water mixture (5 mL) was treated with mercuric acetate or mercuric trifluoroacetate (0.24 mmol) and stirred at room temperature (3 and 6 h for the reaction of **1b** with mercuric acetate and mercuric trifluoroacetate, respectively, and 15 h for the reactions of **1c**). Then 4 N NaOH (0.5 mL) and sodium borohydride (0.027 g, 0.73 mmol) were added and stirring was continued for 10 min. The workup was carried out as described above for the reactions in water, and the residue obtained was analyzed by GLC. Reactions of **1** carried out under the same conditions but stopping after relatively longer contact times (24 h for both **1b** and **1c**) yielded the same product ratio within experimental error.

Reaction of 1b and 1c with Mercuric Acetate and Mercuric Trifluoroacetate in Anhydrous CH_2Cl_2. A solution of the cyclopropane (**1b** or **1c**) (0.26 mmol) in anhydrous CH_2Cl_2 (5 mL) was treated with the mercuric salt (0.24 mmol), stirred at room temperature (30 min for the reactions of **1b** and 24 h and 15 min for the reactions of **1c** with mercuric acetate and mercuric trifluoroacetate, respectively), then diluted with CH_2Cl_2, washed immediately with water, and evaporated. The residue (in the reactions with $Hg(OOCCF_3)_2$, λ (CO) 5.76, 6.20 μm for **1b** and 5.77 and 6.19 μm for **1c**; in the reactions with $Hg(OOCCH_3)_2$, λ (CO) 5.62, 5.95 μm for **1b** and 5.62 and 5.92 μm for **1c**) was taken up in anhydrous ether (10 mL), treated with $LiAlH_4$ (0.050 g, 1.31 mmol), stirred for 10 min at room temperature, and then refluxed for 10 min. The excess hydride was decomposed with a minimum amount of water and 2 N NaOH, and the dried ether layer was evaporated to dryness to yield a residue which was analyzed by GLC. The ratios between **13** and **14** are shown in Table I. Reactions of **1b** and **1c** with each salt carried out under the same conditions but stopping after relatively different contact times (1, 3, and 6 h for the reaction of **1b** with mercuric acetate, 15 min and 1 h for the reaction of **1b** with mercuric trifluoroacetate, 48 h for the reaction of **1c** with mercuric acetate, and 8 min and 3 h for the reaction of **1c** with mercuric trifluoroacetate) yielded the same product composition within experimental error. However, in the case of the reaction of **1b** with mercuric trifluoroacetate, much longer contact times (3 and 6 h) showed an increase of the percentage of the syn adduct due to a slow epimerization at the benzylic carbon.

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Registry No.—**6b** (X = CH_3COO), 64705-90-4; **6b** (X = CF_3COO), 64705-91-5; **6c** (X = CH_3COO), 64705-92-6; **6c** (X = CF_3COO), 64705-93-7; **9**, 5331-08-8; **10b**, 64705-94-8; **11b**, 64705-95-9; **17b**, 64705-96-0; **12c**, 64705-97-1; **13b**, 64705-98-2; **13c**, 64705-99-3; **14b**, 64706-00-9; **4a**, 64706-01-0; **15b**, 1821-23-4; **15c**, 27163-65-1; methylene iodide, 75-11-6; *p*-bromotoluene, 106-38-7; tosyl chloride, 98-59-9; 2-methylcyclohexanone, 583-60-8.

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Elimination of Tertiary α Hydrogens from Tosylhydrazones with Lithium Diisopropylamide: Preparation of Trisubstituted Alkenes

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Tosylhydrazones containing only tertiary α hydrogens react with lithium diisopropylamide (LDA) to yield trisubstituted alkenes. The reaction of these and other tosylhydrazones with LDA shows a high degree of regiospecificity which is controlled by the stereochemistry of the imino bond. The stereochemistry of the reaction is manifested by the dominance of the cis alkene except in cases where isomerization to the trans alkene has a low activation barrier. The reaction of LDA with tosylhydrazones of β-keto esters is also successful.

The reaction of tosylhydrazones with alkyllithium reagents is a convenient method of preparing terminal or disubstituted alkenes.[1] This reaction has not, however, proved to be useful for the preparation of trisubstituted alkenes. Although a few isolated examples of tertiary α-hydrogen elimination have been reported,[2,3] no yield or product distribution was given. We recently reported that isobutyrophenone tosylhydrazone does not undergo elimination with methyllithium in ether at 0 °,[1] but at room temperature substitution at the imino carbon competes effectively with elimination.[4] Although substitution can be inhibited by the use of tetramethylethylenediame (TMEDA) as a co-solvent, the yield of isobutenylbenzene is quite poor.

We now wish to report that trisubstituted alkenes are conveniently prepared from tosylhydrazones which contain only tertiary α hydrogens by the use of lithium diisopropylamide (LDA) instead of methyllithium.[5-7] The moderate product yields (38–66%) are compensated by the convenience and by the mild reaction conditions.[8] Table I shows the data for the production of five trisubstituted alkenes.

The data in Table I show that for products which do not tend to undergo isomerization, TMEDA is the solvent of choice. However, in systems which do tend to isomerize, TMEDA appears to facilitate the rearrangement. For example, 2-methyl-2-norbornene isomerizes to 2-methylenenorbornane,[9] and the tricyclic system behaves similarly. The low

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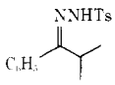
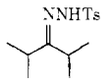
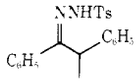
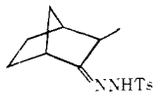
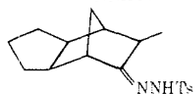
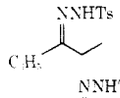
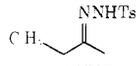
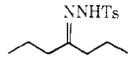
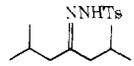
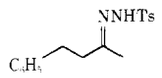
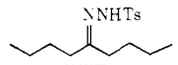
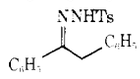
Table I. Trisubstituted Alkenes from Tosylhydrazones and Lithium Diisopropylamide

Tosylhydrazone	Registry no.	Solvent	Product(s)	Registry no.	Yield, %
	56638-11-0	TMEDA	Isobutenylbenzene	768-49-0	57[a]
	17530-00-6	TMEDA	2,4-Dimethyl-2-pentene	625-65-0	54[a]
	54288-47-0	TMEDA	1,2-Diphenyl-1-propene (cis/trans ratio, 16:84)		66[b]
	64884-74-8	Ether	2-Methyl-2-norbornene	694-92-8	38[b]
		TMEDA	2-Methyl-2-norbornene		81[c]
			3-Methylenenorbornene	497-35-8	19[c]
	64884-75-9	Ether	9-Methyltricyclo[5.2.1.0^{2,6}]-8-decene	64937-27-5	43[b]
		TMEDA	9-Methyltricyclo[5.2.1.0^{2,6}]-8-decene		32[b]
			9-Methylenetricyclo[5.2.1.0^{2,6}]-decane	64937-28-6	26[b]

[a] Product isolated by distillation. [b] Product isolated by column chromatography. [c] Ratio by gas chromatography.

Table II. Ratio of *cis*- and *trans*-Alkenes from Tosylhydrazones and LDA/TMEDA

Tosylhydrazone	Registry no.	Product	Registry no.	Cis/trans ratio	Yield, %
	17336-66-2	*trans*-1-Phenyl-1-propene	873-66-5		40[b]
	14195-24-5	*trans*-1-Phenyl-1-propene			40[a]
	36432-88-9	3-Heptene		92:8	55[b]
	64884-76-0	2,6-Dimethyl-3-heptene		92:8	74[b]
	64884-77-1	1-Phenyl-3-butene	768-56-9		75[b]
	64884-78-2	4-Nonene		94:6	72[b]
	19816-85-4	Stilbene		80:20	72[c]

[a] Yield obtained by GC standard method. [b] Product isolated by distillation. [c] Product isolated by column chromatography.

cis/trans ratio observed in the formation of 1,2-diphenyl-1-propene also appears to be the result of some isomerization since higher ratios were observed using ether solvent.[10] For this reason several other tosylhydrazones which would give stable products were tested with the LDA/TMEDA reactant. Table II shows the results of this investigation.

The exclusive formation of *trans*-1-phenyl-1-propene from propiophenone tosylhydrazone with LDA/TMEDA is in direct contrast with the 3:1 cis/trans ratio observed with MeLi/Et_2O.[10] The case of phenylacetone tosylhydrazone is even more striking since the allylbenzene product, obtained with MeLi/Et_2O,[1,4] is not observed at all. The other tosylhydrazones shown in the table give predominantly cis products, a result consistent with the previous observations.[10] From these data, it appears as if an especially active allylic hydrogen is required for product isomerization; whereas the bicyclic and tricyclic internal alkenes appear to be special cases.[9] This argument is supported by the exclusive formation of 1-phenyl-3-butene from 1-phenyl-3-butanone tosylhydrazone.

An explanation for the dominant formation of cis products comes from the recent reports on the stereoselective α-proton abstraction from oximes and their derivatives.[11-13] Scheme I depicts a reasonable mechanism based on the oxime results.

The tosylhydrazone syn dianion, which was proposed by us[4] and confirmed by Dauben,[14] can exist in conformation A or B. Since it appears that the stabilizing force in the dianion is the 6π-electron overlap,[13] it follows that the other nonbonding pair on nitrogen will be repelled and that the electropositive sulfur will be attracted by the electron density on the α carbon. Therefore, any group attached to the α carbon would prefer to be in conformation A. Alternatively, if the lone electron pair is "inside," it may sterically induce the substituent on the α carbon to reside preferentially on the "outside." In either event, the cis-alkene product would be generated.[15]

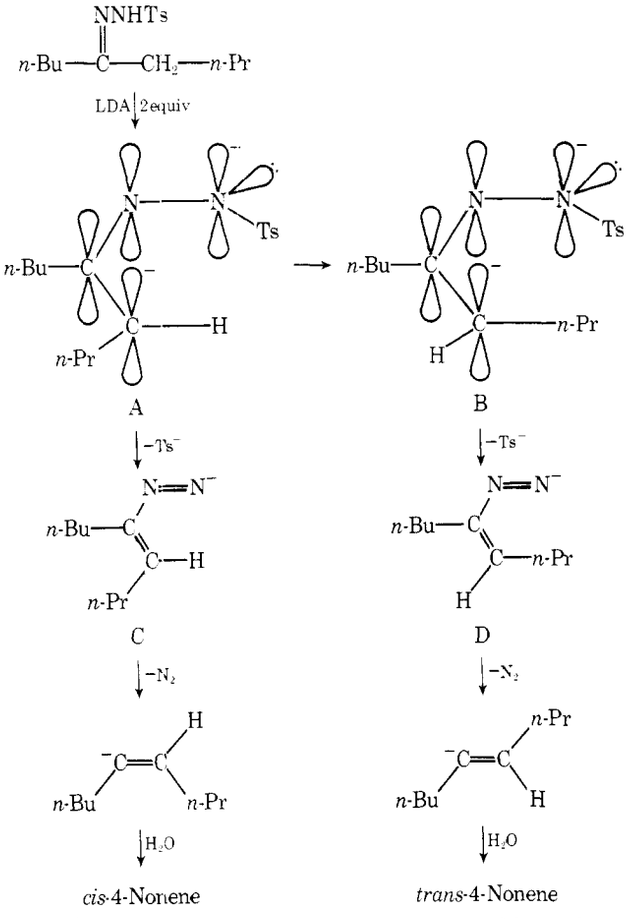
The case of 2-octanone tosylhydrazone represents an interesting example which again demonstrates that the stereochemistry of the carbon–nitrogen double bond controls the regiospecificity of the reaction.[4,14] Highly purified 2-octanone tosylhydrazone consists of a single stereoisomer, and it yields 1-octene exclusively upon reaction with alkyllithium reagents.[16,17] However, in some preparations of 2-octanone tosylhydrazone a second stereoisomer can be detected, albeit

Table III. Physical Constants for Tosylhydrazones

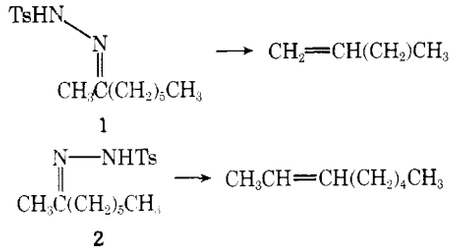
Tosylhydrazone of	Yield, %	Mp, °C	MS *m/e* (relative intensity)
Isobutyrophenone	84	103–104	316 ($M^{+\cdot}$, 6), 119 (100), 117 (42), 139 (29), 91 (29), 132 (26)
2,4-Dimethyl-3-pentanone	64	112–113	282 ($M^{+\cdot}$, 10), 127 (100), 97 (63), 41 (59), 91 (55), 55 (40)
1,2-Diphenyl-1-propanone	57	147–149	378 ($M^{+\cdot}$, 4), 223 (100), 91 (44), 105 (38), 194 (29), 179 (27)
3-Methyl-2-norbornanone	85	130–132	292 ($M^{+\cdot}$, 6), 137 (100), 91 (44), 95 (38), 93 (34), 79 (32)
9-Methyl-8-ketotricyclo-[5.2.1.$0^{2,6}$]decane	65	145–146	332 ($M^{+\cdot}$, 6), 177 (100), 79 (40), 91 (25), 109 (14), 41 (14)
1-Phenyl-2-propanone	93	137–139	302 ($M^{+\cdot}$, 7), 147 (100), 91 (67), 118 (48), 117 (35), 107 (30)
Propiophenone	96	120–121	302 ($M^{+\cdot}$, 9), 147 (100), 118 (62), 119 (60), 43 (50), 91 (43)
4-Heptanone	84	80–81	282 ($M^{+\cdot}$, 16), 127 (100), 44 (86), 42 (63), 41 (54), 43 (42)
5-Nonanone	81	66	310 ($M^{+\cdot}$, 8), 113 (100), 155 (80), 58 (80), 41 (54), 55 (50)
Deoxybenzoin	70	137–138	364 ($M^{+\cdot}$, 6), 91 (100), 92 (33), 65 (23), 209 (20), 180 (15)
2,6-Dimethyl-4-heptanone	76	110–112	310 ($M^{+\cdot}$, 10), 155 (100), 58 (65), 99 (60), 56 (60), 43 (50)
1-Phenyl-3-butanone	92	125–126	316 ($M^{+\cdot}$, 25), 91 (100), 161 (43), 117 (36), 131 (30), 57 (25)

[a] All mass spectra obtained at 70-eV ionizing energy.

Scheme I



in small amounts. In one preparation we were able to obtain a 76:24 mixture of the two stereoisomers as determined by ^{1}H NMR spectroscopy. The major isomer has a syn relationship between the methyl group and the tosylamide function (**1**), and the minor isomer has an anti relationship[18] (**2**). Decomposition of this stereoisomeric mixture with LDA in TMEDA yields a product mixture which contains a mixture of 1-octene and 2-octene in the ratio of 80:20 as determined by gas chromatography. These results are totally consistent with elimination of a syn α hydrogen in the alkene-forming reaction.



Experimental Section

Materials. Ketones, with the exception of 1,2-diphenyl-1-propanone, 3-methyl-2-norbornanone, and 9-methyl-8-ketotricyclo[5.2.1.$0^{2,6}$]decane, were obtained from commercial sources. 1,2-Diphenyl-1-propanone was prepared by phase-transfer alkylation of deoxybenzoin with methyl iodide.[19] 3-Methyl-2-norbornanone was prepared in 71% isolated yield by treating 2-norbornanone with LDA in THF/HMPA at −78 °C followed by reaction with methyl iodide. 9-Methyl-8-ketotricyclo[5.2.1.$0^{2,6}$]decane was prepared by generating the dianion of 8-ketotricyclo[5.2.1.$0^{2,6}$]decane tosylhydrazone and subsequent trapping with methyl iodide. Tosylhydrazine was prepared by treating tosyl chloride with hydrazine.[20] Tosylhydrazones were prepared in 70–95% isolated yield by treating the ketone with tosylhydrazine in 95% ethanol. Best results were obtained when ketones were purified prior to use. Methyllithium in diethyl ether was used to generate LDA and was purchased from Ventron Alfa Products. Diisopropylamine was dried over sodium hydroxide and distilled. Tetramethylethylenediamine (TMEDA) was dried over lithium aluminum hydride and distilled. Elimination reactions were carried out in two solvents, diethyl ether and TMEDA. Diethyl ether was employed to inhibit the isomerization of reactive alkene products. Yields were somewhat lower when diethyl ether was used as a solvent. In cases where alkenes were produced having the cis configuration, 10 equiv of diisopropylamine was employed per equivalent of tosylhydrazone. In all other cases 4 equiv of diisopropylamine were employed, from which 2.5 equiv of LDA was generated. Two workup procedures were employed to remove diisopropylamine and TMEDA from alkene products. One procedure employed aqueous acid washes. In the other, neutral conditions were obtained by first washing the organic phase with water to remove TMEDA, followed by several washes with copper sulfate solution to remove diisopropylamine. The later procedure can be used effectively with acid-sensitive alkenes. Each procedure is outlined below. All glassware was dried at 115 °C prior to use.

The structures of all tosylhydrazones and alkene products were assigned on the basis of their mass spectral, NMR, and IR characteristics. The assignment of the cis configuration to alkenes derived from compounds **1** and **2** was made by comparing their carbon-13 NMR chemical shift data to known literature values.[21] Mass spectral data was obtained on a Varian CH-5 mass spectrometer. ^{1}H NMR spectra were obtained on Varian A60-A and HA-100 NMR spectrometers. Carbon-13 NMR spectra were obtained on a JEOL PFT-100 spectrometer equipped with a Nicolet Model 1080 data system. IR spectra were obtained on a Perkin-Elmer 337 grating infrared spectrometer. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are corrected.

Isobutyrophenone Tosylhydrazone (1): General Procedure. Tosylhydrazine 13.9 g (74 mmol) was dissolved in 30 mL of hot 95% ethanol and isobutyrophenone (10.0 g, 67.5 mmol), and 3 drops of concentrated HCl was added. The solution was boiled for 10 min and cooled. The tosylhydrazone was crystallized and isolated, yield 18.0 g (84%); mp 103–104 °C; IR (KBr) 3200, 2950, 1600, 1340, 1160, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 6), 2.46 (s, 3), 2.72 (septet, 1), 6.9–7.9 (m, 9); mass spectrum, see Table III.

Isobutenylbenzene: General Procedure A. Tosylhydrazones were eliminated by the following general procedure. Diisopropylamine (10.2 g, 101 mmol) and 51 mL of TMEDA (2 mL per millimole of tosylhydrazone) were placed in a 250-mL three-neck flask equipped with a magnetic stirrer, reflux condenser, solid addition tube, N_2 inlet, and drying tube. The solution was blanketed with N_2 gas and cooled to 0 °C. Methyllithium in diethyl ether (39.5 mL, 63.3 mmol) was added over a period of 5 min, and the solution was allowed to stir for 5 min. Isobutyrophenone tosylhydrazone (8.0 g, 25.3 mmol) was then added over a period of 3 min, the cold bath removed, and the solution stirred overnight at room temperature under an N_2 atmosphere. Enough water was carefully added to dissolve lithium salts. The solution was poured into a separatory funnel, the layers were separated, and the aqueous phase was extracted three times with 50 mL of diethyl ether. The organic layers were combined and washed five times with 50 mL of water. The resulting ether layer was washed with 50-mL aliquots of 0.48 M HCl until the aqueous layer maintained a pH of 0.3. The ether layer was washed once with 50 mL of saturated $NaHCO_3$ solution followed by one 50-mL water wash. The organic layer was dried over Na_2SO_4 and filtered, and the ether removed by fractional distillation. The alkene was then distilled to yield 1.9 g of 1-phenyl-2-methylpropene (57%), bp 103–104 °C (43 mm); IR (neat) 3100, 3000, 1650, 1600, 1450, 920, 840, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (s, 3), 1.84 (d, 3), 6.26 (m, 1), 7.22 (s, 5); mass spectrum (70 eV), *m/e* (relative intensity) 78 (8), 65 (12), 77 (12), 39 (14), 115 (35), 91 (37), 132 (M^+, 80), 117 (100).

2-Methyl-2-norbornene: General Procedure B. The following procedure inhibits the isomerization of alkene products. Sensitive alkene products are isolated under nonacidic conditions. Diisopropylamine (4.1 g, 40.8 mmol), TMEDA (2.4 g, 20.4 mmol), and 40 mL of anhydrous diethyl ether were placed in a 250-mL three-neck flask equipped with a magnetic stirrer, reflux condenser, solid addition tube, N_2 inlet, and drying tube. The solution was blanketed with N_2 gas and cooled to 0 °C. Methyllithium in diethyl ether (17.0 mL, 25.5 mmol) was added over a period of 5 min, and the resulting solution was allowed to stir for 15 min. 3-Methyl-2-norbornanone tosylhydrazone (3.0 g, 10.2 mmol) was added over a period of 3 min. The cold bath was removed, and the solution was stirred for 25 h at room temperature under an N_2 atmosphere. Enough water was carefully added to dissolve lithium salts. The solution was poured into a separatory funnel, the layers were separated, and the aqueous phase was extracted three times with 30 mL of diethyl ether. The organic extracts were combined and washed eight times with 30 mL of water. The organic phase was washed with 60-mL aliquots of 5% $CuSO_4$ solution until all the diisopropylamine had been removed; usually four washes are required. The $CuSO_4$ extracts were suction filtered to remove a pasty emulsion, and the resulting filtrate was extracted twice with 30 mL of diethyl ether. The organic extracts were combined and washed once with 20 mL of 5% $CuSO_4$ solution. All the ether extracts were combined, dried over Na_2SO_4, and filtered, and the diethyl ether was removed by fractional distillation. Residual traces of pentane were removed under a gentle stream of nitrogen to yield 2-methyl-2-norbornene, 0.4 g (38%); IR (neat) 2940, 1630, 1400, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–1.70 (m, 6), 1.72 (d, 3), 1.65 (s, 2), 5.50 (s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 39 (14), 91 (18), 108 (M^+, 20), 79 (36), 80 (100).

2,4-Dimethyl-2-pentene. Following general procedure A for alkene preparation, 2,4-dimethyl-3-pentanone tosylhydrazone (8.0 g, 28.4 mmol) and 70.9 mmol of LDA in 57 mL of TMEDA yielded 1.5 g of 2,4-dimethyl-2-pentene (54%), bp 67–68 °C; IR (neat) 2950, 1675, 1470, 1380, 1030, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (d, 6), 1.60 (d, 3), 1.63 (d, 3), 2.44 (broad septet, 1), 4.98 (broad d, 1); mass spectrum (70 eV), *m/e* (relative intensity) 53 (15), 67 (19), 84 (20), 56 (25), 98 (M^+, 28), 39 (45), 41 (65), 55 (79), 83 (100).

1,2-Diphenyl-1-propene. Following general procedure A for alkene preparation, 1,2-diphenyl-1-propanone tosylhydrazone (8.0 g, 21.2 mmol) and 53 mmol of LDA in 43 mL of TMEDA yielded 2.7 g of 1,2-diphenyl-1-propene (66%) after column chromatography through Al_2O_3 employing 100% pentane as the eluent, mp 77–79 °C; IR (KBr) 3020, 1630, 1590, 1480, 1440, 1380, 930, 875, 760, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (d, cis isomer, 3), 2.22 (d, trans isomer, 3), 6.78–7.63 (m, 10); mass spectrum (70 eV), *m/e* (relative intensity) 116 (10), 77 (12), 91 (14), 103 (16), 89 (15), 195 (16), 193 (19), 165 (20), 115 (29), 180 (37), 178 (54), 194 (96), 179 (100).

2-Methyl-2-norbornene and 2-Methylenenorbornane. Following general procedure A for alkene preparation, 3-methyl-2-norbornanone tosylhydrazone (3.0 g, 10.2 mmol) and 25.5 mmol of LDA in 20.4 mL of TMEDA yielded, after chromatography through Al_2O_3 using 100% pentane as the eluent, 0.6 g of a mixture of 2-methyl-2-norbornene and 2-methylenenorbornane (54%, 81:19). Each isomer was collected by preparative gas chromatography on a 10% SE-30 column (3/8 in × 16 ft). Each isomer was subsequently characterized. 2-Methyl-2-norbornene: IR (neat) 2940, 1630, 1400, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–1.70 (m, 6), 1.72 (d, 3), 1.65 (s, 2), 5.50 (s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 39 (14), 91 (18), 108 (M^+, 20), 79 (36), 80 (100).

2-Methylenenorbornane: IR (neat) 2980, 1880, 1670, 1450, 910, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.25 (m, 8), 2.37 (s, 1), 2.70 (s, 1), 4.60 (s, 1), 4.85 (s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 81 (10), 78 (14), 106 (20), 41 (30), 77 (31), 39 (34), 67 (38), 108 (M^+, 45), 80 (75), 66 (77), 79 (100).

9-Methyltricyclo[5.2.1.$0^{2,6}$]-8-decene and 9-Methylenetricyclo[5.2.1.$0^{2,6}$]decane. Following general procedure A for alkene preparation, 9-methyl-8-ketotricyclo[5.2.1.$0^{2,6}$]decane tosylhydrazone (3.0 g, 9.0 mmol) and 22.5 mmol of LDA in 18 mL of TMEDA yielded, after chromatography through Al_2O_3 using 100% pentane as the eluent, 0.7 g of 9-methyltricyclo[5.2.1.$0^{2,6}$]-8-decene and 9-methylenetricyclo[5.2.1.$0^{2,6}$]decane (58%, 55:45). Each isomer was separated and collected by preparative gas chromatography on a 10% SE-30 column and characterized. 9-Methyltricyclo[5.2.1.$0^{2,6}$]-8-decene: IR (neat) 2970, 2850, 1660, 1470, 1440, 1310, 1020, 810, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.48 (m, 12), 1.72 (d, 3), 5.60 (broad s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 43 (10), 91 (13), 39 (14), 41 (14), 67 (15), 77 (15), 148 (M^+, 19), 81 (30), 79 (60), 80 (100).

9-Methylenetricyclo[5.2.1.$0^{2,6}$]decane: IR (neat) 2930, 2880, 1670, 1480, 1470, 1450, 1430, 1280, 1030, 920, 880, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–2.50 (m, 14), 4.57 (s, 1), 4.83 (s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 93 (10), 133 (10), 66 (11), 106 (11), 39 (13), 105 (15), 78 (18), 41 (19), 77 (19), 81 (19), 91 (19), 67 (23), 148 (M^+, 35), 79 (76), 80 (100).

Gas Chromatographic Standardization of *trans*-1-Phenyl-1-propene vs. Bicyclohexyl. *trans*-1-Phenyl-1-propene (0.1021 g, 0.86 mmol) and 0.1400 g of bicyclohexyl were carefully weighed (Mettler balance) into a vial, and 3.0 mL of diethyl ether was then added. This mixture was subjected to the following gas chromatographic conditions: column, 1/8 in × 8 ft, Dow Corning 550 on 80–100 mesh Chromosorb W; injector temperature, 230 °C; detector temperature, 260 °C; column temperature, 80 °C initial, 200 °C final; program rate, 8 °C/min; carrier gas rate (N_2), 50 mL/min; sample size, 15 μL. A series of three chromatograms were obtained from which a molar response factor of 1.026 was calculated (moles of bicyclohexyl vs. moles of *trans*-1-phenyl-1-propene).

***trans*-1-Phenyl-1-propene.** Following general procedure A for alkene preparation, phenylacetone tosylhydrazone (2.990 g, 9.87 mmol), bicyclohexyl (0.7612 g, 4.58 mmol), and 24.7 mmol of LDA in 20 mL of TMEDA were reacted for 23 h at room temperature. Reaction aliquots were removed after 7.5 h and subjected to the gas chromatographic conditions described above. A final reaction aliquot was removed and analyzed after 23 h of reaction time. Percent yield values were determined using the equation $M_x = A_x S_s M_s / A_s S_x$ and a molar response factor of $S_s/S_x = 1.026$ (M_x, moles of substrate; M_s, moles of standard; A_x, peak area of substrate; A_s, peak area of standard; S_x, response of substrate; S_s, response of standard). A 40% yield of *trans*-1-phenyl-1-propene was found to be produced after 7.5 h of reaction time. After 23 h of reaction time only a 20% yield of *trans*-1-phenyl-1-propene was present with no new products present in a gas chromatogram of the reaction mixture.

1-Phenyl-3-butene. Following general procedure A for alkene preparation, 1-phenyl-3-butanone tosylhydrazone (5.0 g, 15.8 mmol) and 39.5 mmol of LDA in 32 mL of TMEDA yielded 1.5 g of 1-phenyl-3-butene (75%), bp 51 °C (10 mm); IR (neat) 2950, 1625, 1580, 1480, 1440, 990, 910, 740, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10–2.86 (m, 4), 4.80–5.20 (m, 2), 5.50–6.18 (m, 1), 7.15 (s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 104 (10), 39 (12), 92 (14), 65 (19), 132 (M^+, 40), 91 (100).

1-Phenyl-1-propene. Following general procedure A for alkene preparation, propiophenone tosylhydrazone (5.0 g, 16.5 mmol) and 41.4 mmol of LDA in 66 mL of TMEDA yielded, after 3.0 h reaction time, 0.9 g of 1-phenyl-1-propene (48%), bp 47–48 °C (5.0 mm); IR (neat) 2920, 2850, 1650, 1580, 1480, 1410, 960, 805, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (d, 3), 5.90–6.60 (m, 2), 7.26 (m, 5); mass spectrum (70 eV), *m/e* (relative intensity) 63 (10), 65 (10), 77 (10), 78 (10), 103 (13), 51 (15), 39 (16), 91 (38), 116 (40), 118 (M^+, 93), 117 (100).

***cis*- and *trans*-3-Heptene.** Following general procedure A for alkene preparation, 4-heptanone tosylhydrazone (8.0 g, 28.4 mmol) and 71 mmol of LDA in 57 mL of TMEDA yielded 1.5 g of *cis*- and *trans*-3-heptene (55%; cis/trans ratio, 92:8 by ^{13}C NMR integration), bp 85–87 °C; IR (neat) 2900, 1650, 1450, 1360, 1060, 960, 890, 870, 790, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63–1.67 (m, 8), 1.67–2.33 (m, 4), 5.30 (m, 2); ^{13}C NMR data was collected and compared with literature

values[21] obtained on authentic samples of *cis*- and *trans*-3-heptene; mass spectrum (70 eV), *m/e* (relative intensity) 43 (16), 70 (17), 39 (20), 42 (20), 98 (M^+, 35), 55 (52), 69 (55), 56 (75), 41 (100).

***cis*- and *trans*-4-Nonene.** Following general procedure A for alkene preparation, 5-nonanone tosylhydrazone (7.0 g, 22.5 mmol) and 56.5 mmol of LDA in 45 mL of TMEDA yielded 2.0 g of *cis*- and *trans*-4-nonene (72%; cis/trans ratio, 94:6 by ^{13}C NMR integration), bp 135–137 °C; IR (neat) 2930, 1650, 1460, 1380, 1055, 970, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.64–1.73 (m, 12), 1.73–2.30 (m, 4), 5.37 (m, 2); ^{13}C NMR data was collected and compared with literature values[21] obtained on authentic samples of *cis*- and *trans*-4-nonene; mass spectrum (70 eV), *m/e* (relative intensity) 57 (11), 67 (12), 97 (14), 83 (17), 84 (18), 42 (16), 43 (26), 69 (28), 126 (M^+, 30), 70 (38), 56 (51), 41 (60), 55 (100).

***cis*- and *trans*-Stilbene.** Following general procedure A for alkene preparation, deoxybenzoin tosylhydrazone (8.0 g, 21.8 mmol) and 54.8 mmol of LDA in 44 mL of TMEDA yielded 2.9 g of *cis*- and *trans*-stilbene after chromatography through alumina (72%). The cis/trans ratio was determined to be 80:20 by gas chromatography. GC conditions were the following: column, 1/8 in × 12 ft, 10% SE-30 (silicon rubber) on 80–100 mesh Chromosorb W; injector temperature, 230 °C; detector temperature, 260 °C; column temperature, 100 °C initial, 240 °C final; program rate, 4 °C/min; carrier gas rate (N_2), 50 mL/min; sample size, 5.0 μL (*cis*- and *trans*-stilbene are injected in chloroform solution). Retention times: *cis*-stilbene, 8 min 48 s; *trans*-stilbene, 10 min 12 s. The trans isomer was allowed to crystallize from the cis/trans mixture and was separated by suction filtration and washed with pentane. The cis isomer was isolated from the filtrate. *cis*-Stilbene: IR (neat) 3000, 2930, 1600, 1490, 1450, 925, 780, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.60 (s, 2), 7.22 (s, 10); mass spectrum (70 eV), *m/e* (relative intensity) 77 (10), 177 (11), 76 (12), 89 (21), 165 (33), 178 (54), 179 (74), 180 (M^+, 100).

trans-Stilbene: IR (KBr) 3000, 1590, 1490, 1450, 970, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (s, 2), 7.39 (m, 10); mass spectrum (70 eV), *m/e* (relative intensity) 177 (10), 76 (14), 89 (19), 165 (30), 178 (50), 179 (74), 180 (M^+, 100).

***cis*- and *trans*-2,6-Dimethyl-3-heptene.** Following general procedure A for alkene preparation, 2,6-dimethyl-4-heptanone tosylhydrazone (8.0 g, 25.8 mmol) and 64.5 mmol of LDA in 52 mL of TMEDA yielded 2.4 g of *cis*- and *trans*-2,6-dimethyl-3-heptene (74%; cis/trans ratio, 92:8 by ^{13}C NMR integration), bp 119 °C; IR (neat) 2900, 1600, 1460, 1360, 1350, 1160, 1100, 1020, 970, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–1.05 (m, 12), 1.10–1.80 (septet, 1), 1.80–2.10 (m, 2), 2.25–2.90 (septet, 1), 4.95–5.40 (m, 2); ^{13}C NMR ($CDCl_3$) from proton-decoupled spectra (see structure I), 22.4 (C-7), 23.2 (C-1), 26.5

$$\overset{1}{(CH_3)_2}\overset{2}{C}\overset{3}{H}\overset{4}{=}\overset{5}{C}\overset{6}{H}\overset{7}{CH_2}CH(CH_3)_2$$

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(C-6), 28.7 (C-2, cis isomer), 31.2 (C-2, trans isomer), 36.6 (C-5, cis isomer), 41.8 (C-5, trans isomer), 126.1 (C-4, cis isomer), 137.7 (C-4, trans isomer), 138.1 (C-3, cis isomer), 138.8 ppm (C-3, trans isomer); mass spectrum (70 ev), *m/e* (relative intensity) 42 (12), 67 (13), 39 (20), 83 (23), 57 (31), 126 (M^+, 32), 70 (43), 43 (57), 41 (75), 56 (85), 69 (95), 55 (100).

1-Octene and *cis*- and *trans*-2-Octene. Following general procedure A for alkene preparation, 2-octanone tosylhydrazone (8.0 g, 27 mmol) and 70 mmol of LDA in 56 mL of TMEDA yielded 2.4 g of a mixture of 1-octene and *cis*- and *trans*-2-octene (80%), bp 110 °C; IR (neat) 2920, 1640, 1460, 1375, 1000, 910, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.30 (m, 13), 4.72–5.20 (m, 2), 5.30–6.20 (m, 1); 1-octene/*cis*-2-octene/*trans*-2-octene ratio, 80:10:10 by GC (GC conditions: column, 1/8 in × 12 ft, 10% SE-30 (silicone rubber) on 80–100 mesh Chromosorb W; injector temperature, 50 °C initial, 200 °C final; program rate, 4 °C/min; carrier gas rate (N_2), 50 mL/min; sample size, 5.0 μL); GC–MS was performed on the reaction mixture and found to be consistent with that obtained for authentic samples;[22] mass spectrum (70 eV), *m/e* (relative intensity) 1-octene, 112 (M^+, 10), 70 (62), 42 (73), 56 (87), 55 (87), 41 (92), 43 (100); *m/e* *cis*-2-octene, 112 (M^+, 19), 43 (21), 42 (53), 70 (51), 56 (53), 41 (95), 55 (100); *m/e* *trans*-2-octene, 112 (M^+, 24), 43 (19), 42 (44), 70 (49), 56 (65), 41 (91), 55 (100).

Registry No.—Isobutyrophenone, 611-70-1; 2,4-dimethyl-3-pentanone, 565-80-0; 1,2-diphenyl-1-propanone, 2042-85-5; 3-methyl-2-norbornanone, 643-51-6; 9-methyl-8-ketotricyclo-[5.2.1.$0^{2,6}$]decane, 64884-79-3; 1-phenyl-2-propanone, 103-79-7; propiophenone, 93-55-0; 4-heptanone, 123-19-3; 5-nonanone, 502-56-7; deoxybenzoin, 451-40-1; 2,6-dimethyl-4-heptanone, 108-83-8; 1-phenyl-3-butanone, 2550-26-7; tosylhydrazine, 1576-35-8; *cis*-1,2-diphenyl-1-propene, 1017-22-7; *trans*-1,2-diphenyl-1-propene, 833-81-8; *cis*-3-heptene, 7642-10-6; *trans*-3-heptene, 14686-14-7; *cis*-4-nonene, 10405-84-2; *trans*-4-nonene, 10405-85-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *cis*-2,6-dimethyl-3-heptene, 20488-35-1; *trans*-2,6-dimethyl-3-heptene, 64884-80-6; 2-octanone tosylhydrazone, 54798-76-4; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; 2-octanone, 111-13-7; lithium diisopropylamide, 4111-54-0.

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