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# The Reaction of Organoboranes with Lithium Salts of Trisylhydrazones of Cycloalkanones Followed by Treatment with Iodine

Tsutomu Baba, Kamlakar Avasthi, and Akira Suzuki*

*Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060*

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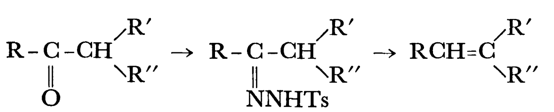
**Synopsis.** The titled reaction proceeds smoothly under mild conditions to give corresponding 1-alkylcycloalkenes in excellent yields. The overall reaction provides a convenient synthetic procedure of cycloalkenes for cycloalkanones, with various alkyl substituents readily available by means of hydrobortation.

Recently, organoborates have been recognized as important intermediates in the formation of carbon–carbon bonds.[1] On the other hand, there are various methods to convert ketones to alkenes,[2] one of which is the conversion through their tosylhydrazones (Bamford-Stevens reaction and the related reactions, Eq. 1).[3] Although such methods are established as

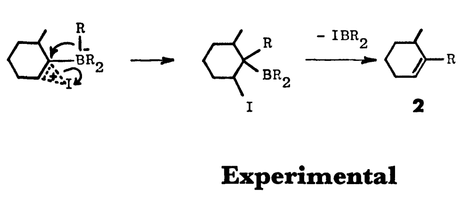


$$\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{R{-}C}}\mathrm{{-}CH}\begin{matrix}\diagup\mathrm{R'}\\ \diagdown\mathrm{R''}\end{matrix} \rightarrow \underset{\underset{\displaystyle\mathrm{NNHTs}}{\|}}{\mathrm{R{-}C}}\mathrm{{-}CH}\begin{matrix}\diagup\mathrm{R'}\\ \diagdown\mathrm{R''}\end{matrix} \rightarrow \mathrm{RCH{=}C}\begin{matrix}\diagup\mathrm{R'}\\ \diagdown\mathrm{R''}\end{matrix} \qquad (1)$$

useful synthetic routes to alkenes with a wide variety of structures, they have unavoidable limitation that only alkenes with the skeltons of the parent ketones are obtained as shown in Eq. 1. Previously, we reported that the reaction of iodine with 1-alkenyltrialkylborates derived from trialkylboranes and 2,4,6-triisopropylphenylsulfonylhydrazones (trisylhydrazones) of methyl ketones provides a novel synthesis of 1,1-dialkylethylenes.[4] However, that procedure did not give satisfactory results for trisylhydrazones of cycloalkanones.

In this paper, we wish to report that the modified procedure by using THF as a solvent gives excellent results for cycloalkanone derivatives. Representative results are summarized in Table 1.

The reaction is considered to proceed through the vinylic anion[5] derived from a trisylhydrazone as reported previously.[4] More interesting examples involve unsymmetrical ketones, which can give rise to geometrically isomeric vinyllithium reagents. As an example of such a type, the derivative (**1**) formed from 2-methylcyclohexanone gives good yields of 1-alkyl-6-methylcyclohexenes (**2**).



(2)

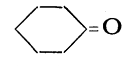
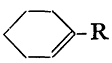
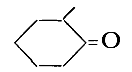
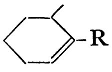
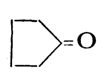
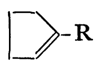
## Experimental

*Materials.* Commercial alkenes and butyllithium were used. THF was purified by distillation from $LiAlH_4$ before use. Trialkylboranes were prepared by the hydroboration of corresponding alkenes with borane in THF.[6] Trisylhydrazones of cycloalkanones were prepared by the reported method[5] from ketones and 2,4,6-triisopropylphenylsulfonylhydrazide.[7]

The IR and NMR spectra were taken on a Hitachi-Perkin Elmer Model 125 spectrophotometer and a Hitach R-22 spectrometer at 90 MHz using tetramethylsilane as an internal standard, respectively.

*General Procedure.* The following procedure for the preparation of 1-propyl-6-methylcyclohexene is representative. A dry 50 ml-flask equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser was flushed with dry nitrogen. The flask was charged under nitrogen with 0.784 g (2.04 mmol) of 2-methylcyclohexanone trisylhydrazone, mp 109 °C (decomp) and 10 ml of a 10% TMEDA solution in THF under stirring. The mixture was cooled to −78 °C, and 2.59 ml (5.03 mmol) of a 1.97 M (1 M=1 mol $dm^{-3}$) solution of butyllithium in ether was added dropwise. The solution was stirred at the temperature for 30 min, and then allowed to warm to 0 °C. The flask was held at the temperature for additional 15 min to ensure the completion of nitrogen evolution. To the mixture again cooled to −78 °C, 0.65 ml (1.43 mmol) of a 2.2 M solution of tripropylborane in THF was added carefully. The mixture was stirred at −78 °C for 60 min followed by 60 min stirring at room temperature. The flask was again cooled to −60 °C and 0.40 g (1.57 mmol) of iodine in 4 ml of THF was added dropwise. The reaction mixture was stirred around −60 °C for 30 min followed by 60 min stirring at room temperature, and a few drops of aqueous sodium thiosulfate solution was added to remove an excess

Table 1. Synthesis of 1-alkylcycloalkenes from cycloalkanones

| Cycloalkanone (Mp $\theta_m$/°C of trisylhydrazone) | Organoborane $R_3B$, R= | Yield/%[a] | of product[b] |
|---|---|---|---|
| <br>(124 decomp) | Propyl | 82 |  |
| | Butyl | 77 | |
| | *s*-Butyl | 96 | |
| | Isobutyl | 67 | |
| | Cyclopentyl | 79 | |
| <br>(109 decomp) | Propyl | 93 |  |
| | Butyl | 92 | |
| | *s*-Butyl | 94 | |
| | Isobutyl | 96 | |
| | Cyclopentyl | 87 | |
| | Hexyl | 92 | |
| <br>(134 decomp) | Butyl | 95 |  |
| | *s*-Butyl | 93 | |
| | Isobutyl | 90 | |
| | Cyclopentyl | 98 | |
| | Hexyl | 96 | |

a) Based on the organoborane used. b) Satisfactory spectral data and elemental analyses were obtained for all products.

of iodine. After the usual alkaline hydrogen peroxide oxidation, the solution was saturated with potasium carbonate. The VPC analysis of the separated organic layer indicated formation of 1-propyl-6-methylcyclohexene in a 93% yield.

*Identification of the Products.* In all cases analytically pure samples were obtained by preparative VPC with Varian autoprep Model-2800 and characterized by NMR, IR, and mass spectra, and elemental analyses.

*Cyclohexanone Trisylhydrazone*: Mp 125 °C (decomp). Found: C, 66.66; H, 9.04; N, 7.38; S, 8.42%. Calcd for $C_{21}H_{34}O_2N_2S$: C, 66.75; H, 9.01; N, 7.42; S, 8.49%. $^1$H-NMR ($CCl_4$): $\delta$ 1.20 (d, 18H), 1.56 (s, 6H), 2.28 (s, 4H), 2.90 (m, 1H), 4.25 (m, 2H), 7.15 (s, 3H).

*2-Methylcyclohexanone Trisylhydrazone*: Mp 108 °C (decomp). Found: C, 67.49; H, 9.25; N, 7.01; S, 7.99%, Calcd for $C_{22}H_{36}O_2N_2S$: C, 67.48; H, 9.20; N, 7.15; S, 8.19%. $^1$H-NMR ($CCl_4$): $\delta$ 0.94 (d, 3H), 1.22 (d, 18H), 1.60—2.15 (m, 10H), 2.85 (m, 1H), 4.25 (m, 2H), 7.06 (s, 2H).

*Cyclopentanone Trisylhydrazone*: Mp 133—134 °C (decomp). Found: C, 65.85; H, 8.85; N, 7.68; S, 8.80%. Calcd for $C_{20}H_{32}O_2N_2S$: C, 65.91: H, 8.92; N, 7.63; S, 8.60%. $^1$H-NMR ($CCl_4$): $\delta$ 1.25 (d, 18H), 1.80 (s, 4H), 2.32 (d, 4H), 2.95 (m, 1H), 4.30 (m, 3H), 7.10 (s, 2H).

*1-Propylcyclohexene*: Found: C, 86.98; H, 13.02%. Calcd for $C_9H_{16}$: C, 87.02; H, 12.98%. Mass: $m/e=124$ ($M^+$). IR (neat): 820, 1665 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.90 (t, 3H), 1.62 (m, 2H), 1.72—2.10 (m, 8H), 3.65 (t, 2H), 5.34 (s, H).

*1-Butylcyclohexene*: Found: C, 86.90; H, 13.10%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass: $m/e=138$ ($M^+$). IR (neat): 820, 1665 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.90 (t, 3H), 1.32 (m, 2H), 1.58 (m, 2H), 1.75—2.05 (m, 8H), 3.64 (t, 2H), 5.35 (s, H).

*1-(s-Butyl)cyclohexene*: Found: C, 86.80; H, 13.23%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass: $m/e$ 138 ($M^+$). IR (neat): 810, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.84 (t, 3H), 0.95 (d, 3H), 1.62 (m, 2H). 1.72—2.05 (m, 8H). 3.68 (t, H), 5.40 (s, H).

*1-Isobutylcyclohexene*: Found: C, 86.72; H, 13.01%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass; $m/e=138$ ($M^+$). IR (neat): 820, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.86 (d, 6H), 1.54—2.05 (m, 9H), 3.68 (t, 2H), 5.35 (s, H).

*1-Cyclopentylcyclohexene*: Found: C, 87.89; H, 12.11%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%. Mass: $m/e=150$ ($M^+$). IR (neat): 820, 1665 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 1.50—2.30 (m, 17H), 5.40 (m,H).

*1-Propyl-6-methylcyclohexene*: Found: C, 86.66; H, 12.95%. Calcd for $C_{10}H_{18}$: C 86.88; H, 13.12%. Mass: $m/e=138$ ($M^+$). IR (neat): 805, 1670 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.89 (t, 3H), 1.02 (d, 3H), 1.20—1.66 (m, 7H), 1.90—2.05 (m, 4H), 5.33 (s, H).

*1-Butyl-6-methylcyclohexene*: Found: C, 86.36; H, 13.01%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%. Mass: $m/e=152$ ($M^+$). IR (neat): 810, 1670 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.89 (t, 3H), 0.96 (d, 3H), 1.15—1.55 (m, 7H), 1.76—2.10 (m, 6H), 5.30 (s, H).

*1-(s-Butyl)-6-methylcyclohexene*: Found: C, 86.65; H, 13.35%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%. Mass: $m/e=152$ ($M^+$). IR (neat): 800, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.86 (d, 6H), 1.00 (d, 3H), 1.30—1.66 (m, 6H), 1.80—2.15 (m, 4H), 5.33 (s, H).

*1-Isobuty-6-methylcyclohexene*: Found: C, 86.80; H, 13.19%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%. Mass: $m/e=152$ ($M^+$). IR (neat): 790, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.88 (t, 6H), 1.02 (d, 3H), 1.18—1.30 (m, 4H), 1.45—1.65 (m, 4H), 1.95 (m, 2H), 5.32 (s, H).

*1-Cyclopentyl-6-methylcyclohexene*: Found: C, 87.69; C, 12.23%. Calcd for $C_{12}H_{20}$: C, 87.73; H. 12.27%. Mass: $m/e=164$ ($M^+$). IR (neat): 800, 1650 cm$^{-1}$. $^1$H-MNR ($CCl_4$): $\delta$ 1.02 (d, 3H), 1.20—2.00 (m, 15H), 2.20 (m, H), 5.38 (s, H).

*1-Hexyl-6-methylcyclohexene*: Found: C, 86.50; H, 13.38%. Calcd for $C_{13}H_{24}$: C, 86.58; H, 13.42%. Mass: $m/e=180$ ($M^+$). IR (neat): 810, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_3$): $\delta$ 0.88 (t, 3H), 0.98 (d, 3H), 1.15—1.58 (m, 11H), 1.75—2.05 (m, 6H), 5.32 (s, H).

*1-Butylcyclopentene*: Found: C, 86.98: H, 12.89%. Calcd for $C_9H_{16}$: C, 87.02; H, 12.98%. Mass: $m/e=124$ ($M^+$). IR (neat): 810, 1650 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.92 (t, 3H), 1.40 (m, 4H), 1.75—2.30 (m, 8H), 5.29 (s, H).

*1-(s-Butyl)cyclopentene*: Found: C, 87.21; H, 12.85%. Calcd for $C_9H_{16}$: C, 87.02; H, 12.98%. Mass; $m/e=124$ ($M^+$). IR (neat): 790, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.88 (t, 3H), 0.92 (d, 3H), 1.48—2.22 (m, 9H), 5.28 (s, H).

*1-Isobutylcyclopentene*: Found: C, 86.94; H, 12.93%. Calcd for $C_9H_{16}$: C, 87.02; H, 12.98%. Mass: $m/e=124$ ($M^+$). IR (neat): 800, 1660 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.90 (t, 6H), 1.50—2.25 (m, 9H), 5.30 (s, H).

*1-Cyclopentylcyclopentene*: Found: C, 88.12; H, 11.82%. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84%. Mass: $m/e=136$ ($M^+$). IR (neat): 800, 1650 cm$^{-1}$. $^1$H-MNR ($CCl_4$): $\delta$ 1.30—1.93 (m, 9H), 2.05—2.35 (m, 6H), 5.30 (s, H).

*1-Hexylcyclopentene*: Found: C, 86.75; H, 13.24%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.04%. Mass: $m/e=152$ ($M^+$). IR (neat): 810, 1650 cm$^{-1}$. $^1$H-NMR ($CCl_4$): $\delta$ 0.88 (t, 3H), 1.28 (m, 10H), 1.75—2.30 (m, 6H), 5.28 (s, H).

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