

- displacement on ethyl tosylate. (b) J. F. Normant and H. Deshayes, *Bull. Soc. Chim. Fr.*, 1001 (1969). (c) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, 9, 24 (1960); solvents and nature of cation drastically effect apparent nucleophilicities. (d) A. J. Parker, *Chem. Rev.*, 69, 1 (1969); a review on protic-dipolar aprotic solvent effects on rates of bimolecular processes.
- (57) Although media effects are important, the alkaline hydrolysis of methyl acetate vs. ethyl acetate exhibits a $k_{\text{CH}_3}/k_{\text{CH}_3\text{CH}_2}$ of about 2 (ref 47a).
- (58) The $k_{\text{CH}_3}/k_{\text{CH}_3\text{CH}_2}$ for a simple ester with $\text{B}_{\text{AL}2}$ cleavage has been reported as 49 using molten thiocyanate salts (ref 54).
- (59) (a) A. J. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 73; average values for a series of $\text{S}_{\text{N}}2$ displacements of about 30. (b) A $k_{\text{CH}_3}/k_{\text{CH}_3\text{CH}_2}$ of 17 was reported for the alkylative decarboxylation of a *N*-carboxypyrazole with Cl^- (ref 30). (c) A $k_{\text{CH}_3}/k_{\text{CH}_3\text{CH}_2}$ of 72 was reported for the decarboxylation of 2-benzyl-2-carboxycyclopentanone with NaCN-HMPT (ref 12a).
- (60) C. L. Liotta and E. E. Grisdale, *Tetrahedron Lett.*, 4205 (1975), and references cited therein.
- (61) (a) A volume containing reprints of important papers in this area has recently been published: R. G. Pearson, Ed., "Hard and Soft Acids and Bases", Dowden, Hutchinson, and Ross, Inc., Stroudsburg, Pa., 1973. (b) T. L. Ho, *Chem. Rev.*, 75, 1 (1975). (c) J. F. Bunnett and J. D. Reinheimer, *J. Am.*

- Chem. Soc.*, 84, 3284 (1962), and references cited therein. (d) For a paper criticizing symbiotic effects, see: W. S. Trahanovsky and M. P. Doyle, *Chem. Commun.*, 1021 (1967). See also ref 56d.
- (62) L. B. Engemyr and J. Songstad, *Acta Chem. Scand.*, 26, 4179 (1972); symbiotic effects are greater for $\text{S}_{\text{N}}2$ displacements in dipolar aprotic solvents than in protic media.
- (63) (a) In ref 12a for displacements of 2-benzyl-2-carboxycyclopentanone in HMPT with LiCl or LiBr the relative reactivities are reported to be 2.4:1. (b) In ref 30 the alkylative decarboxylation of *N*-carboxypyrazoles were studied in Me_2SO and the $k_{\text{X}}/k_{\text{I}^-}$ rate ratios are 5.1, 3.0, and 1.0 for Cl^- , Br^- , and I^- , respectively. (c) R. Fuchs and K. Mahendran, *J. Org. Chem.*, 36, 730 (1971); $\text{S}_{\text{N}}2$ reactions for unassociated X^- for primary alkyl *p*-toluene sulfonates are listed as $\text{Cl}^-/\text{Br}^-/\text{I}^- = 8:3:1$ (Me_2SO) with the tetra-*n*-butylammonium cation.
- (64) A. P. Krapcho, J. Diamanti, C. Cayen, and R. Bingham, *Org. Synth.*, 5, 198 (1973).
- (65) I. Heilbron, et al., Eds., "Dictionary of Organic Compounds", Oxford University Press, New York, N.Y., Vol. 1-5, 1965; all esters are listed except 2 ($\text{R}^1 = \text{R}^2 = n\text{-butyl}$, $\text{R}^3 = \text{ethyl}$) which is reported in M. Rouchi-Laridjani and M. Vilkas, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 254, 1090 (1962), and ester 2 ($\text{R}^1 = \text{phenyl}$, $\text{R}^2 = \text{H}$, and $\text{R}^3 = \text{ethyl}$) which is reported in H. Laato and R. Isotalo, *Acta Chem. Scand.*, 21, 2119 (1967).

Vinylolithium Reagents from Arenesulfonylhydrazones

A. Richard Chamberlin, Jeffrey E. Stemke, and F. Thomas Bond*

Department of Chemistry, University of California at San Diego, La Jolla, California 92093

Received June 6, 1977

2,4,6-Triisopropylbenzenesulfonylhydrazones of a wide range of ketones serve as a convenient source of vinylolithium reagents. Treatment with 2.0–3.0 equiv of alkylolithium reagent at -78°C in TMEDA–hexane followed by warming to 0°C rapidly generates the vinyl anions in most cases. The reagents so formed can be trapped with a variety of electrophiles. This procedure leads to a convenient synthesis of allylic alcohols, di-, tri-, and tetrasubstituted olefins, acrylic acids, acrylic aldehydes, vinylsilanes, and vinyl bromides.

Organolithium reagents have become increasingly important in synthetic organic chemistry.¹ We report here an extremely facile method for generation of a variety of vinylolithium derivatives and trapping of them with an assortment of electrophilic reagents. Our initial studies, portions of which have been reported in preliminary form,^{2,3} used the reaction of tosylhydrazones with excess *n*-butyllithium in TMEDA–hexane solvent systems for generation of vinylolithium reagents. This procedure represented a modification of the valuable and widely used Shapiro olefin synthesis⁴ by allowing the vinyl anion intermediate⁵ to be trapped by externally added electrophiles.

The procedure is illustrated in Scheme I for the tosylhy-

drazone (1) of 2-octanone. Treatment of 1 with excess base generates almost exclusively the 1-octenyl anion (3). In solvents (hexane or ether) normally used for the olefin synthesis, 3 is protonated either by solvent^{4,6} or, in the case of hexane where the reaction is heterogeneous, by the tosylhydrazone.⁷ Use of TMEDA as solvent overcomes this problem, but requires the use of 3 equiv or more of alkylolithium reagent if workup is to produce the desired product. This is shown in Table I for D_2O workup of the reaction. The yield of olefin is invariably high, but deuterium incorporation on workup clearly requires excess base beyond the 2 equiv needed for stoichiometric dianion formation.

The source of this problem has now been shown to be an *o*-aryl hydrogen of the tosyl group.^{3,8} Specifically, treatment of 1 at -78°C with >3.0 equiv of *n*-butyllithium in TMEDA–hexane, followed by D_2O quench, results in the incorporation of two deuterium atoms, one on nitrogen (washed out on workup) and one on the α -methyl group. If, however, the reaction mixture is warmed to 0°C and then quenched before decomposition to 3 becomes significant, trideuterated tosylhydrazone 4 is obtained. NMR examination of the recovered tosylhydrazone shows that metalation⁹ has occurred in the ortho position. A similar directed ortho metalation by an SO_2NHCH_3 group has been reported.¹⁰ Such metalation is facilitated by the use of the strongly basic *n*-butyllithium/TMEDA solvent system and is necessary if 3 is to be trapped by externally added electrophiles. Otherwise, the vinyl anion 3 metalates the remaining dianion, giving 1-octene. Excess *n*-butyllithium (typically 3.5–4.5 equiv) must therefore be used with tosylhydrazones, and this in turn necessitates the use of excess electrophile and the separation of side products which result from attack of the *n*-butyllithium on the electrophile.

These problems can be overcome and the reaction greatly facilitated by the use of easily prepared¹¹ 2,4,6-triisopropyl-

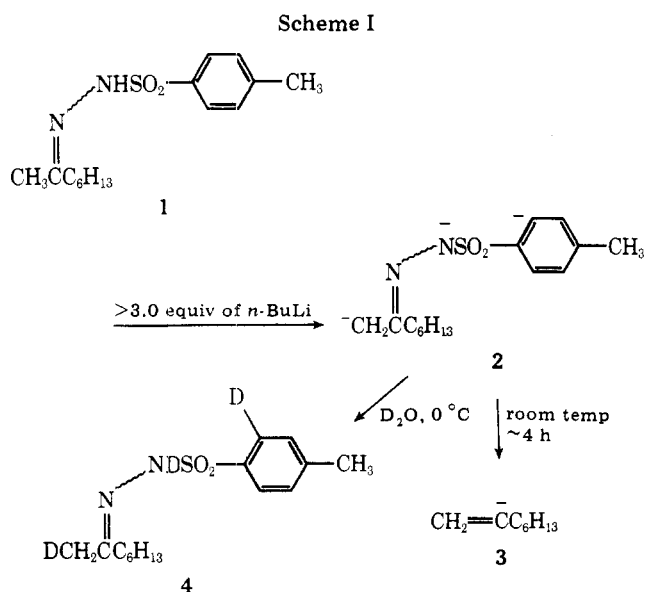
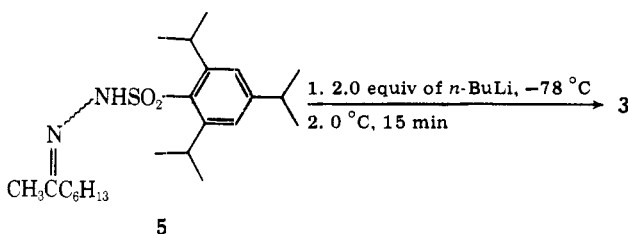


Table I. Deuterium Incorporation As a Function of the Number of Equivalents of *n*-Butyllithium Used to Decompose 1

Equiv of <i>n</i> -BuLi	% yield of 1-octene ^a	% <i>d</i> ₁ ^b
2.0	95-97	<1
2.5	95-97	<1
3.0	95-97	59
4.0	95-97	85
4.5	95-97	95

^a Determined by GLC. ^b Determined by mass spectrometry.

benzenesulfonylhydrazones (trisyldiazones) such as **5**. With these derivatives the desired dianion can be formed at -78°C , except for examples which involve removal of tertiary α -hydrogens, a procedure for which is described later. There is

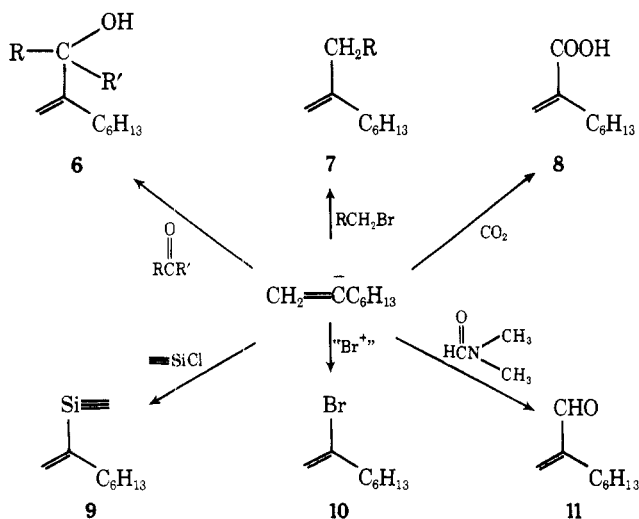


no evidence for benzylic metalation even with excess base, and there is an important added advantage in that dianion decomposition to vinyl anion is accelerated relative to the analogous tosylhydrazone. The latter typically requires 1-8 h at room temperature, whereas the dianion from **5** forms **3** rapidly and conveniently at 0°C . Only 1.0-1.2 equiv of electrophile is then required, and is routinely added as soon as nitrogen evolution ceases. A possible explanation for the enhanced rate of decomposition is discussed in an accompanying note¹² which also demonstrates the utility of trisyldiazones in carbene generation.

The vinyl lithium reagents so generated have been trapped with a variety of electrophiles as shown in Scheme II. The reactions are illustrated for the 1-octenyl anion (**3**), but can be applied to a variety of other reagents, generated as described below.

In our initial studies we reported trapping of **3** (generated from the tosylhydrazone) with D_2O ,^{2,6} with ketones and aldehydes,³ with alkyl halides,^{3,6} and with carbon dioxide.³ In the meantime, we¹³ and others^{14,15} have used chlorotrimethylsilane to generate synthetically useful vinylsilanes such as **9**, and in another application the reaction of organolithium reagents with *N,N*-dimethylformamide¹⁶ has been used on

Scheme II

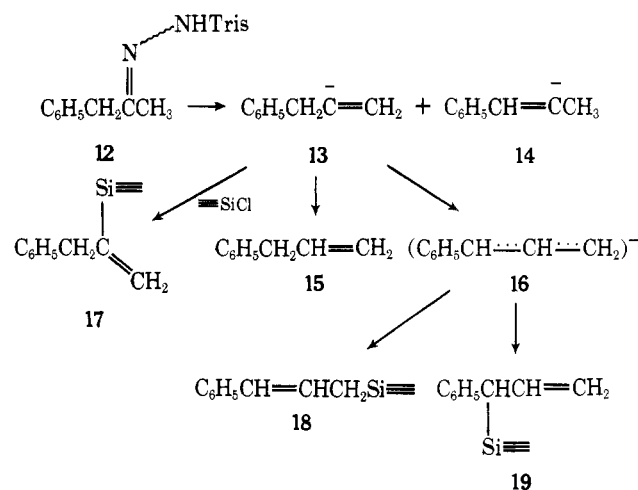


tosylhydrazone derived reagents to give α,β -unsaturated aldehydes such as **11**.¹⁷ All of these reactions are much more conveniently run using trisyldiazone precursors and yields are often higher. In virtually every case examined, isolated yields of 50-70% have been obtained in small-scale reactions with no more than standard bench top precautions for protection from moisture. Allylic alcohols **6**¹⁸ and alkylated olefins such as **7**¹⁹ are particularly useful products of this sequence.

All of the reactions illustrated in Scheme II can be run, of course, on vinyl lithium reagents generated in other ways. The standard route¹ for the preparation of reagents such as **3**²⁰ involves metal-halogen exchange²¹ on a suitable vinyl halide such as **10**.²² The problem with this method, as noted before,²³ is that regiospecific preparation of vinyl halides is often cumbersome. We believe that the preferred route to **10**^{22a} and similar vinyl bromides is actually via trisyldiazone derived vinyl anion **3**, which gives **10** with either allyl bromide or 1,2-dibromoethane.²⁴




The optimum conditions for generation of the vinyl lithium reagent depend on the nature of the α -hydrogen removed and follow the expected order of acidity primary > secondary > tertiary. Conditions for each type are discussed below. Only representative electrophiles are given, as with few exceptions we have been able to use all of the electrophiles shown in Scheme II with all ketone precursors. Alkyl halides appear to be the least reactive, as discussed in the next section.


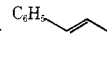
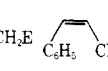
Trisyldiazones such as **5**, in which an α -methyl proton is removed, require 2.0 equiv of *n*-BuLi at -78°C for 20 min, followed by warming to 0°C to generate **3**. Regioselectivity toward C-1 is as high as that observed with tosylhydrazones.⁴ The derivative **12** of benzyl methyl ketone is an interesting



system in which the trisyldiazone offers special advantages. Shapiro et al.⁶ have proposed that the less substituted non-conjugated vinyl anion **13** is formed initially in the tosylhydrazone reaction. Indeed, allylbenzene (**15**) is the sole product of the olefin reaction (methyl lithium-ether), and its dianion precursor could be quenched at the methyl position with a variety of electrophiles. When **13** was generated from the tosylhydrazone using *n*-butyllithium in hexane/TMEDA, however, only alkylation products derived from the rearranged 1-phenylallyl anion (**16**) could be obtained. We have found that decomposition of the dianion of trisyldiazone **12** is much faster and that unrearranged anions **13** and **14** (ratio ca. 9:1) can be trapped by rapid quench using reactive electrophiles. For example, when the anion **13** is quenched with trimethylsilyl chloride after only 5 min at 0°C , **17** is the major product, whereas after 30 min allylic isomers **18** and **19** predominate as shown in Table II. Alkylation, unfortunately, is too slow at 0°C to trap **13**, and with this electrophile the re-

Table II. Products Derived from Trisylhydrazone 12

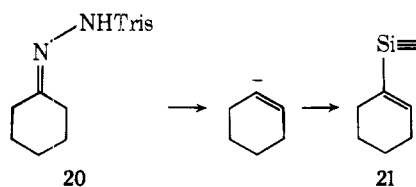
A. Vinyl Anion Quench after 5 min at 0 °C				
% yield ^{a, b}				
Electrophile	E			
D ₂ O	D-	74	5	3
(CH ₃) ₃ SiCl	(CH ₃) ₃ Si-	51	5	2
C ₆ H ₅ CHO	C ₆ H ₅ CHOH-	60	<5	<5

B. Vinyl Anion Quench after 30 min at 0 °C				
% yield ^{a, c}				
Electrophile	E			
D ₂ O	D-	20	52	8
(CH ₃) ₃ SiCl	(CH ₃) ₃ Si-	10	54	5
CH ₃ (CH ₂) ₂ CH ₂ Br	<i>n</i> -Bu-	50	8	2

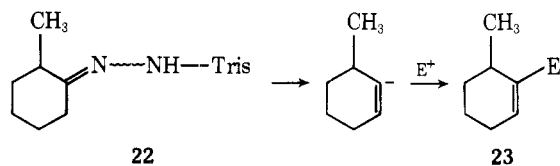
^a Yields determined by calibrated GLC. Products characterized by IR and NMR. ^b Products arising from phenylallyl anion 16 were not detected by GC or NMR. ^c Products arising from vinyl anion 13 were not detected by GC or NMR.

sults of Shapiro et al. are confirmed with the trisylhydrazone.

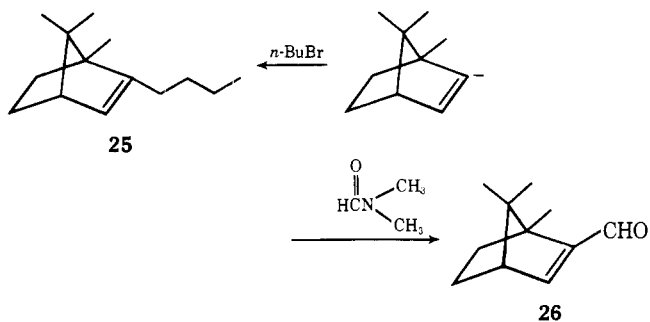
In cases where dianion formation requires the removal of a secondary α -hydrogen, we have used either 2.0 equiv of the stronger base²⁵ *sec*-butyllithium, at -78 °C for 2 h, or excess (3.0 equiv) *n*-butyllithium at the same temperature for 30 min. Removal of the secondary α -hydrogen under these conditions is accelerated by this excess base which, however, is not consumed. Thus, cyclohexanone trisylhydrazone (20) can be converted in 83% yield to vinylsilane 21.^{14,15,26}



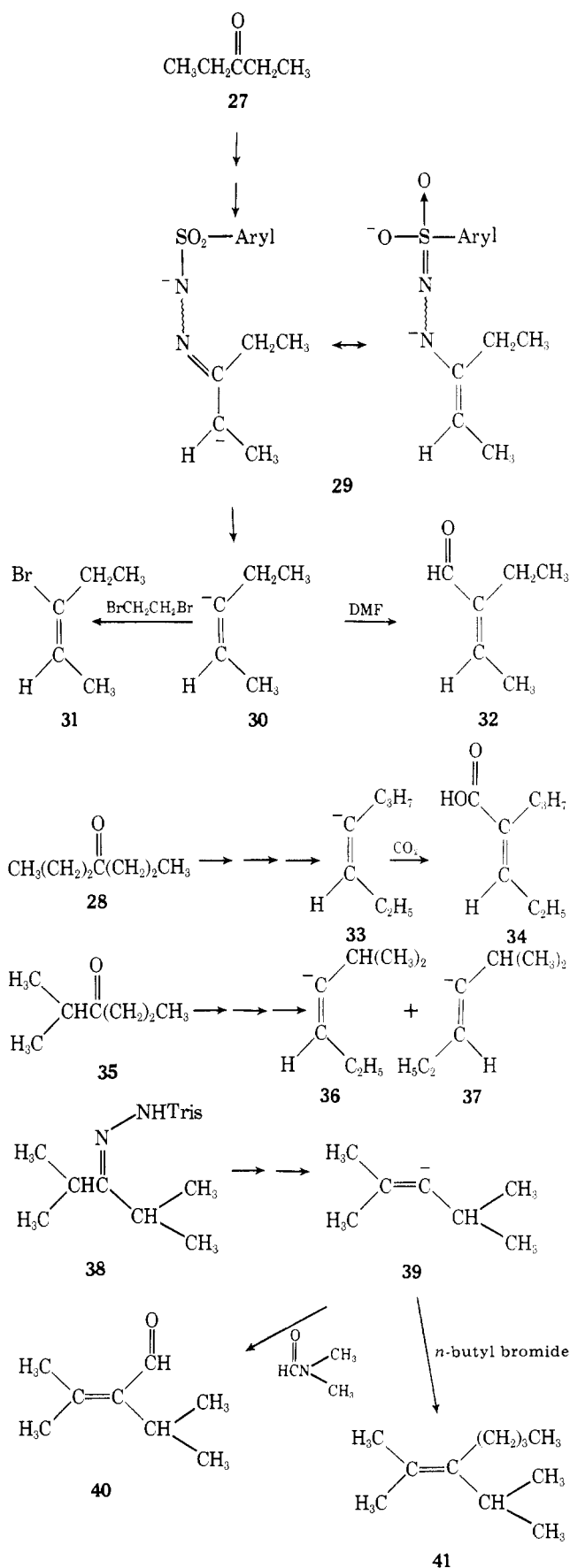
More interesting examples involve unsymmetrical ketones, more hindered ketones, or ketones which can give rise to geometrically isomeric vinylolithium reagents. As an example of the first type, the derivative 22 of 2-methylcyclohexanone behaves similarly to the corresponding tosylhydrazone³ and gives good yields of 23 containing only trace amounts of the



more highly substituted product. Camphor trisylhydrazone (24) (easily prepared; see Experimental Section) is best con-



Scheme III



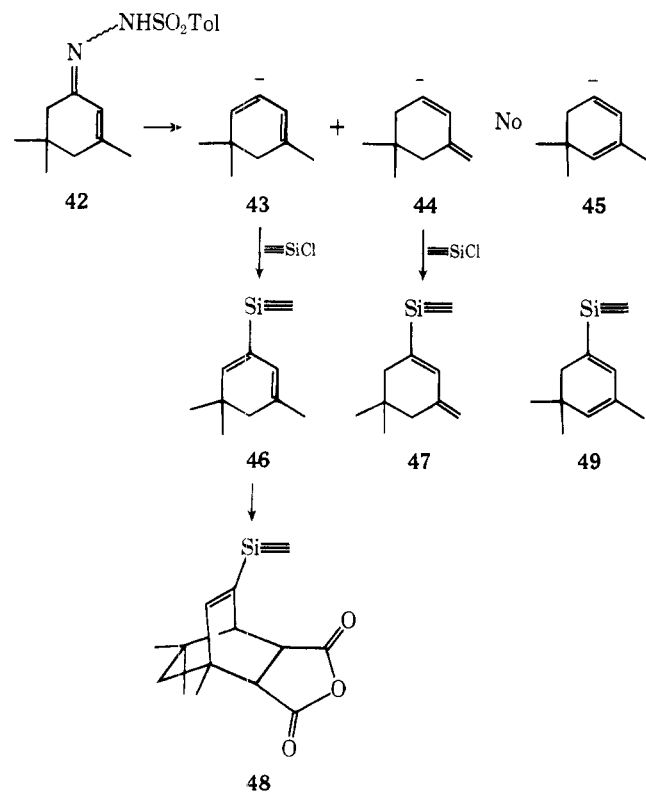
verted into its dianion by treatment with 2.0 equiv of *sec*-butyllithium at approximately -50 °C for 2 h. The solution is then warmed to 0 °C until nitrogen evolution ceases (~20 min), and the electrophile is added. In this way, 25 and 26¹⁷

were obtained in isolated yields of about 60%. The tosylhydrazone route to **26** is far less satisfactory.¹⁷

Symmetrical ketones 3-pentanone (**27**) and 4-heptanone (**28**) are converted exclusively into their *cis*-vinyl lithium reagents as shown in Scheme III. The dianion **29** from **27** controls the stereochemistry of the sequence and generates the configurationally stable **30**. This vinyl lithium reagent was trapped with 1,2-dibromoethane to give **31** and with dimethylformamide to give **32**. Vinyl bromide **31** has spectroscopic properties consistent with the assigned stereochemistry.^{27,28} Aldehyde **32** was assigned the *E* geometry based on the chemical shift of the aldehyde proton at 9.37 ppm. This resonance is characteristically found at about 9.3 ppm for *E*-trisubstituted α,β -unsaturated aldehydes of this type and at about 10 ppm for the corresponding *Z* isomers.^{29,30} Likewise, 4-heptanone (**28**) was converted into **33** and carboxylated to the known³⁰ acid **34**. With 2-methyl-3-hexanone (**35**) the stereoselectivity is lost, however, as a mixture of products derived from **36** and **37** was obtained.

Formation of dianion by removal of a tertiary α -hydrogen is fairly difficult,⁶ as substitution³¹ competes. We have investigated one trisylhydrazone of this type (**38**), and have found that treatment with 3.0 equiv of *sec*-butyllithium at room temperature for 90 min generates **39** in reasonable yield, as shown by trapping with dimethylformamide to give **40** or with *n*-butyl bromide to yield **41**. Some metalation of TMEDA³² is observed under these conditions, but separation of the basic side products so obtained is not difficult. Substitution products were not detected.

The use of tosylhydrazones of α,β -unsaturated ketones in the Shapiro reaction has become a valuable route to 1,3-dienes.³³ In our preliminary report³ we showed that isophorone tosylhydrazone (**42**) could be converted into **43** and



trapped with CO_2 to give derived acid. We have since found, using chlorotrimethylsilane as the electrophile, that both **43** and **44** are formed in approximately a 9:1 ratio. The major product **46** was purified and shown to have the assigned structure rather than **49** by Diels-Alder reaction with maleic anhydride to give a single adduct **48**, the NMR of which clearly

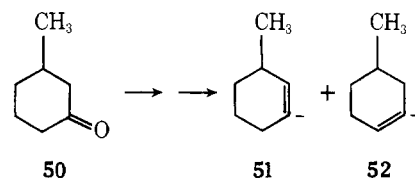
Table III. Relative Olefin Composition from Decomposition of 3-Methylcyclohexanone Tosylhydrazone with Various Bases

Conditions	% product ratio ^a	
<i>n</i> -BuLi/hexane	29	71
<i>tert</i> -BuLi/pentane	33	65
CH_3Li /ether ^b	32	68
<i>n</i> -BuLi/TMEDA-hexane	50	50
<i>t</i> -BuLi/TMEDA-hexane	50	50
/hexane	52	48

^a Product composition was determined by integration of the vinyl and methyl signals in the NMR spectrum of the product. Figures given are the average of three runs and are accurate within $\pm 5\%$, as determined using authentic mixtures of known composition. ^b A mixture of 1,3-dimethylcyclohexanes was a major impurity in this reaction.

distinguishes it from the product derivable from **49**. The trisylhydrazone of isophorone, however, gives a different ratio, approximately 1:1, of **43** to **44**. This is the only example we have encountered of a difference in product distribution between a tosyl and trisyl decomposition. It is clear from the work of Dauben, Yang, et al.³⁴ that the syn-anti stereochemistry of the arenesulfonylhydrazone is a factor in determining the directionality of vinyl anion formation from α,β -unsaturated derivatives. This appears to be the case here, although it is not clear why this should be so with a rigid transoid derivative compared with the cisoidal examples reported previously.

The only other type of ketone which does not lend itself readily to the synthetic methods discussed in this paper is an α,α' -dimethylene system such as derivatives of 3-methylcyclohexanone (**50**). Products are obtained from both isomeric



vinyl anions **51** and **52**. We have examined the effect of base on the olefin forming reaction, as shown in Table III. Tosylhydrazones were used in this study and the product ratio was determined by NMR spectroscopy as the GLC separation of 3- and 4-methylcyclohexene proved difficult.³⁵ The same starting material, approximately a 1:1 mixture of syn and anti isomers which could not be separated, was used in each reaction. It is clear from the data in Table III that bulky aggregated¹ alkyllithium bases give a slight preference for attack at the less hindered methylene position. With RLi/TMEDA systems this preference disappears. There is thus a small base effect in the directionality of this olefin-forming reaction.

In conclusion, trisylhydrazones offer distinct advantages over tosylhydrazones for vinyl anion generation in TMEDA. With the exception of α,β -unsaturated derivatives discussed above, there appears to be no variation in product composition. Tosylhydrazones, however, require an excess of alkyllithium reagent, typically 3.5–4.5 equiv, and a corresponding excess of electrophile. In addition, side products resulting from attack of the alkyllithium reagent on the electrophile are encountered, and these can be difficult to separate. Often, me-

talation of TMEDA³² occurs, giving further side products upon reaction with the electrophile. The faster decomposition of the dianions from trisylhydrazones makes generation of the vinylolithium reagents more rapid and convenient. With tosylhydrazones, the dianion decomposition typically requires 1–8 h at room temperature and is difficult to monitor. For the Shapiro olefin formation trisylhydrazones offer no real advantage, since protonation during the reaction is desired and *n*-butane is easily removed. For trapping with external electrophiles, however, trisylhydrazones are clearly the reagents of choice.³⁶ The derived vinylolithium reagents have been trapped with a wide variety of electrophiles and can be converted into vinyl cuprates as well.³⁷ We are studying further use of these reactions, their application in natural products synthesis, and the utility of the derived alkenes.

Experimental Section³⁸

Preparation of Trisylhydrazones. Trisylhydrazones were prepared by one of two methods. Unhindered ketones are illustrated by method A for cyclohexanone. More hindered ketones were treated as described for camphor in method B, which prevented decomposition¹¹ of the trisylhydrazide. Detailed spectral data are reported only for these two derivatives; all others had properties consistent with the assigned structure, allowing for the possibility of syn-anti isomerism.

A. Cyclohexanone 2,4,6-Triisopropylbenzenesulfonylhydrazone (20). To a stirred suspension of 29.8 g (0.10 mol) of finely ground³⁹ 2,4,6-triisopropylbenzenesulfonylhydrazide¹¹ in 100 mL of methanol was added 9.82 g (0.10 mol) of freshly distilled cyclohexanone. The addition of 1 mL of concentrated hydrochloric acid caused the mixture to clear rapidly, after which a fine granular product began to crystallize. The reaction mixture was chilled overnight and filtered. The product was washed with cold methanol and dried at room temperature at 0.5 Torr to yield 30.8 g (81%) of white crystals, mp 123–124 °C dec.

The IR spectrum shows 3240, 2945, 2880, 1640, 1168, 1155, 1010, and 650 cm⁻¹. The NMR spectrum shows δ 1.25 (d, $J = 7$ Hz, 18 H), 1.57 (br s, 6 H), 2.30 (br s, 4 H), 2.90 (septet, $J = 7$ Hz, 1 H), 4.26 (septet, $J = 7$ Hz, 2 H), 7.18 (2 overlapping s; 3 H (aryl and NH)).

Anal. Calcd for C₂₁H₃₄N₂O₂S: C, 66.64; H, 9.05. Found: C, 66.85; H, 8.89.

B. Camphor 2,4,6-Triisopropylbenzenesulfonylhydrazone (24). To a solution of 33.0 g (0.11 mol) of 2,4,6-triisopropylbenzenesulfonylhydrazide in 100 mL of acetonitrile was added 15.2 g (0.10 mol) of camphor and 10 mL⁴⁰ of concentrated hydrochloric acid. The solution was stirred overnight at room temperature and cooled at 0 °C for 4 h, and the resulting white solid was collected. The crude product was taken up in a minimum amount of chloroform, filtered, concentrated in vacuo, and dried at 0.5 Torr to give 30.3 g (70%) of a white solid, mp 197–199 °C dec.

The NMR spectrum shows δ 0.60 (s, 3 H), 0.80 (s, 6 H), 1.25 (2 overlapping d, $J = 7$ Hz, 18 H), 1.4–2.4 (m, 7 H), 2.88 (septet, $J = 7$ Hz, 1 H), 4.23 (septet, $J = 7$ Hz, 2 H), 7.15 (s, 2 H), 7.45 (br s, 1 H).

Anal. Calcd for C₂₅H₄₀N₂O₂S: C, 69.40; H, 9.32. Found: C, 69.28; H, 9.30.

Other trisylhydrazones were prepared as indicated.

2-Octanone 2,4,6-triisopropylbenzenesulfonylhydrazone (5): method A, mp 87–88 °C dec, yield 92%.

1-Phenyl-2-propanone 2,4,6-triisopropylbenzenesulfonylhydrazone (12): method A, mp 122–124 °C dec, yield 98%.

2-Methylcyclohexanone 2,4,6-triisopropylbenzenesulfonylhydrazone (22): method A, mp 107–109 °C dec, yield 94%.

3-Pentanone 2,4,6-triisopropylbenzenesulfonylhydrazone: method A, mp 115–116 °C dec, yield 79%.

4-Heptanone 2,4,6-triisopropylbenzenesulfonylhydrazone: method A, mp 92–95 °C dec, yield 64%.

2,4-Dimethyl-3-pentanone 2,4,6-triisopropylbenzenesulfonylhydrazone (38): method B, mp 116–122 °C dec, yield 73%.

2-Methyl-3-hexanone 2,4,6-triisopropylbenzenesulfonylhydrazone: method A, mp 103–105 °C dec, yield 72%.

Deuterium Incorporation Studies. A. –78 °C Quench. To a stirred solution of 0.296 g (1.0 mmol) of **1** in 5 mL of TMEDA at approximately –55 °C was added 2.25 mL (4.5 mmol) of 2.0 M *n*-butyllithium in hexane. After stirring for 10 min while cooling with a –78 °C bath, D₂O (1 mL) was added. The reaction mixture was poured into 1 N HCl and the tosylhydrazone recovered quantitatively by ether extraction. The NMR spectrum of recovered tosylhydrazone⁴¹

was identical with that of starting material except for the C-1 methyl singlets at δ 1.74 and 1.88 (from anti and syn isomers), which are broadened and reduced to an area equivalent to 2.0 H.

B. 0 °C Quench. Experiment A was repeated under the above conditions except that the solution was warmed to 0 °C and stirred for 10 min before D₂O quench. Tosylhydrazone was recovered as before. The upfield portion of the NMR spectrum⁴¹ of this material is identical with that described above. In the low-field region the AA'BB' pattern in the aromatic region was changed dramatically. The "doublet" at δ 7.84 is reduced to an area of 1.09 H, and a new singlet bisects the reduced doublet at δ 7.29 (total area 2.0 H).

2-Lithio-1-octene (3). General Procedure. The 2-octanone trisylhydrazone **5** was placed in a flame-dried flask flushed with nitrogen. A solution (10 mL/g of trisylhydrazone) of 10% TMEDA in hexane was added, stirring was begun, and the flask was cooled in a dry ice-acetone bath to –78 °C. *n*-Butyllithium in hexane (2 M, 2.0–2.2 equiv) was then added dropwise, either from a dropping funnel or through a septum via syringe, causing the solution to turn dark orange-red. After stirring at –78 °C for 15 min, the solution was allowed to warm to ~0 °C, during which time it turned light yellow. The reaction flask was then cooled in an ice bath until nitrogen evolution ceased (~10 min), followed by addition of electrophile as described below.

2-*n*-Hexyl-1-phenyl-2-propenol (6, R = Ph, R' = H). A solution of **3** was prepared as described above from 10.0 g (0.0245 mol) of **5** and 25.7 mL (0.0514 mol) of 2.0 M *n*-butyllithium. The solution was treated with stirring at 0 °C with 3.12 g (0.0294 mol) of freshly distilled benzaldehyde. The reaction was stirred for 1 h at room temperature and worked up in the standard manner. GLC analysis (column A at 200 °C) of the crude product showed a single peak in 84% yield, using purified product as standard. Short-path distillation afforded 3.31 g (62%) of **6** as a colorless liquid, bp 135–138 °C (1.0 Torr).

The NMR spectrum shows δ 0.83 (t, $J = 6$ Hz, 3 H), 1.0–1.5 (m, 8 H), 1.85 (m, 2 H), 2.57 (s, 1 H), 4.90 (s, 1 H), 5.03 (s, 1 H), 5.18 (s, 1 H), and 7.28 (s, 5 H). The mass spectrum shows peaks at *m/e* 133 (base) and 218 (parent).

Anal. Calcd for C₁₅H₂₂O: C, 82.52; H, 10.16. Found: C, 82.57; H, 10.18.

2-*n*-Butyl-1-octene (7, R = *n*-Pr). A solution of 2-lithio-1-octene was prepared as described for **6** above, but treated with 4.03 g (0.0294 mol) of *n*-butyl bromide. After stirring at room temperature for 4 h the reaction was worked up in the usual manner (GLC yield 72%, column A at 135 °C). Distillation through a 4-in. Vigreux column afforded 2.39 g (58%) of **7** as a clear liquid, bp 87–89 °C (28 Torr) [lit.⁴² bp 83–84 °C (9 Torr)].

The mass spectrum shows *m/e* 168 (parent) and 56 (base). The NMR spectrum has δ 0.88 (t, $J = 6$ Hz, 6 H), 1.0–1.7 (m, 12 H), 2.00 (t, $J = 6$ Hz, 4 H), and 4.70 (s, 2 H).

2-Trimethylsilyl-1-octene (9). A solution of 2-lithio-1-octene was prepared as described above and treated at 0 °C with 3.18 g (0.0294 mol) of chlorotrimethylsilane. After stirring for 1 h at room temperature the reaction mixture was worked up in the standard method. GLC analysis showed 1-octene (5%) and **9** (71%). The crude material was subjected to short-path distillation, affording 2.50 g (55%) of clear liquid, bp 78–80 °C (14 Torr).

The NMR spectrum shows δ 0.00 (s, 9 H), 0.80 (t, $J = 6$ Hz, 3 H), 1.0–1.7 (m, 8 H), 2.05 (m, 2 H), 5.25 (m, 1 H), and 5.45 (m, 1 H). The mass spectrum shows *m/e* 184 (parent) and 73 (base). Careful GLC-mass spectral analysis shows ~1% of an isomeric product.

Anal. Calcd for C₁₁H₂₄Si: C, 71.65; H, 13.12. Found: C, 71.62; H, 12.97.

2-Bromo-1-octene (10),^{22a} A solution of 2-lithio-1-octene was prepared as described above from 4.1 g of **5** (0.010 mol) and 10.0 mL (0.020 mol) of 2.0 M *n*-butyllithium in hexane. The solution was treated at 0 °C with 2.00 g (0.0106 mol) of 1,2-dibromoethane and stirred until gas evolution ceased. Standard workup followed by short-path distillation afforded 0.83 g (43%) of **10**, bp 70–72 °C (18 Torr).

The NMR spectrum shows δ 0.88 (t, $J = 6$ Hz, 3 H), 1.29 (m, 8 H), 2.41 (br t, $J = 7$ Hz, 2 H), 5.37 (d, $J = 1.3$ Hz, 1 H), and 5.52 (q, $J = 1.3$ Hz, 1 H).

2-Lithio-3-phenylpropene (13). A solution of **13** was prepared as described in the general procedure for **3** by treating 0.415 g (1.0 mmol) of **12** with 1.1 mL (2.2 mmol) of 2.0 M *n*-butyllithium at –78 °C for 15 min. The –78 °C bath was replaced with a 0 °C bath and after 5 min of stirring the solution was treated with electrophiles as described below.

A. D₂O Quench. D₂O quench of the reaction mixture followed by standard workup gave, as shown in Table II, a 74% yield (GLC, column A at 95 °C) of 3-phenyl-1-propene, a 5% yield of (*E*)-1-phenylpropene, and a 3% yield of (*Z*)-1-phenylpropene. The major product, isolated

by preparative GLC, shows virtually quantitative deuterium incorporation at C-2. The NMR spectrum shows δ 3.38 (s, 2.0 H), 5.07 (s, 2.0 H), and 7.22 (s, 5.0 H).

B. Chlorotrimethylsilane Quench. Addition of 0.130 g (1.2 mmol) of chlorotrimethylsilane to a solution prepared as above and standard workup gave a mixture of products as shown in Table II. Preparative GLC collection of the major peak afforded 2-trimethylsilyl-3-phenylpropene (17). The NMR spectrum shows δ 0.00 (s, 9 H), 3.48 (s, 2 H), 5.45 (m, 2 H), and 7.2 (m, 5 H).

C. Benzaldehyde Quench. Similar quench of a solution prepared as above with 0.130 g (1.2 mmol) of benzaldehyde afforded, after standard workup, the mixture shown in Table II. The major product, 2-benzyl-1-phenyl-2-propen-1-ol, was isolated by column chromatography on silica gel. Its NMR spectrum shows δ 3.30 (q, 2 H), 4.90 (s, 1 H), 5.15 (s, 1 H (D₂O exchangeable)), 5.35 (s, 1 H), and 7.3 (m, 5 H).

D. Delayed Quenches. When the procedure described above was carried out exactly as above, but the reaction mixture was allowed to stir at 0 °C for 30 to 60 min, it became heterogeneous and intensely red, and products derived from 16 were obtained as shown in Table II. Chlorotrimethylsilane quench (0.130 g, 1.2 mmol) is typical and gave as the major product (54%) (*E*)-1-phenyl-3-trimethylsilylpropene. The NMR spectrum of the GLC collected product (column B at 180 °C) shows δ 0.00 (s, 9 H), 1.58 (dd, J = 5, 1.5 Hz, 2 H), 6.17 (m, 2 H), and 7.2 (m, 5 H).

1-Trimethylsilylcyclohexene (21). To a stirred solution of 0.378 g (1.0 mmol) of 20 in 10 mL of 50% TMEDA-hexane at -78 °C was added 1.5 mL (3.0 mmol) of 2.0 M *n*-butyllithium in hexane. The solution was allowed to warm to 0 °C and then treated with 0.216 g (2.0 mmol) of chlorotrimethylsilane. After stirring for 1 h the solution was worked up in the normal manner to give 21 (GLC yield 83%, column A at 120 °C). The GLC collected product has properties as reported.^{14,15}

If only 2.0 equiv of *n*-butyllithium was used above the GC yield dropped to 47% and butyltrimethylsilane was detected by GLC. This indicates incomplete dianion formation with stoichiometric quantities of base. With excess base trimethylsilylated TMEDA³² was formed and detected in the basic products.

2-Lithio-3-methylcyclohexene. To a stirred solution of 22 in 50% TMEDA-hexane (10 mL/g) at -78 °C was slowly added 2.0 equiv of *sec*-butyllithium in cyclohexane or 3.0 equiv of *n*-butyllithium in hexane. After stirring at -78 °C for 2 h, the solution was allowed to warm to 0 °C, held there until gas evolution ceased (less than 5 min), and quenched.

A. 2-Deuterio-3-methylcyclohexene (23, E = D). To a solution prepared as above from 0.393 g (1.0 mmol) of 22 and 1.5 mL (3.0 mmol) of *n*-butyllithium was added 1.0 mL of D₂O. Standard workup gave (GLC, column A at 55 °C) 93% 3-methylcyclohexene and 1-2% 1-methylcyclohexene. Integration of the NMR spectrum of the GLC collected major product showed only 1.12 olefinic protons, indicating 88% deuterium incorporation.

B. 2-*n*-Butyl-3-methylcyclohexene (23, E = *n*-Bu). A solution of 2-lithio-3-methylcyclohexene was prepared as above from 10.0 g (0.0255 mol) of 22 and 38.2 mL (0.0764 mol) of 2.0 M *n*-butyllithium. Quenching at 0 °C with 7.0 g (0.0511 mol) of *n*-butyl bromide and standard workup followed by short-path distillation gave 2.3 g (59%) of a clear liquid, bp 76-79 °C (18 Torr).

The NMR spectrum shows δ 1.0 (t, 3 H), 1.1 (d, 3 H), 1.2-2.5 (m, 13 H), and 5.5 (br s, 1 H). GC-mass spectral analysis shows the parent peak at *m/e* 152 and the base peak at *m/e* 95.

Anal. Calcd for C₁₁H₂₀: C, 86.76; H, 13.24. Found: C, 86.60; H, 13.38.

C. 3-Methylcyclohexene-2-carboxaldehyde (23, E = CH=O). A solution of vinyl anion was prepared by treating 10.0 g (0.255 mol) of 22 with 48.7 mL (0.0536 mol) of 1.1 M *sec*-butyllithium in hexane. After the solution had warmed to 0 °C and nitrogen evolution had ceased, 2.05 g (0.0230 mol) of *N,N*-dimethylformamide was added. After stirring for 1 h at room temperature the reaction was worked up in the standard manner. Short-path distillation afforded 1.99 g (63%) of colorless liquid, bp 88-90 °C (26 Torr).

The IR spectrum shows characteristic absorption at 2840, 2735, 1698, and 1650 cm⁻¹. The NMR spectrum has δ 1.07 (d, J = 7 Hz, 3 H), 1.6 (m, 4 H), 2.3 (m, 2 H), 2.67 (m, 1 H), 6.74 (t of d, J = 4, 0.7 Hz, 1 H), and 9.37 (s, 1 H).

2-*n*-Butylbornene (25). A solution of 2-lithiobornene was prepared by treatment of 10.0 g (0.023 mol) of 24 in 100 mL of 50% TMEDA-hexane with 46.2 mL (0.051 mol) of 1.1 M *sec*-butyllithium at ca. -55 °C for 2 h followed by stirring for 30 min at 0 °C. At this time, 3.80 g (0.0277 mol) of *n*-butyl bromide was added and the reaction was stirred overnight at room temperature. Standard workup

(GLC yield 70%, column A at 145 °C) followed by short-path distillation afforded 25, 2.26 g (51%), as a clear liquid, bp 57-59 °C (0.5 Torr).⁴³

The mass spectrum shows the parent peak at *m/e* 192 and the base peak at *m/e* 121. The NMR spectrum shows three singlets at δ 0.73, 0.76, and 0.43 superimposed on a broad multiplet (total 16 H), δ 1.4 (m, 4 H), 1.9 (m, 2 H), 2.19 (t, 1 H), and 5.52 (m, 1 H).

Anal. Calcd for C₁₄H₂₄: C, 87.42; H, 12.58. Found: C, 87.16; H, 12.38.

Bornene-2-carboxaldehyde (26). A solution of 2-lithiobornene was prepared exactly as above and quenched with 2.0 g (0.0277 mol) of *N,N*-dimethylformamide. After stirring for 30 min at room temperature the reaction was worked up by the standard method. GLC analysis (column A at 150 °C) showed a single peak in 79% yield. Vacuum sublimation gave 2.3 g (61%) of 26.¹⁷

(Z)-3-Lithio-2-pentene (30). To a solution of 0.366 g (1.0 mmol) of 3-pentanone 2,4,6-triisopropylbenzenesulfonylhydrazone in 10 mL of 50% TMEDA-hexane at -78 °C was added 1.5 mL (3.0 mmol) of 2.0 M *n*-butyllithium, and the reaction was stirred for 30 min and warmed to 0 °C.

A. Addition of 0.146 g (2.0 mmol) of *N,N*-dimethylformamide and stirring at room temperature for 1 h was followed by standard workup to give a crude product (70% GC yield) which was shown to consist of 98% (*E*)-2-ethyl-2-butenal (32)⁴⁴ (aldehyde C-H proton at δ 9.37) and 2% of the *Z* isomer (aldehyde C-H proton at δ 9.90).

B. To a similarly prepared solution was added 0.376 g (2.0 mmol) of 1,2-dibromoethane. Standard workup after stirring at room temperature for 10 min gave a crude product (GLC yield 69%, column A at 55 °C). Preparative GLC (column B at 50 °C) afforded (*E*)-3-bromo-2-pentene (31).

The NMR spectrum shows δ 1.10 (t, 3 H), 1.65 (d, 3 H), 2.44 (q, 2 H), and 5.81 (q of t, 1 H).

(E)-2-Propyl-2-pentenoic Acid (34). A solution of (*Z*)-4-lithio-3-heptene (33) was prepared in the same manner as 30 from 1.00 g (2.54 mmol) of the trisylhydrazone and 5.0 mL (5.5 mmol) of 1.1 M *sec*-butyllithium in cyclohexane at -78 °C, followed by warming to 0 °C for 20 min. Carbon dioxide was sublimed into the stirred solution via cannula from a flask containing dry ice until gas absorption ceased. The mixture was poured into 1 N HCl, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated salt solution, dried, and concentrated in vacuo to give 1.0 g of a colorless oil which partially crystallized. The NMR spectrum of this product shows it to be a mixture of 2,4,6-triisopropylbenzenesulfonic acid and 34: δ 0.90 (t, J = 7 Hz, 3 H), 1.05 (t, J = 7 Hz, 3 H), 1.40 (m, 2 H), 2.26 (m, J = 7 Hz, 4 H), 6.87 (t, J = 7 Hz, 1 H), and 10.08 (s, 1 H), in addition to signals from the sulfonic acid.¹¹ Attempted separation by distillation led to partial sulfonic acid isomerization of 34 to its *Z* isomer and the formation of 1,3,5-triisopropylbenzene.

3-Lithio-2,4-dimethyl-2-pentene (39). To a stirred solution of 10.0 g (0.0254 mol) of 38 in 100 mL of 50% TMEDA-hexane at -78 °C was added 70 mL (0.077 mol) of 1.1 M *sec*-butyllithium in cyclohexane. The reaction mixture was immersed in a room temperature bath and stirring was continued for 1.5 h.

3-Methyl-2-isopropyl-2-butenal (40). A solution of 39 prepared as above was treated with 3.70 g (0.051 mol) of *N,N*-dimethylformamide. After stirring for 1 h the reaction mixture was worked up in the standard manner to give 40 in a GC yield of 74%. Short-path distillation afforded 1.71 g (53%) of a clear liquid, bp 70-73 °C (25 Torr).

The IR spectrum shows 2810, 2780, 1680, and 1625 cm⁻¹ characteristic bands. The NMR spectrum shows δ 1.15 (d, J = 7 Hz, 6 H), 1.97 (s, 3 H), 2.15 (s, 3 H), 2.9 (septet of d, J = 7, 1.5 Hz, 1 H), and 10.11 (d, J = 1.5 Hz, 1 H).

Anal. Calcd for C₈H₁₄O: C, 76.14; H, 11.18. Found: C, 76.25; H, 11.27.

2-Methyl-3-isopropyl-2-heptene (41). A solution of 39 was prepared as above and treated with 10.44 g (0.0762 mol) of *n*-butyl bromide overnight at room temperature. The reaction was worked up in the standard method to give product in a GC yield of 42% (column A, 120 °C). Short-path distillation afforded 1.2 g (31%) of 41 as a clear liquid, bp 79-80 °C (24 Torr).

The NMR spectrum shows δ 0.91 (d, J = 8 Hz, 9 H), 1.3 (m, 4 H), 1.91 (t, J = 7 Hz, 2 H), 2.62 (s, 6 H), and 2.83 (septet, J = 8 Hz, 1 H). A singlet at δ 6.90 indicates the presence of 3% of triisopropylbenzene.

Tosylhydrazone Decompositions. General Procedure. The tosylhydrazone (or benzenesulfonylhydrazone), typically 0.03 mol, was dissolved in TMEDA (10 mL/g) and the suspension stirred at -78 °C (TMEDA freezes at -55 °C, but melts upon addition of the alk-

yllithium solution) for 10 min, followed by addition of 3.5–4.5 equiv of alkylolithium in hexane over a 10–15-min period. The resulting deep red solution was warmed to room temperature. With tosylhydrazones the solution becomes yellow on reaching room temperature and gradually turns dark brown as vinyl anion is formed. With benzenesulfonylhydrazones a precipitate forms and gradually dissolves on stirring at room temperature. After stirring for 2–8 h at room temperature or 1–4 h at 35 °C, the solution was treated at 0 °C with 3–4.5 equiv of electrophile and the reaction worked up in the standard manner.

1,5,5-Trimethyl-3-trimethylsilylcyclohexa-1,3-diene (46). A solution of vinyl anion 43 was prepared by the above procedure from 10.0 g (0.033 mol) of 42 and 53 mL of 2.4 M *n*-butyllithium in 100 mL of TMEDA. After stirring for 4 h at room temperature the mixture was cooled to 0 °C and 11.0 g (0.10 mol) of chlorotrimethylsilane was added dropwise over a 10-min period. The solution was stirred at room temperature for 90 min and worked up in the standard fashion to give a crude product shown by GLC to consist of 46 and 47 in a 9:1 ratio. Short-path distillation afforded 3.21 g (50%) of the mixture, bp 90–92 °C (26 Torr). The isomers were separated by preparative GLC on column B at 100 °C. The major product, *m/e* 194, has an NMR spectrum consistent with structure 46: δ 0.00 (s, 9 H), 0.85 (s, 6 H), 1.70 (s, 3 H), 1.88 (s, 2 H), 5.46 (br s, 1 H), 5.53 (br s, 1 H). The minor product, *m/e* 194, has an NMR spectrum with δ 0.0 (s, 9 H), 0.80 (s, 6 H), 1.88 (s, 2 H), 1.98 (s, 2 H), 4.70 (s, 1 H), 4.78 (s, 1 H), and 6.28 (s, 1 H) and is assigned structure 47. Structure 49 was ruled out for the major product on the basis of the following experiment.

Reaction of 46 with Maleic Anhydride. A solution of 0.204 g (1.05 mmol) of GLC purified 46 and 0.200 g (2.0 mmol) of maleic anhydride in 5 mL of benzene was heated under reflux for 2 h. The cooled solution was washed with water and the aqueous extracts were back-washed with hexane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated to give 0.305 g (99%) of a colorless oil which showed a single peak on GLC (column A, 190 °C). The NMR spectrum, δ 0.00 (s, 9 H), 0.76 (s, 3 H), 1.0 (m, 5 H), 1.37 (s, 3 H), 2.65 (d, $J = 9$ Hz, 1 H), 2.76 (d, $J = 3$ Hz, 1 H), 3.41 (d of d, $J = 3, 9$ Hz, 1 H), and 6.14 (s, 1 H), is as expected for 48.

Olefin Formation from 3-Methylcyclohexanone Tosylhydrazone. The tosylhydrazone of 3-methylcyclohexanone was prepared in the usual manner,⁴ mp 108–110 °C dec. A solution of 3.0 g (0.01 mol) in 30 mL of solvent was treated at room temperature with 4.0 equiv of base as shown in Table III. After stirring for 3 h at room temperature the reaction was quenched with ice water. The organic layer was separated and dried over magnesium sulfate. After filtration, solvent was removed by distillation through a spinning band column and the olefinic mixture isolated by preparative GLC from a 12 ft \times 1/4 in. SE 30 column. The ratio of 53 to 54 was determined using integration of the vinyl and methyl regions of the 90-MHz NMR spectrum using a calibration curve established with mixtures of known composition which were subjected to the same isolation method.

Acknowledgments. Financial support of this research from the donors of The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. NMR spectra were run on instruments supported in part by National Institutes of Health Grant RR00708 from the Division of Research Resources.

Registry No.—*syn*-4, 63904-78-9; *anti*-4, 63904-79-0; 5, 63883-62-5; 6 (R = Ph, R' = H), 61685-29-8; 7 (R = Pr), 5698-48-6; 9, 63883-63-6; 10, 13249-60-0; 12, 63883-64-7; 17, 63883-65-8; 18, 40595-34-4; 20, 61835-95-8; 22, 63883-66-9; 23 (E = Bu), 61685-33-4; 23 (E = CHO), 41437-90-5; 24, 63883-67-0; 25, 61685-34-5; 30, 63883068-1; 31, 54653-28-0; (E)-32, 63883-69-2; (Z)-32, 63883-70-5; 33, 63883-71-6; 34, 33786-47-9; 38, 63883-72-7; 39, 63883-73-8; 40, 63883-74-9; 41, 63883-75-0; 42, 21195-62-0; 43, 63883-76-1; 46, 63883-77-2; 47, 63883-78-3; 48, 63883-79-4; 50 tosylhydrazone, 63883-80-7; 2,4,6-triisopropylbenzenesulfonylhydrazide, 39085-59-1; cyclohexanone, 108-94-1; camphor, 76-22-2; 3-pentanone trisilylhydrazone, 63883-81-8; 4-heptanone trisilylhydrazone, 63883-82-9; 2-methyl-3-hexanone trisilylhydrazone, 63883-83-0; 2-octanone, 111-13-7; 1-phenyl-2-propanone, 103-79-7; 2-methylcyclohexanone, 583-60-8; 3-pentanone, 96-22-0; 4-heptanone, 123-19-3; 2,4-dimethyl-3-pentanone, 565-80-0; 2-methyl-3-hexanone, 7379-12-6; butyllithium, 109-72-8; benzaldehyde, 100-52-7; butyl bromide, 109-65-9; chlorotrimethylsilane, 75-77-4; 1,2-dibromoethane, 106-93-4; 3-phenyl-2-deuterioprop-1-ene, 60468-24-8; 2-benzyl-1-phenyl-2-propen-1-ol, 63883-84-1; 2-lithio-3-methylcyclohexene, 63883-85-2; *N,N*-dimethylformamide, 68-12-2; 2-lithiobornene,

63883-86-3; *sec*-butyllithium, 598-30-1; maleic anhydride, 108-31-6; 2-lithio-1-octene, 63883-87-4; 2-octanone tosylhydrazone, 54798-76-4; 2-lithio-3-phenylpropene, 63883-88-5.

References and Notes

- (1) (a) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974; (b) D. Seebach and K.-H. Geiss in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, p 1; (c) J. M. Brown, *Chem. Ind. (Ind.)*, 454 (1972).
- (2) J. E. Stenke and F. T. Bond, *Tetrahedron Lett.*, 1815 (1975).
- (3) J. E. Stenke, A. R. Chamberlin, and F. T. Bond, *Tetrahedron Lett.*, 2947 (1976).
- (4) R. H. Shapiro, *Org. React.*, **23**, 405 (1975).
- (5) R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, R. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5737 (1967).
- (6) R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuan, *Tetrahedron Lett.*, 1811 (1975).
- (7) R. H. Shapiro and E. C. Hornaman, *J. Org. Chem.*, **39**, 2302 (1974).
- (8) The possibility of ring metalation was first suggested by E. Vedjejs and R. P. Steiner, *J. Chem. Soc. D*, 599 (1973). The problem is *not* benzylic H abstraction as stated in ref 1b, p 60.
- (9) (a) Reference 1a, p 28; (b) W. W. Langer, Ed., "Polyamine-Chelated Alkali Metal Compounds," American Chemical Society, Washington, D.C., 1974.
- (10) D. W. Slocum and C. A. Jennings, *J. Org. Chem.*, **41**, 3653 (1976), and references cited therein.
- (11) N. J. Cusack, C. B. Reese, A. C. Risius, and B. Roozpekar, *Tetrahedron*, **32**, 2157 (1976).
- (12) A. R. Chamberlin and F. T. Bond, *J. Org. Chem.*, following paper in this issue.
- (13) J. E. Stenke, Ph.D. Thesis, University of California, San Diego, 1975; *Diss. Abstr.*, **36**, 5597 (1976).
- (14) R. T. Taylor, C. R. Degenhart, W. P. Melega, and L. A. Paquette, *Tetrahedron Lett.*, 159 (1977).
- (15) T. H. Chan, A. Baldassare, and D. Massuda, *Synthesis*, 801 (1976).
- (16) Reference 1a, p 140.
- (17) P. C. Traas, H. Boelens, and H. J. Takken, *Tetrahedron Lett.*, 2287 (1976).
- (18) For recent alternative syntheses of allylic alcohols see: (a) P. Jacob III and H. C. Brown, *J. Org. Chem.*, **42**, 579 (1977); (b) H. J. Reich and S. K. Shaw, *J. Am. Chem. Soc.*, **97**, 3250 (1975); (c) W. G. Taylor and J. R. Dimmock, *Can. J. Chem.*, **42**, 2522 (1974); (d) W. Dumont, P. Bayet, and A. Kripf, *Angew. Chem., Int. Ed. Engl.*, **13**, 804 (1974); (e) D. Seebach and A. K. Beck, *ibid.*, **13**, 806 (1974).
- (19) For recent references to alkylation of vinylolithium derivatives see: (a) J. Millon, R. Lorne, and G. Linstrumelle, *Synthesis*, 434 (1975); (b) A. P. Uijtewaal, F. L. Jonkers, and A. van der Gen, *Tetrahedron Lett.*, 1439 (1975); (c) G. Linstrumelle, *ibid.*, 3809 (1974); (d) F. Naf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971); (e) E. M. Schlosser and F. Hammer, *ibid.*, **57**, 2547 (1974).
- (20) Reference 1a, p 62; E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078, 2085 (1951).
- (21) For selected recent examples, see: (a) G. Cahiez, D. Bernard, and J. F. Normant, *Synthesis*, 245 (1976); (b) D. Seebach and H. Neumann, *Chem. Ber.*, **107**, 847 (1974); (c) H. Neumann and D. Seebach, *Tetrahedron Lett.*, 4839 (1965); (d) B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975); (e) D. A. Evans, R. C. Thomas, and J. A. Walker, *Tetrahedron Lett.*, 1427 (1976); (f) K. F. Bernady, J. F. Poletto, and M. J. Weiss, *ibid.*, 765 (1975); (g) P. A. Grieco, Y. Masaki, and D. Bowler, *J. Am. Chem. Soc.*, **97**, 159 (1975).
- (22) For recent references to alternative routes, see: (a) R. K. Boeckman, Jr., and D. M. Blum, *J. Org. Chem.*, **39**, 3307 (1974); (b) J. Hartmann and M. Schlosser, *Helv. Chim. Acta*, **59**, 452 (1976); (c) J. F. Normant, C. Chint, G. Cahiez, and J. Villieras, *Synthesis*, 803 (1974).
- (23) S. Baba, D. E. Van Horn, and E. Negishi, *Tetrahedron Lett.*, 1927 (1976).
- (24) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971).
- (25) Reference 9b, p 10.
- (26) U. F. Mironov, N. G. Maksimova, and U. V. Nepomniva, *Bull. Acad. Sci. USSR*, 313 (1967); *Chem. Abstr.*, **67**, 32719 (1967).
- (27) R. Y. Tien and P. J. Abell, *J. Org. Chem.*, **35**, 956 (1970).
- (28) For an incorrect assignment, see J.-P. Bianchini and E. M. Gaydon, *C. R. Hebd. Seances Acad. Sci., Ser. C.*, **280**, 205 (1975).
- (29) D. J. Faulkner, *Synthesis*, 175 (1971).
- (30) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, **33**, 3382 (1968).
- (31) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968); J. Hertz and C. V. Ortiz, *J. Chem. Soc. C*, 2294 (1971); R. H. Shapiro and T. Gadek, *J. Org. Chem.*, **39**, 3418 (1974); E. Vedjejs and W. T. Stolle, *Tetrahedron Lett.*, 135 (1977).
- (32) D. J. Peterson, *J. Organomet. Chem.*, **9**, 373 (1967).
- (33) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).
- (34) W. G. Dauben, G. T. Rivers, W. T. Zimmerman, N. C. Yang, B. Kim, and J. Yang, *Tetrahedron Lett.*, 2951 (1976).
- (35) The isomers are reported to be separable using a capillary column: G. Schomburg, *J. Chromatogr.*, **23**, 1 (1966).
- (36) We have occasionally detected small amounts of 1,3,5-triisopropylbenzene, presumably formed from the sulfinate, in crude reaction products. Its separation in these cases can be effected by either distillation or chromatography.
- (37) Work in progress with Mr. Sair Hagopian.

(38) Capillary melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken as neat films or CHCl_3 solutions on a Perkin-Elmer Infracord or Beckman IR-18 A-X. Proton magnetic resonance (NMR) spectra were recorded in CDCl_3 or CCl_4 solution on a Varian T-60, EM-390, or HR-220 instrument. Chemical shifts are reported as parts per million (δ) downfield from tetramethylsilane. GLC-mass spectra were obtained on an LKB-9000 instrument using a $1/8$ in. \times 6 ft Dexsil 300 column.

Reagent grade hexane was distilled from lithium aluminum hydride prior to use. Tetramethylethylenediamine (TMEDA) was distilled from lithium aluminum hydride and could be stored, protected from moisture for several weeks. 2,4,6-Triisopropylbenzenesulfonylhydrazide was prepared as reported.¹¹ Alkylolithium reagents were obtained from Alfa-Ventron Corp. and standardized prior to use.

"Standard workup" consisted of pouring the mixture into water, separating the organic layer, and reextracting the aqueous layer with ether. The combined organic layers were washed to neutrality (removing TMEDA) with

water and dried over magnesium sulfate. After concentration of the filtered solution in vacuo, it was diluted to known volume and an aliquot taken for GLC analysis. The aliquot was analyzed on a $1/8$ in. \times 15 ft 6% SE-30 on Chromosorb W column (column A) using solutions of purified product as standard. Preparative GLC was done on a $1/4$ in. \times 5 ft 20% SE-30 on Chromosorb W (column B). Microanalyses were performed by Galbraith Laboratories, Inc.

- (39) Large particles tended to remain undissolved and were occluded in the product as it crystallized.
 (40) Excess acid slows decomposition of the trisylhydrazide to diimide.
 (41) This solution was treated with D_2O prior to recording the spectrum to ensure total N-H exchange.
 (42) C. E. Griffen, *J. Org. Chem.*, **25**, 665 (1960).
 (43) The forerun was 0.44 g of **25** contaminated with about 10% 1,3,5-triisopropylbenzene.
 (44) S. Satsumabayashi, K. Nakajo, R. Soneda, and S. Motoko, *Bull. Chem. Soc. Jpn.*, **43**, 1586 (1970).

Notes

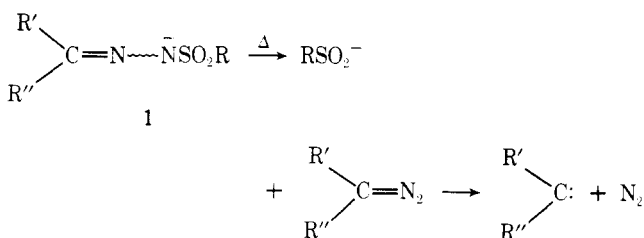
Leaving-Group Variation in Aprotic Bamford-Stevens Carbene Generation

A. Richard Chamberlin and F. Thomas Bond*

Department of Chemistry, University of California at San Diego, La Jolla, California 92093

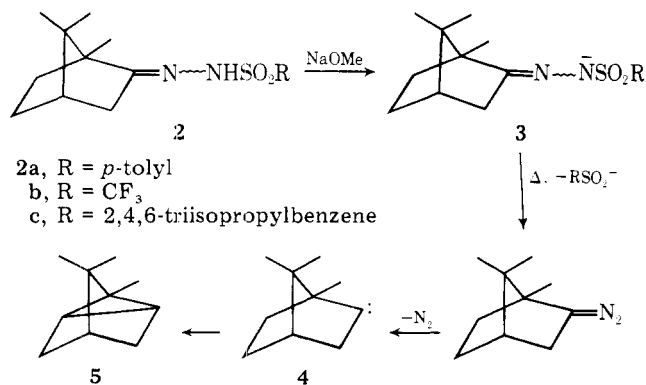
Received June 6, 1977

Thermal decomposition of the monoanions of tosylhydrazones **1** ($\text{R} = p\text{-tolyl}$) in aprotic solvents has become the standard method for generation of dialkyl carbenes.¹ The reaction is typically carried out at temperatures of 130 °C or higher, often in refluxing diglyme (161 °C). Carbenes can also be generated photochemically from **1**,² but the reaction is



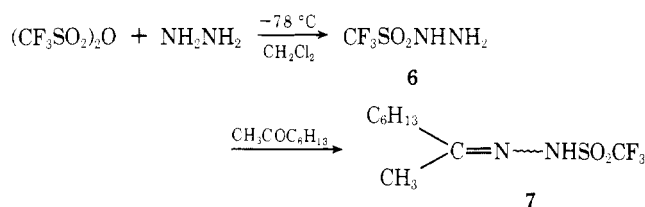
difficult to run on a large scale. In connection with another problem,³ we had reason to investigate the variation of the R group in **1** and report here the results of that study which show that "trisylhydrazones" (**1**, $\text{R} = 2,4,6\text{-triisopropylbenzene}$) decompose at a much lower temperature in this aprotic Bamford-Stevens reaction.

We chose the camphor system **2** for our study, since exclusive formation of tricyclene **5** is a standard test¹ for the intermediacy of **4**. Camphene becomes an important product



under protic conditions, and bornylene is the product of Shapiro reaction^{1b,4} conditions. Indeed, decomposition of **3a** at 161 °C produces **5** in essentially quantitative yield after 40 min.

In seeking a leaving group which would allow the reaction to proceed at a lower temperature, our attention was first directed toward triflylhydrazones **2b**. The enhanced leaving-group ability of the trifluoromethanesulfonate group⁵ has been amply documented, particularly in the solvolytic generation of vinyl cations.⁶ β eliminations of the trifluoromethylsulfonate group from nitrogen and carbon are also accelerated,⁷ but the only reported α elimination, that of benzil monotriflylhydrazones, was merely reported to give the diazo ketone "quickly" at about 0 °C. Direct comparison with the tosylhydrazones was not made.⁸ We initially attempted to prepare triflylhydrazide **6** as shown and were able to trap it in low yield at -78 °C with reactive ketones such as 2-octanone. All attempts at isolation of **6**, however, led to decomposition as first noted by Powell



and Whiting.⁹ Less reactive ketones, including camphor, could not be trapped. Triflylhydrazones **2b** were therefore prepared by treatment of camphor hydrazones¹⁰ with triflyl-anhydride in the presence of base.

Thermal decomposition of the sodium salt of **2b** at 161 °C does indeed produce **5** in a yield comparable with that obtained from **2a**. Unfortunately, the reaction is accelerated only slightly at best as shown in Table I for refluxing glyme (bp 85 °C). At this temperature both **3a** and **3b** decompose too slowly for practical purposes. We conclude that the increased leaving-group ability of the triflate anion is about equally offset by increased stabilization of **3b**, making triflylhydrazones of little value for the aprotic Bamford-Stevens sequence.

We therefore sought an R group which might selectively destabilize the starting anion **3**. The report¹¹ that trisylhydrazide decomposes to diimide faster than tosylhydrazide prompted the study of decomposition of trisylhydrazones **2c**. The preparation of a wide variety of trisylhydrazones has been reported.^{3,11} Indeed, thermal decomposition of the sodium salt **3c** is far faster than that of **3a** or **3b** as shown in Table I. In all