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# CYCLOALKENYLATION OF ALDIMINE USING 1,3-DIENE
## SYNTHESIS OF 4-ALKYLAMINOCYCLOHEXENE DERIVATIVES

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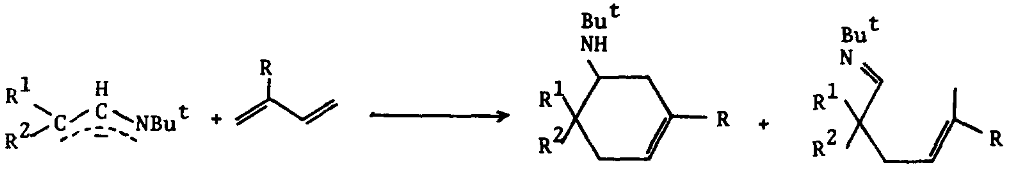
It has been well-known that aldimines are readily metalated with organoalkali metal compounds and the resulting metalated aldimines react with alkyl halides, carbonyl compounds and α-haloketones to give α-alkylated aldimines, α,β-unsaturated carbonyl compounds[1] and pyrrole derivatives[2], respectively. In this communication, we wish to report on the cycloalkenylation of aldimines using 1,3-diene, particularly on the peculiality of the adducts and the application to the synthesis of terpenoids.

Butadiene was allowed to react with N-isobutylidene-t-butylamine (1) in the presence of n-butyl lithium in the benzene-ether solution at 60° for 6.5 hr to give a mixture of 4,4-dimethyl-5-t-butylaminocyclohexene (2) and N-(2,2-dimethyl-cis-4-hexenylidene)t-butylamine (3) with a ratio of 11 : 2 on the glc inspection in a 60% yield.3)

Similar treatments of (1) with isoprene and myrcene at 45° for 20 hr gave 1,4,4-trimethyl-5-t-butylaminocyclohexene (4) and 1-(4-methyl-3-pentenyl)-4,4-dimethyl-5-t-butylaminocyclohexene (5) in 53% and 45% yields, respectively.3)



$R^1$=$R^2$=Me-

(2): R=H-
(4): R=Me-
(5): R=$Me_2C$=CH-$(CH_2)_2$-

(3): R=H-

These reactions were also able to be initiated by means of sodium metal or lithium diisopropylamide in place of n-butyl lithium, in which sodium metal seemed to be preferable to synthesize 4-alkylaminocyclohexene derivatives. Actually, the sodium initiated reaction of isoprene with (1) at 55° for 6 hr afforded (4) in a 70% yield.

For the purpose of the synthesis of terpenoids, the reaction of isoprene with N-(3-methylbutylidene)t-butylamine (6) was also investgated. Isoprene was allowed to react with (6) in the presence of lithium diisopropylamide at 45° for 62 hr to give a 78% yield of a mixture of 5-t-butylamino-p-menthene (7), the aldimine of dihydrolavandulal (8) and N-(5-methyl-2-isopropyl-2-prenyl-4-hexenylidene)t-butylamine (9)4) with a ratio of 5 : 6 : 9 3), but the sodium-initiated reaction at 40° for 20 hr afforded (7) mainly in a 62% yield (ref. Table 1.).

Further work is now in progress to establish details of the scope and mechanism of the reaction.

Table 1. Alkenylation of N-(3-methylbutylidene)t-butylamine (6)a)

| Equiv. isoprene | Metal (mmol) | Benzene (ml) | Temp. (°C) | Time (hr) | Yields b) (%) | Products (%) c) (7) | (8) | (9) |
|---|---|---|---|---|---|---|---|---|
| 4.0 | $LiN(i\text{-}Pr)_2$ (10) | 10 | 45 | 62 | 78 | 25 | 30 | 45 |
| 4.0 | n-BuLi (4) | 5 | 45 | 41 | 70 | 45 | 30 | - |
| 2.2 | $LiN(i\text{-}Pr)_2$ (10) | 5d) | 50 | 30 | 21 | 6 | 92 | - |
| 1.8 | Na 0.1 g | 5 | 40 | 6 | 65 | 7 | 90 | - |
| 1.8 | Na 0.1 g | 5 | 40 | 20 | 62 | 83 | 4 | 13 |

a) (6): 10 mmol. b) Yields are based on (6).

c) The percentage were determined by glc. d) Ether was used as the solvent.

## REFFERENCES AND FOOTNOTES

1) G. Wittig and H. B. Frommeld, Chem. Ber., 97, 3548 (1964).

G. Wittig and H. Reiff, Angew. Chem., 80, 8 (1968).

2) G. Wittig, R. Roderer and S. Fischer, Tetrahedron Lett., 3517 (1973).

3) The structures of all products were verified by compatible spectral data ( ir, nmr and mass spectra).

4) The compound (9) is α-diprenylated product of (6).