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C-ALKYLATION OF ALLYL DITHIOCARBAMATES FOLLOWED BY ALLYLIC REARRANGEMENT

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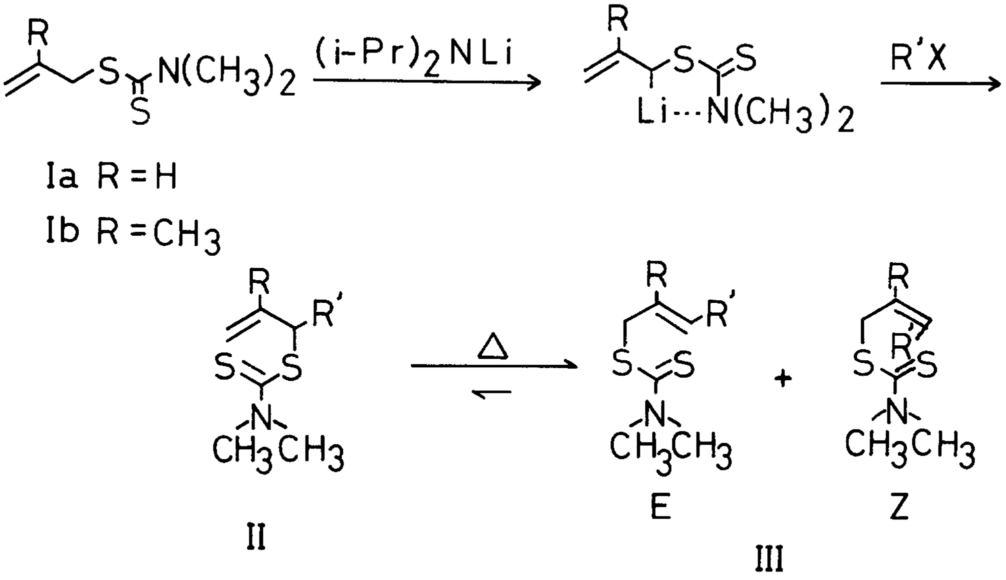
An allylic carbanion stabilized by sulfur has been shown by several investigators to be a useful reagent for olefin synthesis.[1-4] Recently, an elegant application of the cyclic analogs to the stereoselective synthesis of Cecropia juvenile hormones has been reported by two groups.[5,6] The author wishes to report here a novel olefin synthesis involving alkylation with simultaneous allylic rearrangement using allyl N,N-dimethylaminodithiocarbamates (I).

The allyl N,N-dimethylaminodithiocarbamates (I) can be readily prepared from commercially available allyl chlorides, dimethylamine, and carbon disulfide. Treatment of I with lithium diisopropylamide in THF at -60° in a nitrogen atmosphere led to the corresponding lithium salt, which might be stabilized through the contribution of a five-membered chelate ring. This would serve for minimization of possible side reactions such as migration of a double bond and cis-trans isomerization. The alkylation of the lithium salt with a slight excess of n-alkyl iodide gave exclusively the product (II) in an almost quantitative yield, but when isopropyl iodide was used, afforded a slightly less yield. It should be noticed that the reaction did not afford any side product such as a γ-alkylated product and migration of a double bond. The lithium salt also reacted with CO_2, aldehydes, ketones, esters, and acid chlorides in excellent yields. The product (II) gradually rearranged at room temperature, and rapidly over 100° into the product (III) quantitatively. It is outstanding that the thermodynamic equilibrium between II and III is shifted almost completely to the right. It was also



Ia R = H

Ib R = CH3

II

III

Table 1. Reactions of Ia with Alkyl Halides

alkyl halide	Bp (°C/mm)	yield (%)	J_{trans} (Hz)	Ir (cm^{-1})
MeI	116-120/3.5	96	15.3	969
EtI	117-121/3.5	94	15.3	970
n-PrI	130-133/3.5	96	15.3	970
i-PrI	120-125/3.5	90	15.4	972
n-BuI	135-136/3.5	96	15.3	970
$C_6H_5CH_2Br$	184-187/4.0	91	15.4	972

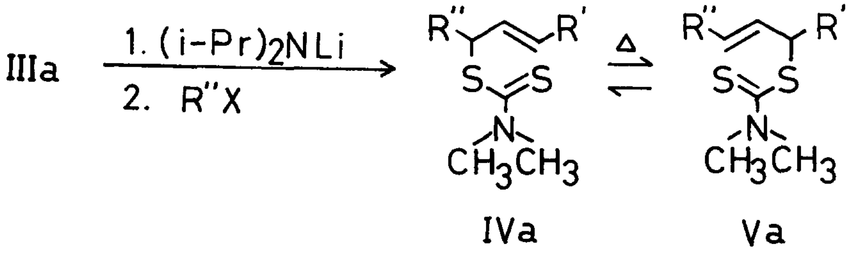
found that IIa rearranged stereoselectively to the *E*-isomer of IIIa, whereas IIb was converted into a stereoisomeric mixture of IIIb. The results were summarized in Tables 1 and 2. The yield of product was calculated from the amount of the distillate of III. The geometric configuration of IIIa was determined as follows.

Table 2. Reactions of Ib with Alkyl Halides

alkyl halide	Bp (°C/mm)	yield(%)	E:Z (%)
MeI	114-116/3.5	92	70:30
EtI	123-127/3.5	90	67:33
n-PrI	131-132/4.0	88	65:35
i-PrI	125-130/4.0	82	60:40
n-BuI	142-144/4.0	92	58:42
CH_3OCH_2Cl	140-141/3.5	84	54:46

The structure of 2-butenyl N,N-dimethylaminodithiocarbamate was confirmed by direct comparison with an authentic sample prepared independantly from commercially available trans-2-butenyl chloride and dimethylammonium N,N-dimethyldithiocarbamate. The sample showed the CH out of plane deformation band at 969 cm^{-1} (neat liquid) and the olefinic proton signals at δ = 5.56 and 5.78 ppm (J = 15.3 Hz, $CDCl_3$ solution). As shown in Table 1, all the products (IIIa) prepared in the work have almost the same J value and CH deformation frequency. Stereoisomeric ratios of IIIb were determined from the integration of the NMR signals. The results are in contrast to the high stereoselectivity of the rearrangement of allyl thionocarbamates and allyl dithiocarbamates (96.5% E and 5% Z isomer).[7]

It is interesting that the rearrangement product (III) can be further alkylated on the α-position to give IV in an excellent yield (Table 3). When R' and R" are the same, only one product was obtained (R'= R" = CH_3). However, in the other cases, distillation of the product afforded a mixture of IV and V.



IVa Va

Table 3. Reactions of IIIa ($R'= CH_3$) with Halides

halides	Bp (°C/mm)	yield (%)	IV:V
MeI	110-112/3.5	88	
EtI	113-118/4.0	86	53.5:46.5
Allyl Cl	120-125/3.5	95	64:36

Therefore, in order to obtain only IV, the product was separated at room temperature by column chromatography.

General Procedure — To a deep red solution of the lithium salt (0.022 mole) of I in 30 ml of THF, which was prepared from an equimoler mixture of I and lithium diisopropylamide below -50° in a nitrogen atmosphere, was slowly added below -45° a solution of alkyl halide (0.028 mole) in 5 ml of THF. When a n-alkyl halide was used, the red color of the solution disappeared within several min. After being stirred at -60° for 1 hr, the temperature was gradually raised to 0°. The solution was washed successively with 2M ammonium chloride and dilute HCl. The organic layer was dried over Na_2SO_4 and then submitted to distillation under reduced pressure or column chromatography.

The repetition of alkylation here outlined might be utilized for the synthesis of insect attractants and 1,5-dienes.

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