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 reported[1] 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 $C_{13}H_{18}Si$: C, 77.23; H, 8.91. Found: C, 77.38; H, 8.93.

3-Methyl-3-phenylbut-1-yne (IX).—A solution of trilithiophenylpropyne 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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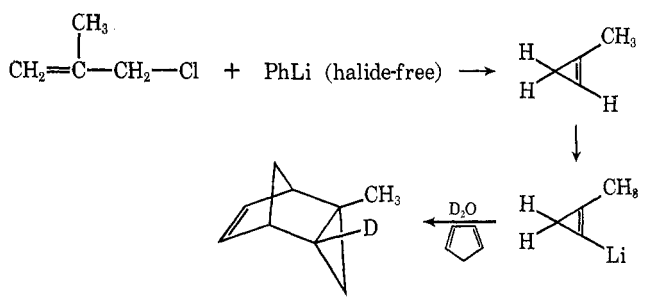
Several syntheses for cyclopropene and its simple derivatives have been reported, by far the most useful of which is the sodium amide induced α elimination of an allylic chloride.[2] This method, however, suffers from the relatively low yields, the difficultly purified product, and the necessity of performing 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).

sources of halide-free phenyllithium (such as the commercial material or that prepared from chlorobenzene and lithium shot) give similarly high yields of the stable lithium derivative.

Experimental Section

Instruments.—Analytical glpc was performed on a Perkin-Elmer Model 800 gas chromatograph (flame ionization detector). Product yields were determined by quantitative glpc using the internal standard method; peak areas were measured with a Disc integrator and the response ratios for all products and standards were determined Preparative glpc was performed on a Varian Aerograph Model 202-1B gas chromatograph (thermal conductivity detector). Nmr spectra were obtained on a Varian Associates A-56/60A spectrometer.

Materials.—β-Methylallyl chloride was obtained from Matheson Coleman and Bell and was distilled at atmospheric pressure before use. Iodobenzene was purchased from either Matheson Coleman and Bell or J. T. Baker Chemical Co.; the former gave by far the better and more consistent results. Phenyllithium in benzene–ether was obtained from Alfa Inorganics, Inc., and *n*-butyllithium in hexane from Foote Mineral Co. Lithium shot was prepared from lithium rod by the method of Worden and Burgstahler.[5] Organolithium reagents were analyzed for carbon-bound lithium by either "double titration"[6a] or the triphenylmethane method[6b] (see below); analysis for inorganic halide was done by Volhard titration. All reactions involving lithium reagents were run under an argon atmosphere.

Preparation of Crystalline Phenyllithium.—The procedure of Scholosser and Ladenberger[4] gave phenyllithium yields of the order of 60%, as judged by titration of an aliquot either by the "double titration" method[6a] using 1,2-dibromoethane or, more conveniently, by the addition of a two- to threefold excess of triphenylmethane in tetrahydrofuran followed by titration of the blood-red solution to a pale yellow end point with ethanol in benzene.[6b] Volhard titration of the aqueous layer from the neutralization of an aliquot of solution showed the absence of halide ion.

Synthesis of 1-Methylcyclopropene.—A solution of 2.75 g (0.030 mol) of β-methylallyl chloride in 50 ml of ether (dried over sodium) was added over *ca.* 30 min at room temperature to a stirred solution of a two- to threefold excess of phenyllithium (crystalline) in ether containing cyclooctane as an internal standard. The mixture was stirred for an additional 30 min. An aliquot was quenched with water and quantitatively analyzed by glpc (20 ft × 1/8 in., Hi-Pak silicone rubber W98 column) for β-methylallylbenzene for which a total yield of 0.051 g (1.4%) was calculated. A second aliquot was treated with cyclopentadiene and water. Analysis on the same column for *endo*-2-methyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene, the Diels–Alder adduct of 1-methylcyclopropene, gave a total yield of 2.92 g (80%); the structure was confirmed by comparison of glpc retention time and nmr spectrum with that of an authentic sample.[2a] Small amounts of β-methylallyl chloride could be detected, indicating that the yield of products may be even higher. In other runs, the yield of coupling product was in the range of 1.8–3.2% and that of Diels–Alder adduct from 54 to 73%.

The remainder of the reaction mixture was placed in the freezer for 3 months. Aliquots were then removed and analyzed as described above giving calculated yields for β-methylallylbenzene and Diels–Alder adduct of 4.5 and 76%, respectively. The remainder of this material was quenched with deuterium oxide and cyclopentadiene. The aqueous layer was extracted several times with ether, and the combined organic phases were washed with saturated NaCl, dried over $MgSO_4$, and concentrated with a rotary evaporator. Preparative glpc (10 ft × 3/8 in., XF-1150 column) gave the completely monodeuterated Diels–Alder adduct (total absence of nmr absorption at δ 1.0); mass spectral analysis confirmed that the sample was better than 95% monodeuterated.

For the purpose of further reaction, 1-methylcyclopropene may either be generated by aqueous neutralization of the lithiocyclopropene and used in the original reaction vessel, or generated and driven into a suitable trap, as illustrated for formation of its Diels–Alder adduct, where the reaction vessel was fitted with a condenser which was connected by a length of Tygon tubing to an ice-cooled gas-washing tower containing cyclopentadiene, pentane, and cyclooctane (internal standard). The reaction vessel was cooled (ice bath) while absolute ethyl alcohol was slowly added; a stream of argon was swept through the flask and into the trap. Upon completion of the neutralization, the reaction flask was slowly warmed until ethanol began to reflux, and gentle reflux was maintained for 2.5 hr. Quantitative glpc analysis for the Diels–Alder adduct indicated that 84% of the methylcyclopropene originally present in the reaction flask had been driven over and converted into the Diels–Alder adduct.

Registry No.—1-Methylcyclopropene, 3100-04-7.

(5) L. R. Worden and A. W. Burgstahler, *J. Chem. Educ.*, **45**, 425 (1968).

(6) (a) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964); (b) R. M. Magid, S. E. Wilson, T. C. Clarke, and C. D. Duncan, unpublished results.

1,2,3,4-Tetrahydroquinoline 8-Sulfones[1,2]

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Sulfuric acid has been known to cause rearrangement or hydrolysis[3] of arylsulfonanilides. The utilization of the rearrangement technique as a synthetic route to difficultly accessible sulfones has received little attention. Hydrolysis is the predominant reaction for sulfonamides, while either hydrolysis or rearrangement, depending on acid concentration, is possible for the N-substituted sulfonanilides. In their original investigations, Witt and Uermenyi[3] found that high acid concentration with sulfonanilides led primarily to the formation of *o*-amino sulfones rather than the expected hydrolytic products.

Additional work by Witt[4] and later by Halberkamm[5] defined several of the parameters which favored the rearrangement reaction. Where the *N*-alkylaniline was either unsubstituted or possessed *p*-methyl, *p*-methoxy, or *p*-chloro substituents, ortho rearrangement predominated. If, however, the para substituents were amino, nitro, or sulfonic acid, virtually no sulfone was formed and only hydrolytic products were observed. One case of a para rearrangement was reported by Witt[3] in which *N*-ethyl-*p*-toluenesulfono-*o*-toluidide resulted from the rearrangement of *N*-ethyl-4-(*p*-toluenesulfonyl)-*o*-toluidine. Halberkamm, however, observed only ortho rearrangement.

Thus, the rearrangement is generally ortho and appears to be favored by electron-donating groups on the aniline moiety and suppressed by electron-withdrawing groups.

Recently, this reaction has been reinvestigated in this laboratory with a view toward expanding its utility as a synthetic tool. Instead of employing sulfonanilides, the amines were selected such that the amino nitrogen was incorporated in a heterocyclic ring. Thus the heterocyclic sulfonamide **1** would give rise to an aromatic sulfone **2a**. Initially, the rearrangement

(1) Supported by a grant (MH 11489) from the National Institutes for Mental Health.

(2) Presented at the 5th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1, 1970.

(3) O. N. Witt and D. Uermenyi, *Ber.*, **46**, 296 (1913).

(4) O. N. Witt and H. Truttwin, *ibid.*, **47**, 2786 (1914).

(5) (a) J. Halberkamm, *ibid.*, **54**, 1665, 1833 (1921); (b) *ibid.*, **55**, 3074 (1922).