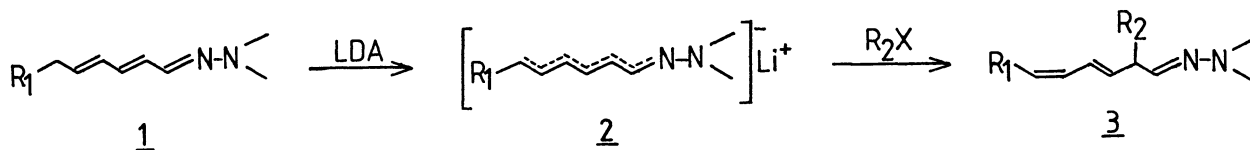


α -Alkylation of Lithiated (2E,4E)-2,4-Alkadienal Dimethylhydrazones.Preparation of α -Alkylated (3E,5Z)-3,5-Alkadienal Dimethylhydrazones

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Alkylation of lithium salts of (2E,4E)-2,4-alkadienal dimethylhydrazones with alkyl halides afforded α -alkylated (3E,5Z)-3,5-alkadienal dimethylhydrazones with the rearrangement of two double bonds in good yields.

Dimethylhydrazone derivatives of ketones and aldehydes are useful intermediates in organic synthesis because of their unique reactivity.¹⁾ In the previous paper, we have reported that the alkylation of α,β -unsaturated aldehyde dimethylhydrazones gives α -alkylated β,γ -unsaturated aldehydes after hydrolysis with the rearrangement of a double bond.²⁾ In this communication, we wish to report the novel regiospecific alkylation of (2E,4E)-2,4-alkadienal dimethylhydrazones (1) and the rearrangement of their two double bonds to α -alkylated (3E,5Z)-3,5-alkadienal dimethylhydrazones (3) (Scheme 1). To our knowledge, no selective alkylation of 2,4-alkadienals has been reported.

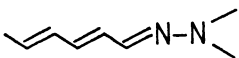

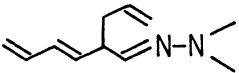
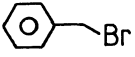
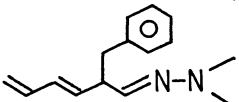

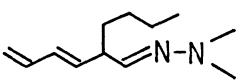
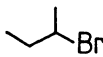
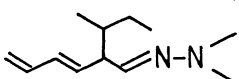

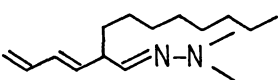
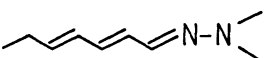

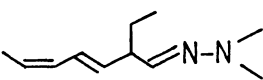
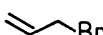
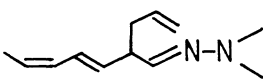
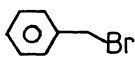
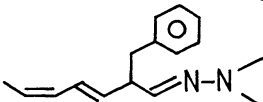


Scheme 1.

Condensation of (2E,4E)-2,4-alkadienals and N,N-dimethylhydrazine in benzene gave the corresponding hydrazones 1 in high yields. A typical procedure for the alkylation of these hydrazones 1 is as follows: To a solution of lithium diisopropylamide (LDA) (5.7 mmol) in tetrahydrofuran (THF) (10 ml) was added (2E,4E)-2,4-heptadienal dimethylhydrazone (5.5 mmol) at -5 °C under argon atmosphere, and the stirring was continued for 1 h at -5 °C. After cooling to -78 °C, benzyl bromide (5.7 mmol) was added, and the reaction mixture was further stirred for 1.5 h at ambient temperature and then treated with brine. After usual work up, (3E,5Z)-2-benzyl-3,5-heptadienal dimethylhydrazone (coupling constants: J_{3,4}=15.2 Hz, J_{5,6}=10.5 Hz)³⁾ was obtained in 62% yield by column chromatography (hexane: ethyl acetate=9:1) as a yellowish liquid.

Lithium derivatives (2) of (2E,4E)-2,4-alkadienal dimethylhydrazones 1 reacted with a variety of alkyl halides, accompanying rearrangement of two double bonds simultaneously, to give α -alkylated (3E,5Z)-3,5-alkadienal dimethyl-

Table 1. Alkylation of (2E,4E)-2,4-alkadienal dimethylhydrazones

Run	Substrate	Alkylating agent	Product ^{a)}	Yield/% ^{b)}
1				80
2				79
3				76
4				66
5				79
6				57
7				60
8				62

a) All compounds were identified by their IR, ¹H-NMR, and mass spectra.

b) Isolated yields.

hydrazones 3 exclusively. No isomeric products could be detected by TLC analysis. These results were summarized in Table 1.

The present new alkylation reaction of 1 to the α-alkylated (3E,5Z)-3,5-alkadienal dimethylhydrazones 3 can be realized to be of considerable synthetic potential because of the regioselectivity, high yields and the simple operations. Moreover, this reaction is a new tool for the synthesis of dienes with functional groups such as carbonyl group.

Further studies of this reaction and the applications of these products to the synthesis of naturally occurring compounds are under progress.

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(Received July 25, 1988)