afford a viscous oil which on distillation provided a fraction, bp 100–105° (0.1 mm), which crystallized on cooling to yield 0.6 g (5%) of a wax-like material, mp 67–74°. This material could be sublimed *in vacuo* [70–90° (0.1 mm)] to provide pure product, mp 74–76°. This material was homogeneous by vpc analysis, ir (KBr) 1060 cm^{-1} (S=O). The mass spectrum of this material exhibits a parent ion at *m/e* 136.0007 (calcd for $C_4H_8OS_2$, *m/e* 136.0016).

Registry No.—**2**, 18321-15-8; **3**, 24308-29-0; **4**, 7153-76-6; **5**, 1633-83-6.

Acknowledgment.—We wish to thank the National Research Council of Canada for financial support of this work and Professors J. T. Edward and A. S. Perlin for helpful discussions.

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[16] Reference 3, p 375.

[17] W. Kwestroo, F. A. Meijer, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **73**, 717 (1954).

[18] R. U. Lemieux and N. J. Chu, Abstracts, 133rd National Meeting of the American Chemical Society, New York, N. Y., 1958, 31N.

[19] Müller has recently carried out semiempirical calculations on analogous heterocyclic systems which indicate that diaxial lone-pair repulsions are also significant (5–6 kcal/mol): K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

[20] D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

[21] This phosphine has been used to desulfurize a wide variety of organosulfur compounds: see D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968); D. N. Harpp and B. A. Orwig, *Tetrahedron Lett.*, 2691 (1970); D. N. Harpp and D. K. Ash, *Chem. Commun.*, 811 (1970).

Formation and Transannular Reactions of Cyclopropane Half-Cage Alcohols[1a]

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Dechlorination of hexachloro half-cage alcohol **1** with lithium and *tert*-butyl alcohol in tetrahydrofuran[2] gave a solid alcohol mixture that consisted of 55% of the known[2,3] half-cage alcohol **2** and 45% of a new alcohol, cyclopropane half-cage alcohol **3**. In the nmr spec-

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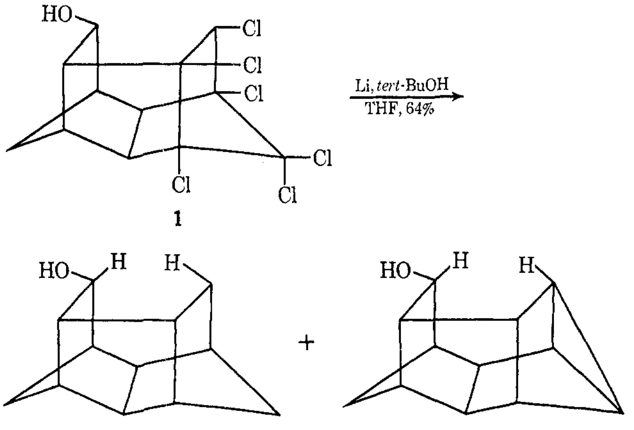
[1] (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (b) Address inquiries to this author. (c) Deceased Nov 23, 1969.

[2] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (*London*), 405 (1960).

[3] L. de Vries and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 5363 (1960).

trum the α protons of the two alcohols appeared as slightly broadened singlets at τ 5.41 and 5.59, respectively. Both signals are at unusually low field due to strong deshielding that arises from severe steric congestion[4,5] of the α protons with the opposed transannular hydrogen atoms. This deshielding in half-cage alcohols has been discussed previously.[5]

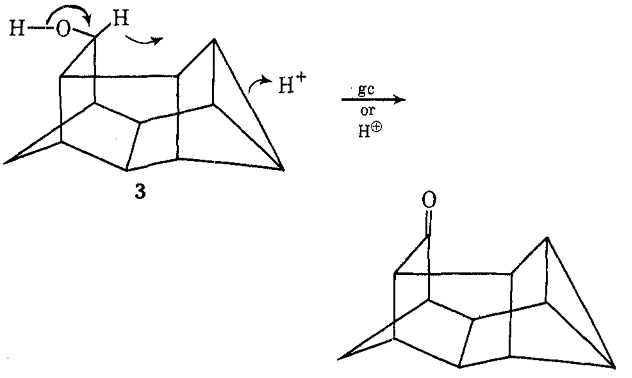


1

2, 55%

3, 45%

Alcohol 3 could not be isolated in pure form either by alumina chromatography, fractional crystallization, or preparative gas chromatography. The mixture of alcohols decolorized bromine in carbon tetrachloride but did not react with potassium permanganate in acetone, indicative of the presence of the cyclopropane ring in 3. Pure 2 does not decolorize bromine in carbon tetrachloride. Attempted gas chromatographic separation of the alcohol mixture led to conversion of 3 to half-cage ketone 4 as determined by infrared spectra of the two materials, 2 and 4, collected from the gas chromatograph. This conversion also occurred quantitatively within a few hours when an ether solution of the alcohol mixture was stirred with dilute sulfuric acid. From a 55:45 mixture of alcohols there was obtained a 55:45 mixture of half-cage alcohol 2 and half-cage ketone 4.

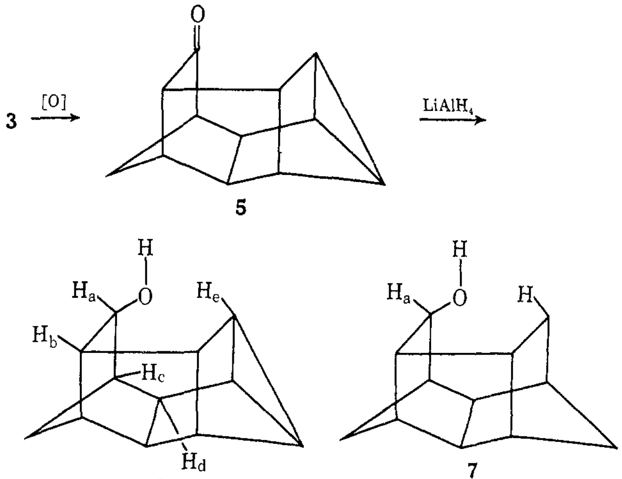


3

4

The quantitative conversion of 3 to 4 is consistent only with the proposed cyclopropane half-cage alcohol structure. The acid-catalyzed cyclopropane ring opening occurs in the direction of the least strained structure; cleavage of either of the other two cyclopropane ring bonds would lead to a highly strained structure containing a cyclobutane ring. The hydride shift may possibly be concerted with and may facilitate the ring opening.

Oxidation of a 53:47 mixture of the two alcohols with chromium trioxide in pyridine gave a 57:43 mixture of the corresponding ketones in 78% yield. A pure sample of the cyclopropane half-cage ketone 5 was obtained by gas chromatographic purification. The carbon–hydrogen analysis of this ketone was consistent with an empirical formula of $C_{12}H_{12}O$. The ketone instantly decolorized bromine in carbon tetrachloride but did not react with potassium permanganate in acetone, as expected for the presence of the cyclopropane ring. Furthermore, the infrared spectrum exhibited cyclopropane C–H stretching at 3067 and 3040 cm^{-1} and a carbonyl frequency of 1746 cm^{-1}, exactly the same as that of 4. Lack of a methylene group adjacent to the carbonyl was indicated by the lack of absorption at 1410–1420 cm^{-1}, an absorption that is characteristic[6] of α-methylene ketones.



5

6

7

Reduction of 5 with lithium aluminum hydride in ether followed by a work-up that involved no trace of acid gave the oxygen-inside cyclopropane half-cage alcohol 6 in 91% yield. In the nmr spectrum ($CDCl_3$) the α-proton signal appeared at τ 6.02 as a doublet, $J = 8.5$ Hz, with both components of the doublet split into triplets, with an apparent J of 2 Hz. The major splitting is due to coupling of the α proton with the eclipsed H_b proton. Additional small coupling of the α proton with H_c and long-range coupling with H_d result in the 2-Hz splitting. The severely congested transannular hydrogen atom H_e is strongly deshielded and appeared as a broad signal at τ 6.96. In the nmr spectrum (CCl_4) of oxygen-inside half-cage alcohol 7, the α-proton signal appeared at τ 6.08, and the strongly deshielded transannular hydrogen atom signal appeared at τ 6.45.[5]

After the chloroform-*d* solution of 6 was allowed to stand overnight, the nmr spectrum of the solution revealed very nearly complete conversion of 6 to cage ether 8. Removal of the solvent gave impure cage ether; after purification the solid had an infrared spectrum, gas chromatographic retention time, and melting point which were identical with those of authentic 8.[4] Chloroform-*d* usually contains traces of acid. The

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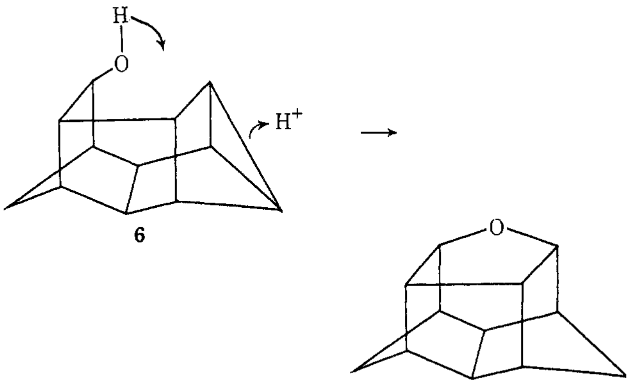
(4) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, **83**, 2938 (1961).

(5) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, **87**, 5247 (1965).

(6) S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

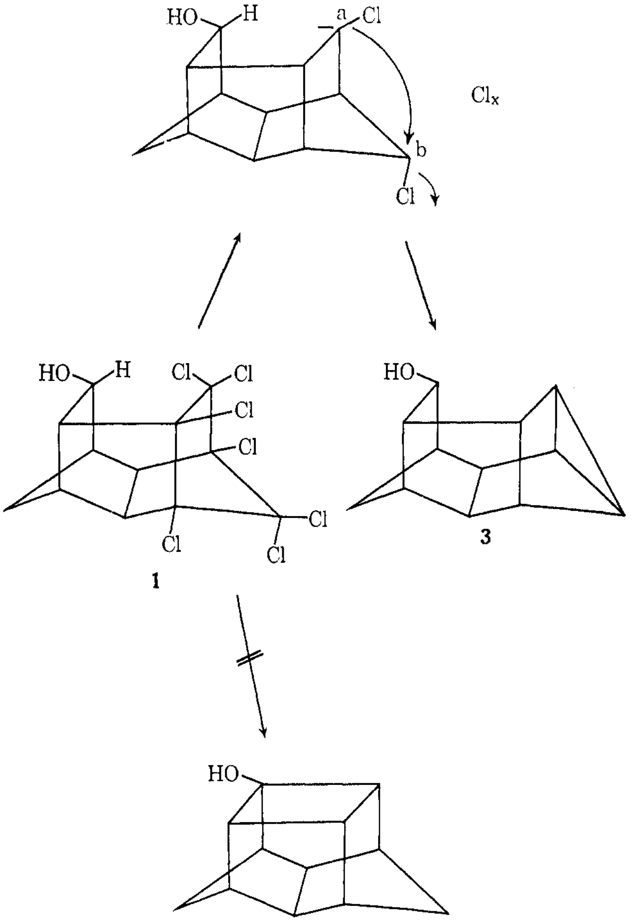


6

8

conversion of **6** to **8** probably occurred by acid-catalyzed cyclopropane ring opening, possibly with oxygen participation, and ring closure to the ether. This conversion further supports the structural assignments for the two cyclopropane alcohols and the ketone **5**.

Formation of **3** from hexachloro half-cage alcohol **1** could occur either by a carbene mechanism or by an internal carbanion displacement of chlorine. The carbene mechanism would involve abstraction of the hydrogen α to chlorine at C_a by lithium *tert*-butoxide formed in the dechlorination, followed by α elimination of chloride anion to form a carbene. Insertion of the carbene into the proximate C_b–Cl bond or the C_b–H bond formed in the dechlorination would ultimately give rise to **3**. If the carbene mechanism were operative, insertion into the opposed transannular carbon–hydrogen bond to give bird-cage alcohol **10**[7] might be expected also. In fact, there is less than 0.3% bird-cage alcohol in the crude product mixture from dechlorination. It thus appears that the carbanion displacement of chlorine is responsible for the cyclopropane ring formation. The only chlorine atom in a suitable stereochemical position for displacement is the *anti*-chlorine atom on C_b.[8] Carbanion formation at C_a could occur either by proton abstraction by lithium *tert*-butoxide or by exchange of the chlorine atom with lithium.



1

3

10

Experimental Section

Melting points are corrected. Infrared spectra were determined with a Perkin-Elmer Model 421 spectrometer; frequencies are accurate to within ±2 cm^{-1}. Nmr spectra were determined with a Varian A-60 spectrometer.

3. Dechlorination of 1.—To a magnetically stirred solution of 28.5 g of pure hexachloro half-cage alcohol **1**, mp 203–203.5° (lit.[9] mp 204°), and 158 g of *tert*-butyl alcohol in 500 ml of tetrahydrofuran under dry nitrogen was added 30 g of lithium wire cut into 0.25-in. lengths so that the freshly cut pieces fell directly into the 3-l. flask. After a few minutes a vigorous, exothermic reaction began that required cooling with an ice bath. The mixture was allowed to reflux spontaneously with stirring until the reaction subsided (90 min). The mixture was held at reflux on a steam bath for an additional hour. The hot reaction mixture was poured through a wire screen to remove residual lithium. Ice and then 2 l. of water were added. The mixture was extracted with 500 ml of ether and then with two 250-ml portions of ether. The ether layers were combined, extracted with three 200-ml portions of saturated sodium chloride solution, dried (Na_2SO_4), and concentrated to an oil. The oil was heated several minutes on a steam bath under aspirator vacuum. Upon cooling, the oil solidified. Gc analysis ($^1/_8$ in. × 5 ft column of 25% SE-30 at 155°) indicated that the mixture consisted of 93% **2** and **3**, with less than 0.3% bird-cage alcohol **10** (none detected). The solid, 12 g, exhibited α-proton signals at τ 5.41 (55%) and 5.59 (45%) in the nmr spectrum ($CDCl_3$ solvent).

Repeated attempts to crystallize the sample from hexane and from aqueous ethanol were unsuccessful. In each case the material separated as an oil. After removal of the solvent, the material was chromatographed on a 2.5 × 40 cm column of activity III alumina. The first 250 ml of eluate (20% ether in pentane) yielded an oil. The next 1250 ml of eluate yielded 7.1 g (54% yield) of a mixture of 55% **2** and 45% **3** (nmr analysis). Elution with 50% ether in pentane and then 100% ether yielded more oil. The combined oils were rechromatographed on a 2.5 × 37 cm column of activity III alumina with 15% ether in pentane. An additional 1.3 g (10% yield) of a 65:35 mixture of **2** and **3** was obtained. Fractional crystallization of 6.2 g of the 55:45 mixture of alcohols from hexane and then aqueous ethanol gave 1.07 g of pure **2**, mp 130–131° (lit.[3] 130–131°), and a 40:60 mixture, constant mp 124–125°, of **2** and **3**. Both the 55:45 and 40:60 mixtures of **2** and **3** decolorized bromine in carbon tetrachloride and did not react with potassium permanganate in acetone. Pure **2** did not decolorize bromine in carbon tetrachloride.

Acid Treatment of 3.—A solution of 6.0 g of a 55:45 mixture of **2** and **3** in 100 ml of ether and a solution prepared from 10 ml of concentrated sulfuric acid and 90 ml of water were stirred together for 8 hr. The aqueous layer was extracted with two 50-ml portions of ether. The ether layers were combined, extracted with three 50-ml portions of saturated sodium bicarbonate solution and 100 ml of water, and dried (Na_2SO_4). The solvent was distilled off through a Vigreux column. Gc analysis (0.25 in. × 2 m column of 20% Apiezon L at 170°) and ir analysis indicated the product mixture to consist of 55% of **2** and 45% of **4**.

The mixture was chromatographed on a 2.5 × 28 cm column of activity I alumina. The ketone, 2.2 g (37% yield), was eluted

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[7] P. Carter, R. Howe, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 914 (1965).

[8] The facile replacement of this chlorine atom by hydrogen *via* alkoxide attack on halogen in a number of similar compounds has been reported: C. H. M. Adams and K. Mackenzie, *J. Chem. Soc. C*, 480 (1969).

[9] C. W. Bird, R. C. Cookson, and E. Crundwell, *ibid.*, 4809 (1961).

with 20% ether in pentane. Sublimation at 85° (0.05 mm) gave 1.87 g of **4**, mp 165–167° (lit.[10] 167–169°). The infrared spectrum of this solid was identical with that of authentic **4**.[10] Elution of the alumina column with 100% ether gave 3.25 g (54% yield) of **2**.

In a control experiment, a solution of 50 mg of **2** in 10 ml of ether was stirred 4 hr with an acid solution prepared from 1.0 ml of concentrated sulfuric acid and 9.0 ml of water. Work-up yielded 47 mg of solid; the infrared spectrum of this material showed it to be pure **2** with no trace of carbonyl absorption.

Cyclopropane Half-Cage Ketone 5.—A 1.0-g sample of a 53:47 mixture of **2** and **3** was added to 2.0 g of CrO_3 in 11 ml of pyridine. The mixture was stirred for 11 hr. Then water was added, and the mixture was extracted three times with pentane. The pentane extracts were combined, washed well with water, dried (Na_2SO_4), and concentrated to 0.77 g (78% yield) of ketone mixture that consisted of 57% of **4** and 43% of **5** (gc analysis on 2-m column of 20% XF-1150 at 180°). A small amount of **5** was purified by gas chromatography and then was sublimed at 80° (0.03 mm) to give 20 mg of pure **5**: mp 176–177°; positive test with Br_2–CCl_4; negative test with $KMnO_4$–acetone; ir (CCl_4) 3067 (m), 3040 (m), 2965 (s), 2875 (m), 1746 (s) cm^{-1}, no absorption at 1400–1440 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.77; H, 7.12.

6. Rearrangement of 6 to 8.—A 59-mg sample of **5**, mp 173–175°, that contained 0.8% of **4**, was treated with a large excess of lithium aluminum hydride in ether After 30 min the reaction mixture was cooled in ice water, and excess hydride was decomposed by dropwise addition of water. Then 30 ml of water was added and the mixture was allowed to stand 1.5 hr. The layers were separated and the aqueous layer was extracted with two 25-ml portions of ether. The ether layers were combined, washed twice with water, dried (Na_2SO_4), and concentrated under vacuum to give 53.5 mg of **6**, mp 199–201°, with softening at 191°. This material instantly decolorized bromine in carbon tetrachloride.

The nmr spectrum of a solution of 51 mg of **6** in $CDCl_3$ was taken immediately after preparation of the solution: τ 6.02 (dt, 1, J = 8.5 Hz, J = 2 Hz, HCOH), 6.71 (s, 1, OH), 6.96 (m, 1, transannular H), 7.08–8.8 (m, 11). The solution was allowed to stand 17 hr at room temperature, and another nmr spectrum was taken; this spectrum was identical in all respects with that of authentic cage ether except for trace signals at τ 8.8 and 9.15. There was <5% of **6** (none detected) as judged from complete absence of the α-proton signal of **6**. Removal of the solvent and sublimation of the residue at 70° (0.03 mm) gave 23 mg of cage ether, mp 165–175°. The infrared spectrum of this material was identical in all respects with that of authentic cage ether except for an extremely weak hydroxyl absorption and an extremely weak carbonyl absorption. A pure sample of cage ether, mp 191.5–192.5° (sealed capillary; authentic cage ether[4,11] has mp 191–193°), was obtained by gas chromatography on an XF-1150 column. The retention time of the sample was identical with that of authentic cage ether.

Registry No.—**5**, 28229-16-5; **6**, 28229-17-6.

[10] R. Howe and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 915 (1965).

[11] P. Bruck, private communication.

Metalation Reactions. VIII. Evidence for the Sequence of Reactions of Dilithiophenyl-1-propyne

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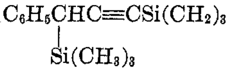
Received August 26, 1970

We have found recently[1] that the reactions of dilithiophenyl-1-propyne (I) with deuterium oxide or trimethylsilyl chloride are accompanied by a rearrangement and give respectively II and III. It was inferred indirectly that the observed hydrogen shift occurred after the first step that was supposed to be an attack on the carbon next to the phenyl group.

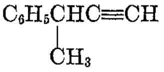
We now report reactions proving the attack on the benzylic carbon of I as the first step and present further examples of this rearrangement. The dilithio derivative I reacted with excess methyl bromide for 20 min and then with water yielding 3-phenylbut-1-yne (IV). When the addition of methyl bromide was followed by that of trimethylsilyl chloride, the product obtained was V. The intermediate acetylide VI was apparently slow to react with methyl bromide but reacted rapidly with trimethylsilyl chloride. This acetylide was obtained on rearrangement of the initial product of the reaction (VII).

$[C_6H_5C{\equiv}CCH]Li_2$ I $C_6H_5CHDC{\equiv}CD$ II



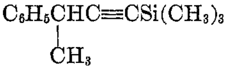
$C_6H_5CH(Si(CH_3)_3)C{\equiv}CSi(CH_2)_3$

III



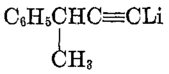
$C_6H_5CH(CH_3)C{\equiv}CH$

IV



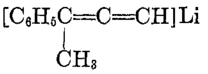
$C_6H_5CH(CH_3)C{\equiv}CSi(CH_3)_3$

V



$C_6H_5CH(CH_3)C{\equiv}CLi$

VI



$[C_6H_5C(CH_3){=}C{=}CH]Li$

VII

The reaction of trilithiophenylpropyne[1,2] (VIII) with methyl bromide for 20 min and subsequent treatment with water gave 3-methyl-3-phenylbut-1-yne (IX); the addition of trimethylsilyl chloride 20 min after the addition of methyl bromide to VIII gave X. The structures of the products were supported by their analyses and spectra.

$C_6H_5C_3Li_3$ VIII $C_6H_5C(CH_3)_2C{\equiv}CH$ IX $C_6H_5C(CH_3)_2C{\equiv}CSi(CH_3)_3$ X

IV showed infrared bands at 3275 and 2100 cm^{-1} supporting the presence of a terminal acetylene group; λ_{max} 242 nm (ϵ 720) shows lack of direct conjugation between the phenyl group and the triple bond. The nmr spectrum showed a doublet at τ 8.53 for the methyl with a coupling of 7 Hz. The benzylic proton at τ 6.37 appeared as an octet and the acetylenic proton at τ 7.91 was a doublet with a coupling constant of 2 Hz.

V did exhibit an acetylenic band at 2170 cm^{-1} but no ≡CH stretching. The lack of conjugation was supported by its uv spectrum with maxima at 252 nm (ϵ 240), 258 (260), and 264 (205). The methyl group appeared in the nmr at τ 8.52 as a doublet with a coupling constant of 7 Hz. The benzylic proton was found at τ 6.28 as a quartet and the trimethylsilyl protons at τ 9.80 (s).

The infrared absorption of IX was similar to that of IV with bands at 3285 and 2110 cm^{-1}, λ_{max} 252 nm (ϵ 220) and 266 (180), and two singlets in the nmr at τ 8.47 (6 H) and 7.85 (1 H) confirmed this structure.

The spectral properties of X were similar to those of IX with differences resulting from the substitution of a trimethylsilyl group for an ethynyl hydrogen: λ_{max}

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[1] J. Klein and S. Brenner, *Tetrahedron*, **26**, 2345 (1970).

[2] J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967).