HOMOLYTIC ADDITION OF THIOPHENOL TO TRIVINYLMETHANE AND RELATED COMPOUNDS

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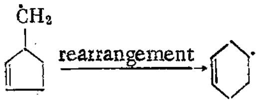
The rearrangement of homoallylic radicals of type A to radicals of type B [Scheme (1)] is of great interest, since the rearrangements of radicals, with a cleavage of the C – C bonds, have received little study:

$$\underset{A}{CH_2{=}CHCR_2\dot{C}HR'} \xrightarrow{\text{rearrangement}} \underset{B}{CH_2{=}CHCHR'\dot{C}R_2}. \qquad (1)$$

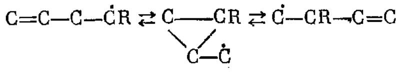
The possibility of such a rearrangement was first indicated in [1] while studying the complex process for the formation of p-xylene during the gas-phase dehydrogenation of 2,4,4-trimethyl-2-pentene with iodine at 450-500°. Subsequently it was shown that the Δ^2-cyclopentenylmethyl radical, formed during the decomposition of tert-butyl-Δ^2-cyclopentenyl peroxyacetate at 140°, undergoes isomerization to the 4-cyclohexenyl radical [2]:



(2)

In [3] the theory was expressed that the previously described rearrangement of the alkenyl radicals, formed during the addition of the isopropyl and tert-butyl radicals to either acetylene [4] or propyne [5], includes the step of the isomerization of the homoallylic radical C, with the intermediate formation of the cyclopropylcarbinyl radical D according to Scheme (3).

A rearrangement that proceeds easily is described in a series of papers [6-9], which formally represents 1,2-migration of the vinyl group; for example, the formation of 1-pentene, together with 3-methyl-1-butene, in the decarbonylation of either 3-methyl-4-pentenal or 2-methyl-4-pentenal [6]. The authors postulate that the rearrangement goes in two steps: first the homoallylic radical C is converted to the cyclopropylcarbinyl radical D, in which the opening of the ring leads to the formation of both the starting radicals C and the rearranged radicals E:



$$C{=}C{-}C{-}\dot{C}R \rightleftarrows \underset{C-\dot{C}}{C{-}CR} \rightleftarrows \dot{C}{-}CR{-}C{=}C \qquad (3)$$

C D E

The authors state that they were unable to reliably identify the intermediate formation of radicals of the D type, since in the mentioned cases of the decarbonylation of 2-methyl-4-pentenal and 3-methyl-4-pentenal the formation of 1,2-dimethylcyclopropane, if it did occur, did not exceed a yield of 0.12% of theory (identified by gas – liquid chromatography (GLC) only from the retention time). The formation of the corresponding cyclopropyl derivatives failed to occur during the decarbonylation of trans-3-methyl-4-hexenal [7], trans-2-methyl-4-hexenal [7], 4-pentenal-2,2-d_2 [8] and cis-4-pentenal-5d [8, 9].

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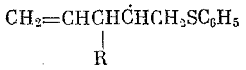
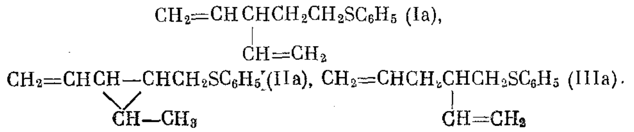
In order to study the behavior of homoallylic radicals of the type



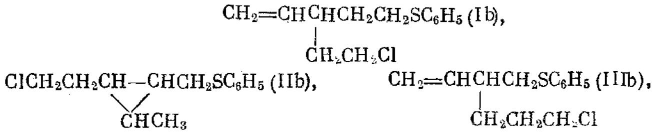
$CH_2{=}CHCH(R)\dot{C}HCH_2SC_6H_5$ R = $CH_2{=}CH{-}$, $ClCH_2CH_2{-}$, $C_6H_5SCH_2CH_2{-}$

we studied the homolytic addition of thiophenol to trivinylmethane, 5-chloro-3-vinyl-1-pentene and 5-phenylthio-3-vinyl-1-pentene. In the first case (R = $-CH=CH_2$) the formation of products with the following structure could be expected:



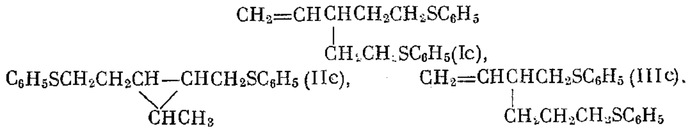
(Ia), (IIa), (IIIa).

In the case of 5-chloro-3-vinyl-1-pentene (R = $ClCH_2CH_2-$) the corresponding products would have the structure:



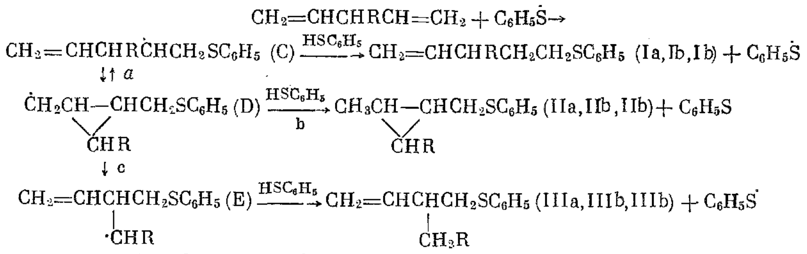
(Ib), (IIb), (IIIb),

and in the case of 5-phenylthio-3-vinyl-1-pentene (R = $-CH_2CH_2SC_6H_5$) the structure:



(Ic), (IIc), (IIIc).

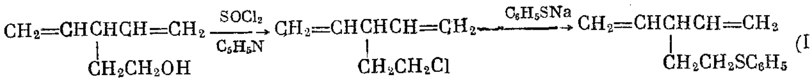
In this connection it seemed most important to us to identify the intermediate formation of the cyclopropylcarbinyl radicals of the D type [see Scheme (3)]. In selecting a method for generating the homoallylic radicals we started with the following considerations. In the formation of radicals by the homolytic addition of any addenda to suitable unsaturated compounds the possibility exists of varying the rate of chain transfer as a function of the nature of the taken addendum. In the generation of the starting radicals by the decarbonylation of aldehydes the transfer of the chain is accomplished only via a relatively inefficient chain carrier, which an aldehyde is. The selection of trivinylmethane excludes the possibility of migration of any other groups, except vinyl, in the initially formed C radicals, and, in addition to this, these radicals are doubly homoallylic. The selection of thiophenol – an efficient chain carrier – as the addendum gave hope that the formation of the intermediate radicals of the D type could be fixed as the compounds (IIa), (IIb), and (IIc), since the rate of chain transfer by the D radicals [step b, Scheme (4)] could prove to be faster than the rate of the competing reactions of ring opening (steps *a* and c).



(4)

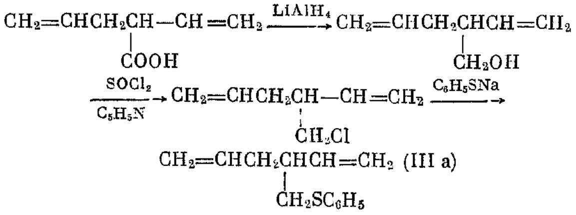
a—R = $CH_2{=}CH{-}$; b)—R = $ClCH_2CH_2{-}$; c)—R = $C_6H_5SCH_2CH_2{-}$

The most interesting results were obtained by us when studying the reaction of thiophenol with trivinylmethane, which was run either at 80° in the presence of benzoyl peroxide, or at 25° with UV-illumination. The reaction mixture was analyzed by GLC and by the paramagnetic resonance (PMR) method. In order to identify the reaction products we synthesized compounds (Ia) and (IIIa) [see Scheme (4), R = $-CH=CH_2$) by an independent route. 5-Phenylthio-3-vinyl-1-pentene (Ia) was obtained according to Scheme (5):



$$CH_2{=}CHCH(CH_2CH_2OH)CH{=}CH_2 \xrightarrow[C_5H_5N]{SOCl_2} CH_2{=}CHCH(CH_2CH_2Cl)CH{=}CH_2 \xrightarrow{C_6H_5SNa} CH_2{=}CHCH(CH_2CH_2SC_6H_5)CH{=}CH_2 \text{ (Ia)} \quad (5)$$

3-(Phenylthiomethyl)-1,5-hexadiene (IIIa) was obtained according to Scheme (6):



$$\underset{\displaystyle COOH}{CH_2{=}CHCH_2CH}{-}CH{=}CH_2 \xrightarrow{LiAlH_4} CH_2{=}CHCH_2\underset{\displaystyle CH_2OH}{CH}CH{=}CH_2 \xrightarrow[C_5H_5N]{SOCl_2} CH_2{=}CHCH_2\underset{\displaystyle CH_2Cl}{CH}{-}CH{=}CH_2 \xrightarrow{C_6H_5SNa} CH_2{=}CHCH_2\underset{\displaystyle CH_2SC_6H_5}{CH}CH{=}CH_2 \text{ (III a)} \qquad (6)$$

The constants of the obtained new compounds are given in Table 1, while their structure was verified by the PMR spectra [10]. Using synthetic mixtures, a method was developed for the quantitative determination of small amounts of product (IIIa) in admixture with product (Ia) employing GLC and the PMR method. The accuracy of these methods was 1-2 absolute %.

An analysis of the reaction mixtures by GLC disclosed that thiophenol adds to trivinylmethane with considerable difficulty: in 10 h the yield of addition products is 8-12% of theory; 5-phenylthio-3-vinyl-1-pentene (Ia) was identified in all of the experiments, while 3-(phenylthiomethyl)-1,5-pentadiene (IIIa) was not found. The PMR spectra of the reaction mixtures made it possible to identify in the mixture, together with unreacted trivinylmethane and product (I), also the presence of compounds containing the methyl and cyclopropyl groups. This gives us reason to postulate the formation of the expected 1-methyl-2-vinyl-3-phenylthiocyclopropane (IIa). By means of control experiments it was shown that neither trivinylmethane nor product (Ia) undergo any changes under the reaction conditions. A comparison of the PMR spectra of trivinylmethane with the spectra of molecules of the type of (Ia) and (IIIa), made by us in [10], made it possible to establish that neither of these products gives signals in a stronger field than 1.3 δ.

Consequently, the appearance in the PMR spectrum of the reaction mixture, obtained by the reaction of trivinylmethane with thiophenol, of signals in the region from 0.3 to 1.5 δ can be satisfactorily explained only by assuming the appearance in the reaction mixture of substances containing cyclopropyl and methyl groups. Conclusive proof in support of the cyclopropyl origin of the main portion of these signals is the shape of the envelope line, the great width, and also the position of the "centers of gravity" of the signals (~0.85 and 1.25 δ). The maximum on the envelope line of the PMR spectrum of cyclopropane is found at 0.3 δ [11]. At the same time, in the methyl ester of cyclopropanecarboxylic acid this maximum is shifted to 0.93 δ [11]. In allylcyclopropane [12] the signals of the cyclopropyl protons are found in the region from 0.2 to 1.33 δ; in methylthiomethylcyclopropane [13] this region is bounded by the values 0.2 ≤ δ ≤ 0.9. The vinyl signals in allylcyclopropane and methylthiovinylcyclopropane are found in the region from 4.8 to 5.9 δ. As a result, the signals observed by us fall in a range that is limited by the indicated

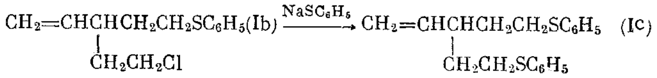
TABLE 1

Formula	Yield, % of theory	Bp., °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found					Calculated				
					MR	C, %	H, %	Cl, %	S, %	*MR*	C, %	H, %	Cl, %	S, %
$CH_2{=}CH\underset{CH_2CH_2Cl}{CH}CH{=}CH_2$	60	66 (60)	1,4525	0,9167	38,48	64,32 64,09	8,60 8,49	26,70 26,79	— —	38,46	64,37	8,49	27,14	—
$CH_2{=}CH\underset{CH_2CH_2SC_6H_5}{CH}CH{=}CH_2$	73	104 (2)	1,5541	0,9864	66,40	75,87 76,21	7,97 7,85	— —	15,24 15,37	66,10	76,41	7,89	—	15,69
$CH_2{=}CHCH_2\underset{CH_2OH}{CH}CH{=}CH_2$	90	59 (11)	1,4560	0,8655	35,22	74,54 74,74	10,84 11,00	—	—	35,13	74,95	10,81	—	—
$CH_2{=}CHCH_2\underset{CH_2Cl}{CH}CH{=}CH_2$	77	76 (74)	1,4549	0,9223	38,42	64,25 64,46	8,58 8,58	27,00 26,70	—	38,46	64,37	8,49	27,14	—
$CH_2{=}CHCH_2\underset{CH_2SC_6H_5}{CH}CH{=}CH_2$	66	90 (1)	1,5570	0,9916	66,33	75,95 76,16	7,85 7,95	— —	15,75 15,78	66,10	76,41	7,89	—	15,69

members of the cyclopropyl derivatives. The great width of the observed line and the complexity of the structure of this portion of the spectrum can be associated with the formation of stereoisomeric trisubstituted cyclopropanes in the reaction process.

The remaining signals in the PMR spectra are easily identified in harmony with the data given in [10]. Thus, the presence of a characteristic quadruplet ($\delta = 3.33$), with traces of further complex splitting, proves the presence of the trivinylmethane molecule in the mixture, while the signals with shifts of 1.6 and 2.74 δ have a shape and position that coincide well with the signals of the methylene protons in 5-phenylthio-3-vinyl-1-pentene (Ia). Integration of the spectrum of the reaction mixture disclosed that it contains approximately equal amounts of cyclopropyl products and 5-phenylthio-3-vinyl-1- pentene. Taking into account the total yield of adducts (8-12%), it must be assumed that the yield of 5-phenylthio-3-vinyl-1-pentene (Ia) and 1-methyl-2-vinyl-3-phenylthiomethylcyclopropanes (IIa) is each equal to 4-6%.

The addition of thiophenol to 5-chloro-3-vinyl-1-pentene and 5-phenylthio-3-vinyl-1-pentene in the presence of benzoyl peroxide at 80° went smoothly, and 1-chloro-3-vinyl-5-phenylthiopentane (Ib) and 3-vinyl-1,5-(bisphenylthio)pentane (Ic) were respectively obtained in good yields. A study of the reaction mixtures by the PMR method disclosed that if the formation of the cyclopropyl products (IIb and IIc, respectively) did take place, then their yield was insignificant. Apparently, the initially formed C radicals [see Scheme (4), R = $-CH_2CH_2Cl$ (a), R = $-CH_2CH_2SC_6H_5$ (c)] react very rapidly with thiophenol. The structure of products (Ib) and (Ic) was proved by the PMR method. In addition, product (Ib) was converted to (Ic) by the scheme:



$$\underset{\displaystyle CH_2CH_2Cl}{CH_2{=}CHCHCH_2CH_2SC_6H_5}\,(Ib) \xrightarrow{NaSC_6H_5} \underset{\displaystyle CH_2CH_2SC_6H_5}{CH_2{=}CHCHCH_2CH_2SC_6H_5}\ (Ic)$$

The PMR spectra of the products (Ic), obtained by the two methods, are identical.

EXPERIMENTAL

Addition of Thiophenol to Trivinylmethane. A solution of 0.94 g of trivinylmethane in benzene (2 M solution) and 1.10 g of thiophenol were heated with benzoyl peroxide (5 mole %) in a sealed ampul for 10 h at 80°. The experiments using UV-illumination were run in a quartz ampul at 25°. Analysis of the reaction mixtures by GLC was run using a flame-ionization detector, a 3-meter column with an inside diameter of 2 mm, Celite-545 as the solid phase, high-vacuum silicone grease (5%) as the stationary phase, nitrogen as the carrier gas, a flow rate of 15 ml/min, a column temperature of 105°, and a vaporizer temperature of 190°. The following were identified in the reaction mixtures by GLC: trivinylmethane, 5-phenylthio-3-vinyl-1-pentene (Ia), thiophenol, and diphenyl disulfide.

Analysis by the PMR method was run using "Hitachi H-60" and Perkin – Elmer P-12 spectrometers. The chemical shifts are given on the δ-scale (the signal for tetramethylsilane is taken as equal to zero), while hexamethyldisiloxane ($\delta = 0.05$) was used as the internal standard. Besides the enumerated compounds, cyclopropane derivatives were found in the reaction mixtures by the PMR method.

Addition of Thiophenol to 5-Phenylthio-3-vinyl-1-pentene. A solution of 2.0 g of 5-phenylthio-3-vinyl-1-pentene in benzene (2 M solution) and 1.1 g of thiophenol were heated with benzoyl peroxide (5 mole %) at 80° for 10 h in an argon stream. The solvent was removed by distillation. Vacuum-distillation of the residue gave, besides the starting product, 1.0 g (30% of theory) of (Ic), bp 188° (1 mm): n_D^{20} 1.6030; d_4^{20} 1.0928. Found: C 72.42; 72.40; H 6.98; 6.99; S 20.41; 20.16%; MR 98.85. $C_{19}H_{22}S_2$. Calculated: C 72.56; H 7.05; S 20.39%; MR 99.07.

In the PMR spectrum of compound (Ic) are observed the AA'BB' signals from the methylene protons in the $CH_2CH_2SC_6H_5$ groups ($\delta_A = 1.55$; $\delta_B = 2.72$), the complex multiplet of a methine proton with $\delta = 2.20$, and the signals of the ABC system from the vinyl group with a center of gravity of $\delta \approx 5$. The integral intensities corroborate the validity of the assignments.

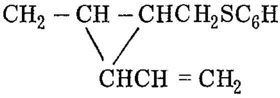
Addition of Thiophenol to 5-Chloro-3-vinyl-1-pentene. The experiment was run in the same manner as the preceding. Here from 1.3 g of 5-chloro-3-vinyl-1-pentene and 1.1 g of thiophenol, after distillation, was obtained 1.45 g (60%) of (Ib), bp 130° (2 mm); n_D^{20} 1.5653; d_4^{20} 1.0944. Found: C 65.19; 65.00; H 6.88; 6.82; S 13.31; 13.45%; MR 71.70. $C_{13}H_{17}SCl$. Calculated: C 64.84; H 7.11; S 13.32%; MR 71.43.

In the PMR spectrum of compound (Ib) are observed the same lines as in the spectrum of 3-vinyl-1,5-(bisphenylthio)pentane, with the addition of the signals of the methylene protons of the CH_2Cl group, $\delta = 3.32$. The chemical shifts of the β-protons of the $-CH_2CH_2Cl$ and $-CH_2CH_2SC_6H_5$ groups approximately coincide, $\delta \approx 1.6$. The integral intensities corroborate the validity of the assignments.

Preparation of 3-Vinyl-1,5-(bisphenylthio)pentane. Sodium thiophenolate (from 0.23 g of sodium, 5 ml of absolute ethanol and 1.1 g of thiophenol) was added, with stirring, at 70°, to 2.4 g of 1-chloro-3-vinyl-5-phenylthiopentane. The reaction mixture was heated for 1 h, after which it was diluted with water and extracted with ether. Distillation gave 2.6 g (82%) of 3-vinyl-1,5-(bisphenylthio)pentane, bp 207° (2 mm); n_D^{20} 1.6037; d_4^{20} 1.0917.

CONCLUSIONS

1. A study was made of the homolytic addition of thiophenol to trivinylmethane, 5-chloro-3-vinyl-1-pentene and 5-phenylthio-3-vinyl-1-pentene.

2. The initially formed homoallylic radical $(CH_2=CH)_2CH\dot{C}HCH_2SC_6H_5$ is cyclized to the cyclopropylcarbinyl radical  $\dot{C}H_2-CH-CHCH_2SC_6H_5$ (ring closed through $CHCH=CH_2$). These radicals are fixed by reaction with thiophenol, with the formation of 5-phenylthio-3-vinyl-1-pentene and 1-methyl-2-vinyl-3-phenylthiomethylcyclopropane. The latter was identified in the reaction mixture by the PMR method.

3. 1-Chloro-3-vinyl-5-phenylthiopentane and 3-vinyl-1,5-(bisphenylthio)pentane were respectively obtained by the reaction of 5-chloro-3-vinyl-1-pentene and 5-phenylthio-3-vinyl-1-pentene with thiophenol.

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