# SYNTHESIS OF DIVINYL DERIVATIVES OF 5-SUBSTITUTED

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1,2,4-TRIAZOLE-3-THIONES
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Derivatives of 1,2,4-triazole-3-thione containing two vinyl groups are promising monomers for the preparation of cross-linked copolymers with a high content of nitrogen and sulfur heteroatoms having ion-exchange and complexation properties [1]. We have previously described the synthesis of two divinyl derivatives of unsubstituted triazolethione [2]. In order to expand the range of such compounds, we studied the reaction of 5-methyl- (I), 5-phenyl- (II), and 5- $\alpha$ -furyl-1,2,4-triazole-3-thione (III) with acetylene.

Triazoles (I) and (III) in the presence of alkali add one acetylene molecule [3]. An increase in the reaction time yields the product of the addition of two acetylene molecules to (I) in yields up to 50%. The substitution of the alkaline catalyst by CuCl facilitates the formation of divinyl derivatives [2]. However, the use of CuCl in this case led to a decrease in the yield of the desired product. N-Vinyl-3-vinylthio-5-methyl-1,2,4-triazoles (IVa) and (IVb) were obtained in yields up to 64% in the presence of cadmium acetate. On the other hand, the use of CuCl as the catalyst facilitates the synthesis of N-vinyl-3-vinylthio-5-phenyl- (Va) and (Vb) and N-vinyl-3-vinylthio-5- $\alpha$ -furyl-1,2,4-triazoles (VIa) and (VIb). The yield of divinyl monomers (VIa) and (VIb) was only 9% due to the significant tar formation, apparently as a result of the presence of the furyl substituent.



Preparative gas-liquid chromatography was used to isolate isomers (IVa) and (IVb). As a consequence of the high boiling points of the divinyl products of (V), (VIa), and (VIb), separate isomers could not be isolated. These isomers were identified by PMR spectroscopy. Analysis of these spectra (Table 1) showed that the products of the reaction of (I)-(III) with acetylene are mixtures of two divinyl isomers. In the compounds synthesized (IV)-(VI), two groups of vicinal coupling constants were found between the vinyl fragment protons,  ${}^{3}J_{AX} = 8.7-8.8$  Hz,  ${}^{3}J_{BX} = 15.2-15.6$  Hz,  ${}^{3}J_{AX} = 9.5-9.9$  Hz, and  ${}^{3}J_{BX} = 17.0-17.2$  Hz, which indicates the existence of two vinyl groups at different nitrogen and sulfur atoms, respectively [4, 5].

In one of the isomers, the difference of the chemical shifts for  $H_A$  and  $H_B$  ( $\Delta\delta_{AB}$ ) is 0.09-0.12 ppm less, the <sup>2</sup>J<sub>AB</sub> coupling constant is 0.6-0.8 Hz greater while the shielding of the H<sub>X</sub> nucleus is 0.15-0.19 ppm greater than for the second isomer (see Table 1). Comparison of these parameters in the compounds synthesized (IVa)-(VIa), (IVb)-(VIb), and in unsubstituted 3-vinyl-3-vinylthio-1,2,4-triazole (VIIa) and 1-vinyl-3-vinylthio-1,2,4-triazole (VIIb) [2] indicates that (IVa)-(VIa) are the N<sup>2</sup>,S-divinyl derivatives, while (IVb)-(VIb) are the N<sup>1</sup>,Sdivinyl derivatives.

### EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-497 spectrometer at 100 MHz in CDCl<sub>3</sub> with HMDS as the internal standard. The IR spectra were taken neat on a Specord IR-75 spectrophotometer.

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TABLE 1. PMR Spectral Parameters for

						нх	$\mathbf{H}_{\mathbf{A}}$	
	N- mail	δ, ppm				Coupling constant J, Hz		
Compound	group position	A	В	x	$\Delta\delta_{AB}$	<sup>2</sup> J <sub>АВ</sub> *	<sup>3</sup> J <sub>AX</sub>	₅J <sub>BX</sub>
(IVa)	-2 3	4,94 5,50	<b>5</b> ,66 <b>5</b> ,48	.6,86 6,69	$-0,72 \\ 0,02$	$-0,9 \\ -0,6$	8,8 9,6	15,4 17,1
(ІVъ)	1 3	$4,95 \\ 5,38$	$5,68 \\ 5,45$	6,88 6,88	$-0,73 \\ -0,07$	-0,7 0	8,8 9,9	15,4 17,0
(Va)	$\frac{2}{3}$	$5,00 \\ 5,48$	5,83 5,47	$6,98 \\ 6,82$	$-0,83 \\ 0,01$	$-0.8 \\ -0.6$	8,7 9,5	15,2 17,0
(V <sub>b</sub> )	1 3	$4,96 \\ 5,40$	$5.83 \\ 5,51$	$^{6,96}_{7,00}$	$-0,87 \\ -0,11$	-0,6	8,7 9,6	15,2 17,2
(VIa)	23	5,08 5,57	$5,88 \\ 5,56$	7,01 6,85	$-0,80 \\ 0,01$	-1,1 -0,8	8,8 9,6	15,4 17,2
(VIb)	1 3 2	<b>5</b> ,07 5,48 5,00	5,90 5,57 5,73	7,61 7,00 6,95	0,83 0,09 0,73	$ \begin{array}{c c} -0.9 \\ 0 \\ -0.9 \end{array} $	8,8 9,9 8,8	15,3 17,2 15,4
(VIIa)	3	5,49	5,47	6,73	0,02	-0,7	9,5	17,0
(VIIb)	1 3	4,97 5,41	$5,69 \\ 5,48$	6,95 6,88	$^{-0,72}_{-0,07}$	$\begin{vmatrix} -1,3\\0 \end{vmatrix}$	8,8 9,8	15,6 17,2

\*The negative sign for the coupling constant  ${}^{2}J_{AB}$  was assigned in accord with previous work [5].

Preparative gas-liquid chromatography was carried out on a PAKhV-0.7 chromatograph with a column packed with 20% PKhMS-4 on Chromaton. The column temperature was 190°C.

<u>N-Vinyl-3-vinylthio-5-methyl-1,2,4-triazoles (IVa) and (IVb)</u>. A mixture of 6 g (0.05 mmole) triazole (I), 1.2 g (20%) cadmium acetate, and 100 ml dioxane was added to a rotating steel autoclave. Acetylene was introduced from a tank with 15 atm initial pressure. The reaction mixture was heated for 2 h at 180°C. At the end of the reaction, the precipitate was filtered off. The solvent was distilled off, and the residue was distilled in vacuum to give a fraction of 5.8 g (64%) with bp 88-153°C (2 mm). Preparative gas-liquid chromatography was used to separate 65% isomer (IVa),  $n_D^{20}$  1.5650, and 35% isomer (IVb),  $n_D^{20}$  1.5748. IR spectrum: 1645 (NCH=CH<sub>2</sub>), 1590 cm<sup>-1</sup> (SCH=CH<sub>2</sub>). Found: C 50.6; H 5.4; N 24.9; S 18.9%. Calculated for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>S: C 50.3; H 5.4; N 25.1; S 19.2%.

<u>N-Vinyl-3-vinylthio-5-phenyl-1,2,4-triazoles (Va) and (Vb)</u>. A mixture of 10 g (0.06 mole) triazole (II), 1 g (10%) CuCl, and 200 ml dioxane was saturated with acetylene and heated in an autoclave for 6 h at 160°C. After removal of the dioxane, the residue was distilled in vacuum to give 3.9 g (69%) of a fraction with bp 150-167°C (2 mm),  $n_D^{20}$  1.6250. IR spectrum: 1650 (NCH=CH<sub>2</sub>), 1585 cm<sup>-1</sup> (SCH=CH<sub>2</sub>). Found: C 62.8; H 4.9; N 18.3; S 13.8%. Calculated for  $C_{12}H_{11}N_3S$ : C 62.8; H 4.8; N 18.3; S 14.02%.

N-vinyl-3-vinylthio-5- $\alpha$ -furyl-1,2,4-triazoles (VIa) and (VIb) were prepared by analogy to the procedure for the preparation of (V). The reaction time was 0.5 h. Column chromatography on alumina using benzene as the eluent gave 0.7 g (9%) of a liquid fraction with np<sup>20</sup> 1.5880. IR spectrum: 6140 (NCH=CH<sub>2</sub>), 1598 cm<sup>-1</sup> (SCH=CH<sub>2</sub>). Found: C 54.6; H 4.0; N 19.0; S 14.0%. Calculated for C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>SO: C 54.8; H 4.1; N 19.2; S 14.6%.

# CONCLUSIONS

The reaction of 5-methyl-, 5-phenyl- and 5- $\alpha$ -furyl-1,2,4-triazole-3-thiones with acetylene gave their N<sup>1</sup>, S- and N<sup>2</sup>, S-divinyl derivatives.

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### $\alpha$ -ORGANYLTHIOCROTONALDEHYDES

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 $\alpha$ -Organylthio-substituted  $\alpha$ , $\beta$ -unsaturated carbonyl compounds are useful intermediates in organic synthesis [1]. The reported methods for the preparation of  $\beta$ -alkyl- $\alpha$ -organylthioacroleins entail numerous steps and not readily available starting reagents [2].

We have developed a method for the synthesis of  $\alpha$ -organylthiocrotonaldehydes based on the ipso-substitution of a chlorine atom in an  $\alpha$ -chlorocrotonaldehyde:

 $\begin{array}{c} \text{CH}_{3}\text{CH} = \text{CCI}-\text{CHO} + \text{RSH} \xrightarrow{\text{K}_{3}\text{CO}_{3}} \text{CH}_{3}\text{CH}(\text{SR})\text{CCICHO} \rightarrow \\ (I) \\ \text{CH}_{3}\text{CH}(\text{SR})\text{CH}(\text{SR})\text{CHO} \rightarrow \text{CH}_{3}-\text{CH} = \text{C}(\text{SR})\text{CHO} \\ (\text{III}) \\ (\text{III}) \\ \end{array}$ 

R = Bu (a), Ph (<sup>b</sup>).

In the case of 40-50° reaction temperature and a stoichiometric reagent ratio, the yield of (II) is 60-70%. At 20°C with excess butyl mercaptan, the major reaction product is 2,3-bis(butylthio)butyraldehyde (IIIa) in 50% yield. This result indicates that in the case of excess mercaptan and reduced temperature, the loss of thiol in the last step is hindered. The yields, physical constants, and elemental analysis data of the compounds synthesized are given in Table 1, while the PMR and IR spectral parameters are given in Table 2.

 $\alpha$ -Organylcrotonaldehydes condense with hydrazine derivatives such as 2,4-dinitrophenylhydrazone or thiosemicarbazone in acid medium. In contrast to  $\alpha$ -alkoxyacroleins, this reaction proceeds only with the participation of the carbonyl group without subsequent hydrolysis of alcoholysis [3]:

 $\begin{array}{ll} CH_{3}CH=C(SR)CHO\ +\ H_{2}NNHR'\ \rightarrow\ CH_{3}CH=C(SR)CH=NNHR'\ +\ H_{2}O\ & (IV)\\ R\ =\ Bu,\ R'\ =\ C_{6}H_{3}(NO_{2})_{2}\ (a);\ R\ =\ Ph,\ R'\ =\ C_{6}H_{3}(NO_{2})_{2}\ (b);\ R\ =\ Ph,\\ R'\ =\ C(S)NH_{3}\ (c). \end{array}$ 

The reaction of  $\alpha$ -butylthiocrotonaldehyde with tetraethoxysilane at 20°C in the presence of  $H_3PO_4$ , according to our previous work [4], leads to acetal (V):

$$(IIa) + (EtO)_4Si \xrightarrow{C_2H_3OH} CH_3CH = C(SBu)CH(OEt)_2$$
(V)

PMR spectroscopy indicates that the yield of (V) was 60%, but this product could not be isolated by distillation.

In contrast to  $\alpha$ -alkylthioacroleins,  $\alpha$ -butylthiocrotonaldehyde does not undergo cyclodimerization even at 100°C for 11 h [5].

# EXPERIMENTAL

The PMR spectra were taken on a Jeol FX-90 X spectrometer at 89.95 MHz in CCl<sub>4</sub>. The IR spectra were taken neat on a UR-20 spectrometer.

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