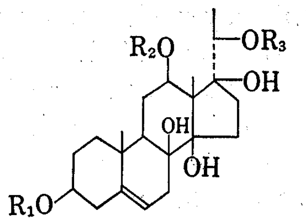
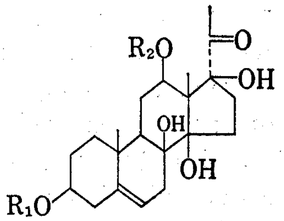
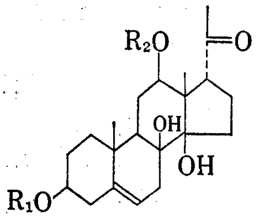
From these results, it is deduced that descinnamoylwilforine (one of the above ikemaoylsarcostins) is formed first from (IV) and the subsequent migration of the ikemaoyl group causes the formation of another ikemaoylsarcostin under the alkaline conditions.



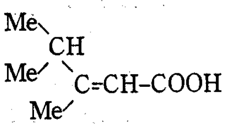
I: $R_1=R_2=R_3=H$
IV: $R_1=H$, $R_2=$cin, $R_3=$ikem
V: $R_1=R_3=H$, $R_2=$cin
X: $R_1=$Ac, $R_2=$cin, $R_3=$ikem
XII: $R_1=$Ac, $R_2=$ikem, $R_3=H$
XIII: $R_1=$Ac, $R_2=$ikem, $R_3=$cin
cin: cinnamoyl
ikem: ikemaoyl



II: $R_1=R_2=H$
VI: $R_1=H$, $R_2=$ikem
VII: $R_1=H$, $R_2=$cin
XI: $R_1=$Ac, $R_2=$ikem



III: $R_1=R_2=H$
IX: $R_1=H$, $R_2=$ikem



$$(CH_3)_2CH-C(CH_3)=CH-COOH$$

VIII

In order to confirm the position of the ester linkages of IV the following experiments were carried out. Caudatin acetate (XI)[5] was reduced with $NaBH_4$. The product (XII) mp 193—199°, δ 1.16 (3H, d, $J=6$ Hz, C-21-Me), 3.62 (1H, q, $J=6$ Hz, C-20-H), was treated with cinnamoyl chloride in pyridine to give 3-O-acetyl, 12-O-ikemaoyl, 20-O-cinnamoyl sarcostin (XIII) which was not identified with wilforine acetate (X) on TLC. The finding suggests that the structure of wilforine is given in terms of the formula (IV).

Acknowledgement We wish to express our thanks to Professor Dug-Ryong Hahn (Seoul) for collection of the plants. Thanks are due to Mrs. Araki for 100 MHz spectral measurement, to Miss Kakizaki for elemental analysis, and to Miss Takahashi for mass spectral measurement.

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Chemistry of 2-Substituted Thiothiazoline. V. Reaction of Dianion of 2-Propargylthiothiazoline with Benzaldehyde

In the preceding communication we reported the unique reactivities of the dianion of proparglythiothiazoline and the 1,5-diyne system synthesis using these 2-alkynylthiothiazolinelithium species.[1] It is of interest to investigate further the properties of these species in the reactions with other electrophiles such as aldehyde. In this viewpoint, we studied the reactions of 2-proparglythiothiazolinelithium and 2-phenylproparglythiothiazolinelithium with benzaldehyde.

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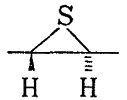
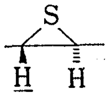
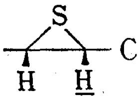
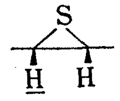
[1] K. Hirai and Y. Kishida, *Tetrahedron Letters*, 1972, 2117.

A white precipitated dilithium salt (IIa), prepared by the reported procedure, was treated with an equimolar benzaldehyde at −60° in THF and then the reaction temperature was gradually raised to 0°. The whole mixture was poured into ice–water and extraction with ethyl acetate gave mainly three products (III, IV and VI) (Chart 1). The separation of the mixture was performed by preparative silica gel thin–layer chromatography.[2] The least polar part (20% yield) consisted of two components (IIIa and IVa). One component (IIIa) was found to be a *ca* 1:1 mixture of two geometrical isomers by the nuclear magnetic resonance (NMR),[3] and the *trans*-isomer was separated by an exhaustive re-chromatography. The infrared (IR) of this isomer showed a strong $C\equiv C$-H stretching vibration at 3340 cm^{-1} and the mass spectrum showed the molecular ion peak at *m/e* 160 which corresponded to $C_{10}H_8S$ and the characteristic base peak at *m/e* 128 (M-32) which arised by extrusion of the sulfur atom. The NMR showed the signals at δ 2.25 (1H, d, J=2 H_z, ≡-H), 3.35 (1H, d of d, J=2 and 5 Hz,  C≡),[4] 4.05 (1H, d, J=5 Hz,  C≡) and 7.0—7.5 (5H, C_6-$\underline{H}_5$-). From these data this isomer was determined as *trans*-4-phenyl-1-butyn-3,4-episulfide (IIIa-*trans*). The counterpart of the isomer showed its NMR signals at δ 2.04 (1H, d, J=2 Hz, -$C\equiv C$-$\underline{H}$), 3.55 (1H, d of d, J=2 and 7 Hz,  C≡), 4.0 (1H, d, J=7 Hz,  C≡) which resembled those of the *trans*-isomer of IIIa. Thus this isomer was determined as *cis*-4-phenyl-1-butyn-3,4-episulfide (IIIa-*cis*). Furthermore this *cis-trans* mixture (IIIa) was desulfurized to IVa under the distillation condition (110°/10 mmHg, 20 min) [conversion ratio: 53% determined by the elemental analysis and NMR]. These facts strongly suggested that IVa was the secondary product which would be formed in the isolation process.

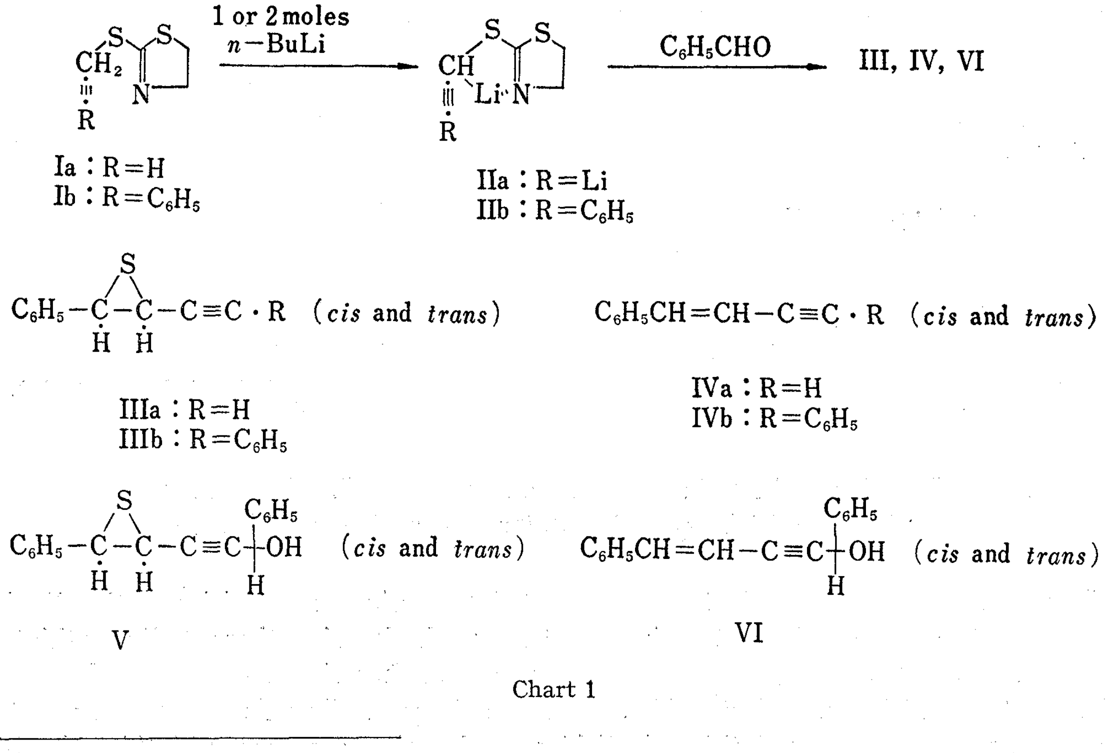


Chart 1

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[2] Merck Preparative TLC-plates Silica Gel F_{254} pre-coated, layer thickness 2 mm were used.

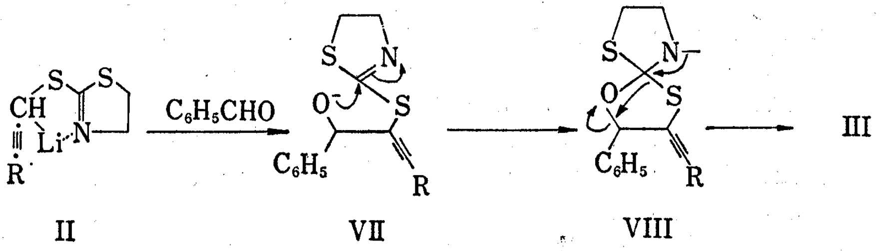
[3] NMR spectra were taken in $CDCl_3$ on Varian A-60 instrument and chemical shifts are reported in δ, ppm, downfield from TMS as an internal standard, s: singlet; d: doublet; t: triplet.

[4] K. Tori, T. Komeno, and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964) and the references cited therein.

The component, IVa, showed M+ peak at m/e 128, which corresponded to $C_{10}H_8$. The IR showed a strong C≡C-H stretching vibration at 3320 and 2100 cm^{-1}, and the UV maxima at 227 and 277 nm in EtOH. The NMR indicated that IVa was again a 1:1 mixture of two geometrical isomers. A precise analysis of the spectrum suggested that the *trans*-isomer exihibited its signals at δ 3.0 (1H, d, J=1.8 Hz, ≡$\underline{H}$), 6.10 (1H, d of d, J=17 and 1.8 Hz, $-\overset{\text{H}}{\text{C}}{=}\underset{\underline{\text{H}}}{\text{C}}-\text{C}{\equiv}$), 7.0 (1H, d, J=17 Hz, $-\overset{\underline{\text{H}}}{\text{C}}{=}\underset{\text{H}}{\text{C}}-\text{C}{\equiv}$), 7.2—7.5 (5H) and that the *cis*-isomer exhibited its signals at δ 3.30 (1H, d, J=1.8 Hz, ≡$\underline{H}$), 5.65 (1H, d of d, J=11 and 1.8 Hz), 6.66 (1H, d, J=11 Hz), 7.2—7.5 (3H). The rest of the two aromatic protons at δ 7.85 (2H, d of d, J=7 and 3.5 Hz) would be assigned to the *ortho*-protons in the benzene ring and the chemical shift in such a low field would be due to the effect of anisotropy of the triple bond in *cis*-IVa. Thus IVa was determined to be a mixture of *cis*- and *trans*-4-phenyl-2-buten-1-yne.[5] The structure of the third product (25% yield) was determined as 1,5-diphenyl-4-penten-2-yn-1-ol (VI) by usual manners. [UV: λ_{max}^{EtOH} 229 and 285 nm. IR: ν_{max}^{film} 3200—3650 (OH), 2200 (C≡C), 1600 (C=C), 700 cm^{-1}. Mass Spectrum: M+ at m/e 234 ($C_{17}H_{14}O$). NMR: δ 5.65 (1H), 5.37 (1H, d of d, J=11 and 1.4 Hz), 6.70 (1H, d, J=11 Hz) and 7.20—7.90 (5H,) for *cis*-isomer, 6.20 (1H, d of d, J=17 and 1.4 Hz), 7.0 (1H, d, J=17 Hz), 7.20—7.90 (5H) for *trans*-isomer]. The isolation of the episulfide (V), which would be a precursor of VI, was not successful partly because of the contamination of VI, but the presence of V was strontly suggested by the mass spectrometry [M+ at m/e 266 ($C_{17}H_{14}OS$) and the base peak at 234 (M-32)] and NMR.

Parallel results were obtained with 2-phenylproparglythiothiazolinelihium (IIb) and mainly two products were isolated. The less polar product (20% yield) was *trans*-1,4-diphenyl-1-butyn-3,4-episulfide (IIIb) [M+ at m/e 236 ($C_{16}H_{12}S$), base peak at 204 (M-32). NMR: δ 3.65 (1H, d, J=5 Hz), 4.17 (1H, d, J=5 Hz) and 7.25—7.55 (10H, $C_6\underline{H}_5\times2$)]. The isolation of the products corresponding to *cis*-IIIb and en-yne (IVb) in pure state was unsuccessful. The second product (20% yield) was a crystalline, mp 132—134° and found to be identical with d, 1-benzoin in all respects.

The formation of episulfides (IIIa, b) would be considered as described in Chart 2. Nucleophilic attack at C=O function of benzaldehyde by the lithium salt (II) would occur to give VII, which cyclized spontaneously affording a spiro-intermediate VIII. The intermediate (VIII) would then collapsed to give episulfides (IIIa, b) (*not epoxide !*), and further to the en-yne derivatives (IVa, b) by a thermal process in the isolation stage.



(R=Li or C_6H_5)

Chart 2

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[5] H. Igeta, T. Tsuchiya, and T. Nakai, *Tetrahedron Letters*, **1969**, 2667.