## HOMOLYTIC ADDITION OF THIOPHENOL TO

ETHYL (β-PHENYLTHIO)CROTONATE

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As an expansion of our studies on the free-radical rearrangement of mercaptols with 1,2-migration of the thiyl groups we studied the chemical transformations of the diphenyl-mercaptol of acetoacetic ester (I) and ethyl( $\beta$ -phenylthio)crotonate (II), which were obtained by reacting acetoacetic ester (AAE) with thiophenol in the presence of HCl; their structure was confirmed by the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

Previously, for the examples of the dibutylmercaptols of AAE [1] and ethyl pyruvate [2] it was shown that the presence of electron-acceptor groups in the mercaptol leads to a decrease in the yields of the rearranged products and an increase in the yields of the products due to competing reactions. A comparison of the behavior of the dibutyl- and diphenylmercaptols of AAE makes it possible to compare the migration ability of the BuS and PhS groups in radicals of structure  $\dot{C}H_2-C(SR)_2CH_2CO_2Et$  and  $CH_3C(SR)_2\dot{C}HCO_2Et$  (R = Bu and Ph).

It proved that (I), in contrast to the dibutylmercaptol of AAE, practically does not undergo rearrangement with 1,2-migration of the PhS group either when heated (130°C, 30 h,  $C_6H_5Cl$ ) or when treated with tert-butyl peroxide (TBP) and does not form compounds (III) and (IV). This apparently indicates that the PhS group has a lower migration ability, which, in combination with the electron-acceptor  $CO_2Et$  group, makes progress of the rearrangement extremely difficult.

 $\begin{array}{c|c} & \xrightarrow{} CH_3CH(SPh)CH(SPh)CO_2Et \\ (III) \\ & \downarrow \\ TBP (I) \\ CH_3C(SPh)_2CHCO_2Et(A) \rightarrow CH_3C(SPh) = CHCO_2Et + PhS| \\ (II) \\ & \downarrow \\ (PhS)_2 \end{array}$ 

When mercaptol (I) is treated with TBP, the main reaction products are (II) and  $(PhS)_2$  in approximately the same yield (70%). It is possible that when the reaction is initiated by peroxide the intermediately formed radicals (A) [due to cleavage of an H atom from the CH<sub>2</sub> group of (I)] are stabilized by fragmentation with the formation of (II) and PhS radicals, which dimerize to (PhS)<sub>2</sub>. The thermolysis of (I) (130°, C<sub>6</sub>H<sub>5</sub>Cl) leads in  $\sim$ 100% yield to (II) and thiophenol.

It seemed of interest to study the reaction of thiophenol with (II) in order to ascertain the ease of reaction and the orientation of the addition. Here the formation of either adducts (I) or (III), or of their mixture, could be expected.

TABLE 1. PMR Spectral Data

Compound	δ, ppm (from TMS)							
	СН	CH2COO	CH₂SR	CH <sub>3</sub> C (SPh) <sub>2</sub>				
(I) (II) (IV) (VI) *	( 5,35 3,60 3,06	2,78 	- 2,85 2,53	1,55 2,45 				
*Data from	n [1].							

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TABLE 2. <sup>13</sup>C NMR Spectral Data

	δ, <sup>13</sup> C, ppm (from TMS)									
Compound		C2	Ca	C4	C2	Ce	s			
		ç					Cı	C²	C3	C4
CH <sub>8</sub> C(SPb) <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> Et (I)		59,8	46,2	168,9	59,8	14,0	14,0 131,0 13,6 134,6 132,9	137,0 128, 129,6 128, 131,5 128,	<b>1</b> 28,4	129,2 125,8 127,1
PhSCH <sub>2</sub> CH(SPh)CH <sub>2</sub> CO <sub>2</sub> Et (IV)		43,9	37,4	169,9	59,8	13,6			128,3 128,3	
BuSCH <sub>2</sub> CH(SBu)CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (VI)*		40,4	38,0	169,7	59,0	12,5	_	—		_

\*Data from [3].

 $[CH_2=C(SPh)CH_2CO_2Et] (V) \xrightarrow{PhSH} (IV)$ 

Only one adduct, namely ethyl  $\beta,\gamma$ -bis(phenylthio)butyrate (IV), is formed in high yield when thiophenol is added to (II) using peroxide initiation (TBP, 130°). Such an unexpected direction of the reaction toward the formation of adduct (IV), and not to either the  $\beta$ , $\beta$  or  $\alpha$ , $\beta$ adducts, possibly proceeds in two steps. First compound (II) undergoes allylic rearrangement with migration of H and the formation of (V), and then the addition of thiophenol to the latter at the terminal double bond. Adduct (IV) is formed when the reaction of (II) with PhSH is initiated photochemically.

If (II) is reacted with PhSH without initiation, with careful removal of traces of air in the ampul, then neither the addition of thiophenol nor the isomerization of (II) to (V) takes place. This makes it possible to assume that the postulated allylic rearrangement with H migration bears a free-radical character.

The structure of the studied compounds was confirmed by the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Tables 1 and 2). In Table 1 are included only the chemical shifts of the protons of the groups that determine the structure of the indicated compounds, which are found in regions known for analogous compounds [1]. The spectrum of compound (IV) (see Table 1) lacks the signals of other  $CH_3$  groups, except the  $CH_3$  triplet of the carbethoxyl group, and also lacks a doublet that corresponds to the  $CH_3-CH$  signal, which should be present in the spectrum of compound (III). In addition, a similarity exists in the PMR spectra of compounds (IV) and (VI). Some differences in the chemical shifts of the corresponding groups are related to the effect of the SPh and SBu groups. The integral intensities of the signals correspond to the proposed structure.

The <sup>13</sup>C NMR spectrum of compound (IV) (see Table 2) lacks the signals of compound (I) and the signals, expected in the 18-21 ppm region [3], for the  $CH_3$  group of the  $CH_3$ -CH(SPh). fragment. All of this confirms the fact that compound (IV) is pure and is not contaminated with isomers (I) and (III).

Consequently, the reaction of (II) with PhSH does not lead to adducts (I) and (III), which could be formed without allylic rearrangement.

## EXPERIMENTAL

The PMR spectra of compounds (I), (II), and (IV) were obtained on a Hitachi-Perkin-Elmer R-20 spectrometer (60 MHz) using 50% CC14 solutions of the compounds and TMS as the internal standard. The <sup>13</sup>C NMR spectra of (I) and (IV) were recorded on a Bruker HX-90 spectrometer (22.635 MHz) at 20° using 70% CHCl<sub>3</sub> solutions of the compounds; the chemical shifts were measured relative to  $CHCl_3$  and were recalculated to TMS ( $\delta$   $CHCl_3$  77.17 ppm). The GLC analysis was run on an LKhM-8MO chromatograph with detection based on the heat conductivity; the 1 m  $\times$  3 mm column was packed with 5% Silicone XE-60 deposited on Chromaton NN-AW. The internal standards were: 1,2-dibutylthioethane for (II), and 1,3-diphenylthiopropane for (IV).

Diphenylmercaptol of Acetoacetic Ester (I). A stream of dry HCl was passed for 2 h at 15° through a mixture of 6.5 g of acetoacetic ester (AAE) and 11 g of PhSH. We obtained

13.5 g (84%) of mercaptol (I), mp 53° (from petroleum ether). Found: C 65.08; H 6.05; S 19.70%. C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>. Calculated: C 65.02; H 6.02; S 19.28%.

Ethyl ( $\beta$ -Phenylthio)crotonate (II). To 11 g of PhSH, saturated with dry HCl (10 min), at  $\sim 20^{\circ}$  was added 6.5 g of AAE. Here the temperature rose to 50-60°. The mixture was heated for 1 h at 45° to give 7 g (63%) of (II), bp 172° (4 mm), np<sup>2°</sup> 1.5690, d4<sup>2°</sup> 1.1069. Found: C 64.85; H 6.32; S 14.59%. C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>S. Calculated: C 64.85; H 6.30; S 14.41%.

Ethyl  $\beta,\gamma$ -Bis(phenylthio)butyrate (V). A mixture of 10 g of ester (II), 20 g of PhSH, and  $\overline{0.5}$  g of TBP was heated for 6 h at 130°. After distilling off the volatiles the residue was chromatographed on a silica column. Here the (PhS)<sub>2</sub> was eluted with hexane, and adduct (IV) was eluted with a 1:1 hexane—benzene mixture. The yield of (IV) was 75%. Found: C 65.16; H 6.06; S 18.97%. C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub>. Calculated: C 65.02; H 6.02; S 19.28%.

After exposing a mixture of ester (II) and thiophenol to UV light we isolated, as described above, adduct (IV) in 53% yield.

## CONCLUSIONS

1. When initiated by either peroxide or photochemically, thiophenol adds to ethyl  $(\beta$ -phenylthio)crotonate to give ethyl  $\beta,\gamma$ -bis(phenylthio)butyrate. The homolytic allylic isomerization of the unsaturated ester with hydrogen migration was postulated.

2. In contrast to the dibutylmercaptol of acetoacetic ester, the diphenylmercaptol of acetoacetic ester fails to undergo rearrangement with 1,2-migration of the phenylthio group.

## LITERATURE CITED

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