

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 CrO₃ 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 (Na₂SO₄), 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 Br₂-CCl₄; negative test with KMnO₄-acetone; ir (CCl₄) 3067 (m), 3040 (m), 2965 (s), 2875 (m), 1746 (s) cm⁻¹, no absorption at 1400–1440 cm⁻¹.

Anal. Calcd for C₁₂H₁₂O: 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 (Na₂SO₄), 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 CDCl₃ 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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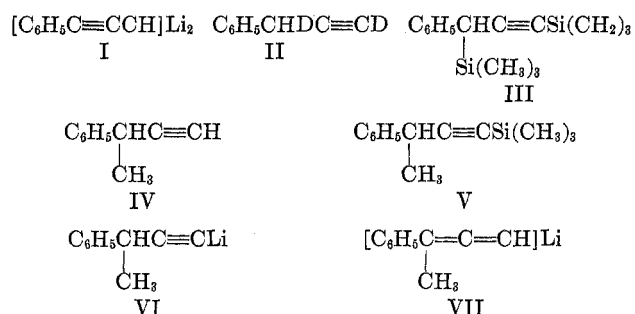
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Received August 26, 1970

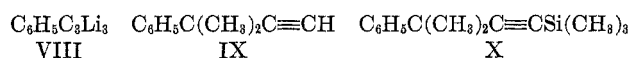
We have found recently¹ that the reactions of dilithiophenyl-1-propyne (I) with deuterium oxide or tri-

methylsilyl 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).



The reaction of trilitiophenylpropyne^{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 struc-



tures of the products were supported by their analyses and spectra.

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}

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

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

252 nm (ϵ 760), 257 (740); nmr τ 8.46 (s, 6 H) and 9.82 (s, 9 H).

Experimental Section

3-Phenylbut-1-yne (IV).—A solution of dilithio-1-phenylpropyne was prepared as reported¹ from 1 g of 1-phenylpropyne and 14.5 ml of 1.2 *F* butyllithium in ether. This solution was cooled in an acetone–Dry Ice bath and gaseous methyl bromide was bubbled through it during 15 min. The reaction mixture was allowed to reach room temperature and poured on ice, and the ether layer separated. The reaction product, containing 80% of IV and 20% of 1-phenylpropyne, was separated into its components by glpc.

Anal. Calcd for $C_{10}H_{10}$: C, 92.31; H, 7.69. Found: C, 92.42; H, 7.81.

1-Trimethylsilyl-3-phenylbut-1-yne (V) was prepared as above but trimethylchlorosilane was added after the product of reaction with methyl bromide reached room temperature. The solution was left overnight and poured on water and the product in the ether layer purified by glpc on Apiezon L on Chromosorb, yield 80%.

Anal. Calcd for $C_{13}H_{13}Si$: C, 77.23; H, 8.91. Found: C, 77.38; H, 8.93.

3-Methyl-3-phenylbut-1-yne (IX).—A solution of trilitio-phenylpropyne VIII was prepared^{1,2} from 1 g of 1-phenylpropyne and a sixfold mole ratio of 1.2 *F* butyllithium in ether. This solution was treated with methyl bromide and worked up as in the preparation of IV. The product IX was obtained in 90% yield and was purified by glpc on polydiethyleneglycol succinate.

Anal. Calcd for $C_{11}H_{12}$: C, 91.67; H, 8.33. Found: 92.05; H, 8.39.

1-Trimethylsilyl-3-methyl-3-phenylbut-1-yne (X) was prepared as above but trimethylchlorosilane was added after methyl bromide. The product X was obtained in 90% yield and purified by glpc on Apiezon L.

Anal. Calcd for $C_{14}H_{20}Si$: C, 77.78; H, 9.26. Found: C, 77.96; H, 9.09.

Registry No.—I, 28129-02-4; IV, 4544-28-9; V, 28129-04-6; IX, 28129-05-7; X, 28129-06-8.

An Efficient and Convenient Synthesis of 1-Methylcyclopropene^{1a}

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Received October 2, 1970

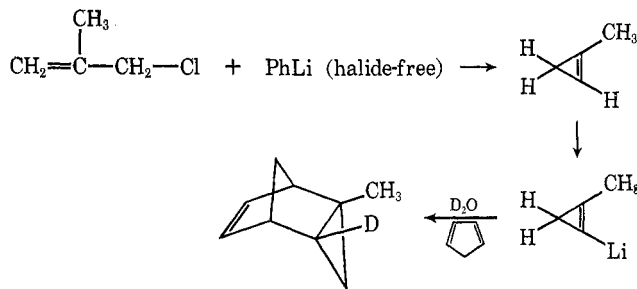
Several syntheses for cyclopropene and its simple derivatives have been reported, by far the most useful of which is the sodium amide induced α elimination of an allylic chloride.² This method, however, suffers from the relatively low yields, the difficultly purified product, and the necessity of performing the reaction each time a fresh sample of the cyclopropene is required.

In the course of our mechanistic study of the reaction between phenyllithium and allyl chloride, we demonstrated that α elimination is a major process and that the cyclopropene thus produced undergoes either of two

subsequent reactions to roughly equal extents: addition of phenyllithium across the double bond, eventually producing phenylcyclopropane, and abstraction of an olefinic proton yielding 1-lithiocyclopropene.³ Since the yield of cyclopropene was considerably higher than that in the Closs and Krantz procedure,^{2b} we decided to investigate the action of phenyllithium on other allylic chlorides. We now describe a procedure which not only leads to 1-methylcyclopropene in consistently high yields, but which also produces it as a stable derivative which can be stored apparently indefinitely.

When β -methylallyl chloride is allowed to react with phenyllithium prepared in the conventional manner (bromobenzene and lithium), both the coupling product and 1-methylcyclopropene (detected as its Diels–Alder adduct with cyclopentadiene) are formed, normally in comparable amounts but in rather unreproducible yields. It was soon discovered that the presence of either lithium bromide or nonphenyllithium base (such as lithium alkoxide) is a major factor in inhibiting cyclopropene formation. In fact, when an ether solution of crystalline phenyllithium, prepared from iodobenzene and *n*-butyllithium,⁴ is employed in this reaction, the yield of coupling product is dramatically reduced and 1-methylcyclopropene is formed in yields typically in the 60–80% range. In and of itself, this is only a modest improvement over the yield claimed by Fisher and Applequist.^{2a} The distinct advantages of this new method lies in the following observations.

1. Unlike the parent compound, 1-methylcyclopropene undergoes no detectable addition of phenyllithium across the double bond; instead, complete loss of the olefinic proton occurs, as demonstrated by the formation of totally monodeuterated Diels–Alder adduct when deuterium oxide is used in the neutralization.



2. This lithiocyclopropene can be quenched under conditions such that 1-methylcyclopropene either remains in the reaction vessel or is driven over into a suitable trap (see Experimental Section).

3. Most important, the lithiocyclopropene in ether solution is stable in the freezer for at least 3 months; work-up at this time with deuterium oxide generates the same amount of completely monodeuterated 1-methylcyclopropene as had been present immediately after its synthesis. Thus, one can prepare and store large quantities of the stable organolithium in solution, aliquots of which can then be neutralized to produce the desired quantity of 1-methylcyclopropene.

Although the enormous advantage gained by excluding extraneous lithium salts from the starting material is not understood, it should be noted that other

(1) (a) Partial support of this work by the Robert A. Welch Foundation is gratefully acknowledged as is the assistance of the National Science Foundation in the purchase of a Varian Associates A-56/60A spectrometer; (b) to whom inquiries should be addressed at the Department of Chemistry, The University of Tennessee, Knoxville, Tenn. 37916; (c) National Science Foundation Undergraduate Research Participant, 1968–1969.

(2) (a) F. Fisher and D. A. Applequist, *J. Org. Chem.*, **30**, 2089 (1965); (b) G. L. Closs and K. D. Krantz, *ibid.*, **31**, 638 (1966); (c) R. Köster, S. Arora, and P. Binger, *Angew. Chem., Int. Ed. Engl.*, **8**, 205 (1969).

(3) R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **90**, 5211 (1968).

(4) M. Schlosser and V. Ladenberger, *J. Organometal. Chem.*, **8**, 193 (1967).