REACTION OF THIONOCARBOXYLATE ESTERS WITH PHENYLAZOTRIPHENYLMETHANE

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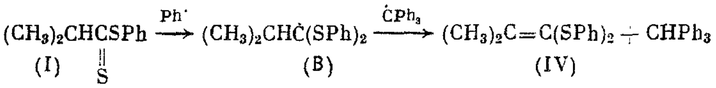
Aryl radicals add readily to the sulfur atom in a variety of thiocarbonyl compounds $\genfrac{}{}{0pt}{}{X\diagdown}{Y\diagup}\mathrm{C{=}S}$ (X, Y = Alk, Ar, NHR, OR, SR) with the formtion of radical adducts $\genfrac{}{}{0pt}{}{X\diagdown}{Y\diagup}\dot{\mathrm{C}}\mathrm{{-}SAr}$ (A), the subsequent chemical fate of which is determined predominantly by the nature of groups X and Y [1-3]. We have previously suggested that the nature of the arylating agent also plays an important part in the formation of the products in these reactions [4]. Specifically, the sources of phenyl radicals used, N-nitrosoacetanilide (NAA) and phenylazotriphenylmethane (PAT) differ in that decomposition of the first compound gives diazoxyl radicals $\mathrm{Ph{-}N{=}N{-}\dot{O}}$ in addition to phenyl radicals [5], while the second gives triphenylmethyl radicals $\mathrm{Ph_3\dot{C}}$, and these "side" radicals also react. For example, in the reaction of thiocarbonyl compounds with NAA, in some instances the "oxidized" products $\genfrac{}{}{0pt}{}{X\diagdown}{Y\diagup}\mathrm{C{=}O}$ are formed. It has been suggested that these are formed by recombination of the radical adducts A with the $\mathrm{PhN{=}N\dot{O}}$ radicals, followed by reaction of the resulting unstable diazoesters [4]. If this were the case, it would be expected that replacement of NAA by PAT would give products of the reaction of radicals A with the $\mathrm{Ph_3\dot{C}}$ radicals.

We have now examined the reaction of PAT with some thiocarboxylate esters which give substantial amounts of "oxidized" products on reaction with NAA [4]. Table 1 shows the principal products of the reactions of phenyl dithioisobutyrate (I), ethyl thionomalonate (II), and ethyl thionoacetate (III) with PAT. The high overall yields of products containing the PhS group (Table 1) confirm the formation of radical adducts $\genfrac{}{}{0pt}{}{Y\diagdown}{X\diagup}\dot{\mathrm{C}}\mathrm{{-}SPh}$ by regioselective addition of phenyl radicals to the thione sulfur. As will be seen from Table 1, in the reaction of (I) with PAT the principal products are dimethylketene diphenylmercaptal (IV) and triphenylmethane. It appears that in this case the adduct radicals B for the most part disproportionate with the $\mathrm{Ph_3\dot{C}}$ radicals, thus clearly facilitating the removal of tertiary hydrogen from the β-position to the radical center:



$$\underset{(\mathrm{I})}{(\mathrm{CH_3})_2\mathrm{CH}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SPh}} \xrightarrow{\mathrm{Ph}^{\cdot}} \underset{(\mathrm{B})}{(\mathrm{CH_3})_2\mathrm{CH}\dot{\mathrm{C}}(\mathrm{SPh})_2} \xrightarrow{\dot{\mathrm{C}}\mathrm{Ph_3}} \underset{(\mathrm{IV})}{(\mathrm{CH_3})_2\mathrm{C{=}C(SPh)_2}} + \mathrm{CHPh_3}$$

This mode of stabilization of the radicals B by "cross"-disproportionation has also been observed in the reaction of (I) with NAA, and is generally highly characteristic of adduct radicals of type A, which contain labile β-hydrogen atoms [1-3].

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*Deceased.

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TABLE 1. Reactions of Thiocarboxylate Esters with PAT (60°C, acetone, 8 h)

Starting material*	Conversion, %	Identified products (yield, %**)
(I)	88	$(CH_3)_2C{=}C(SPh)_2$ (73), $(CH_3)_2CHC(O)SPh$ (2), Ph_2S_2 (2), Ph_3CH
(II)	35	$EtO_2CCH{=}C(CPh_3)OEt$ (31), Ph_2S_2 (32), $PhSCPh_3$, Ph_3CH
(III)	65	$CH_3CH(SPh)OEt$ (19), CH_3COCPh_3 (21), $PhSCPh_3$ (20), Ph_2S_2 (4), Ph_3CH

*For synthesis of (I), see [3], of (II) and (III), [4].
**Determined by GLC.

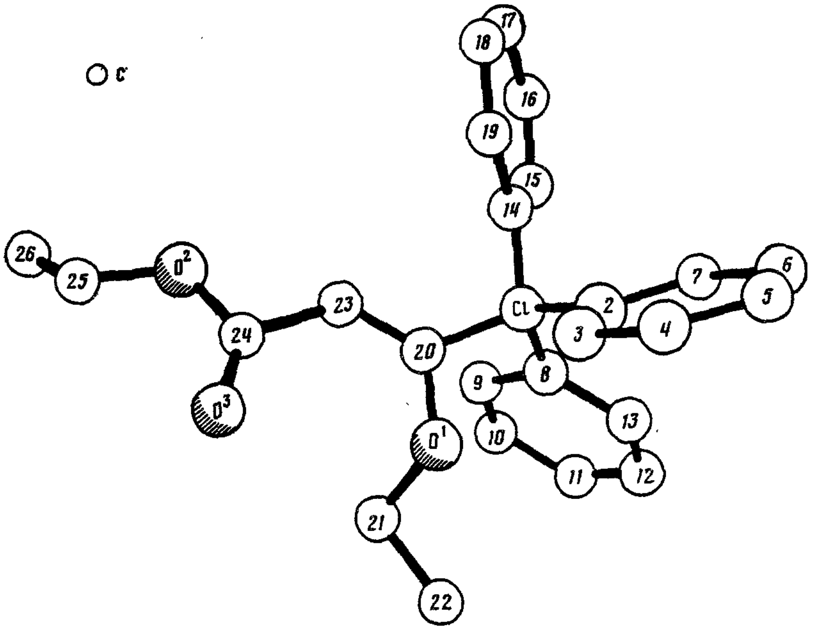
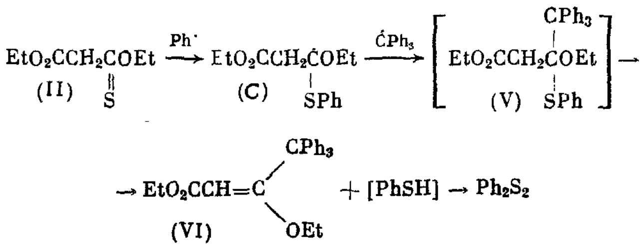


Fig. 1. Molecular structure of $EtO_2CCH{=}C(OEt)CPh_3$.

In the reactions of the thione esters (II) and (III) with PAT, no ketene mercaptals are formed. This may be due to the lesser lability of the secondary or primary β-hydrogens in the radical adducts $EtO_2CCH_2\dot{C}(SPh)OEt$ (C) and $CH_3\dot{C}(SPh)OEt$ (D), hindering cross disproportionation.

The principal products in the reaction of (II) with PAT are 1-ethoxycarbonyl-2-ethoxy-2-triphenylmethylethylene (VI) and diphenyl disulfide (Table 1). The formation of these products may be represented by a sequence in which the adduct radicals C recombine with $Ph_3\dot{C}$ radicals:

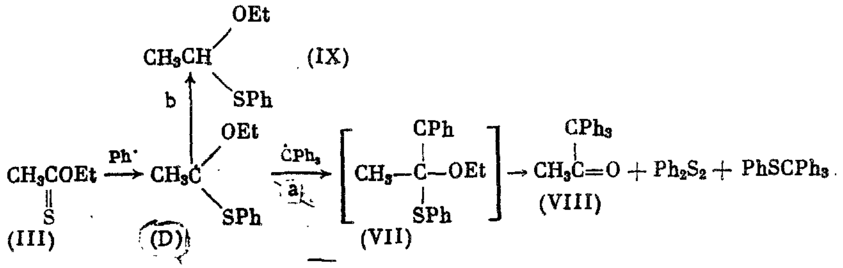


$$\underset{(II)}{EtO_2CCH_2\overset{\displaystyle S}{\overset{\|}{C}}OEt} \xrightarrow{Ph^{\cdot}} \underset{(C)}{EtO_2CCH_2\underset{\displaystyle SPh}{\underset{|}{\dot{C}}}OEt} \xrightarrow{\dot{C}Ph_3} \left[\underset{(V)}{EtO_2CCH_2\overset{\displaystyle CPh_3}{\overset{|}{\underset{\displaystyle SPh}{\underset{|}{C}}}}OEt}\right] \rightarrow$$

$$\rightarrow \underset{(VI)}{EtO_2CCH{=}C\begin{matrix}CPh_3\\OEt\end{matrix}} + [PhSH] \rightarrow Ph_2S_2$$

The intermediate hemiketal could not be isolated. It seems that it readily loses thiophenol (cf. [6]), and it was shown in separate experiments that under the reaction conditions thiophenol is converted quantitatively into diphenyl disulfide. The structure of (VI) was confirmed by X-ray diffraction analysis (Fig. 1), and confirmed by ^{13}C NMR and mass spectroscopy.

It may be assumed that in the reaction of ethyl thionoacetate (II) with PAT also, recombination of the radical adducts D with $Ph_3\dot{C}$ radicals takes place. The formation of methyl triphenylmethyl ketone (VIII), and of Ph_2S_2 and $PhSCPh_3$ (Table 1) may in this instance be due to further reactions of the unstable hemiketal (VII).*



It is noteworthy that in this reaction there appears to be a further mode of stabilization of the intermediate adduct radical, namely by removal of hydrogen from a molecule of the solvent (path b), as shown by the formation of substantial amounts of 1-ethoxy-1-phenylthioethane (IX) (the structures of (VIII) and (IX) were confirmed by ^1H and ^{13}C NMR, and by mass spectroscopy).

These results show the general nature of the behavior of radical adducts of A formed in the reactions of thiocarbonyl compounds with different sources of phenyl radicals. When labile hydrogen is present in the β-position to the radical center, these radicals mostly disproportionate, but in the absence of such hydrogen they recombine with the radicals formed together with the phenyl radicals in the decomposition of the radical source compounds. In the case of NAA, recombination with diazoalkoxyl radicals $Ph{-}N{=}\dot{N}{-}O$ gives rise to oxygen-containing compounds, and in the case of PAT, triphenylmethylated compounds.

EXPERIMENTAL

^1H and ^{13}C NM spectra were obtained on a Bruker WP-200SY spectrometer in $CDCl_3$ relative to TMS. Mass spectra were obtained on an MS/DS-50 with a direct introduction system, sample inlet temperature 20°C, ionization chamber 150°C, ionizing voltage 70 eV.

X-ray diffraction analysis was carried out on a Sinteks $P\bar{1}$ automatic diffractometer, λMoK_α, graphite monochromator, $\theta/2\theta$ scanning.

Quantitative determinations of the yields of reaction products (Table 1) were carried out by GLC, catharometer (column 1m ×3 mm), 15% SKTFT on Chromatone N-AW (0.16–0.20) in a stream of helium. Preparative separation of the mixtures was effected on glass columns (0.6 m × 20 mm) with silica gel L40/100.

Reaction of $(CH_3)_2CHC(S)SPh$ (I) with Phenylazotriphenylmethane (PAT). A solution of 4 g of (I) and 7.1 g of PAT in 80 ml of acetone was boiled under argon for 8 h. The residue after removal of the acetone was separated on silica gel to give (in order of elution), eluent hexane: a) Ph_2S_2 (mp 60°C): b) PH_3CH (mp 89°C); c) $(CH_3)_2C{=}C(SPh)_2$ (IV), oil, 3.7 g. Found: C 70.57; H 5.94; S 23.45%. $C_{16}H_{16}S_2$. Calculated: C 70.59; H 5.89; S 23.52%. ^{13}C NMR spectrum (δ, ppm): 24.1 (CH_3), 121.8 [$(CH_3)_2C{=}$], 125.9, 128.3, 129.3, 135.6 (p-, m-, o-, and i-arom. C), 150.7 [$(PhS)_2C{=}$]. Eluent hexane–benzene (5:1): d) starting (I), and e) $(CH_3)_2$-$CHC(O)SPh$ (X).

Reaction of $EtO_2CCH_2C(S)OEt$ (II) with PAT. The experiment was carried out as in the preceding example. From 2 g of (II) and 8.4 g of PAT there were obtained (in order of elution), eluent hexane: a) Ph_2S_2; b) Ph_3CH. Eluent hexane–benzene (1:1): $EtO_2CCH{=}C(OEt)CPh_3$ (VI) (1.3 g), mp 113°C (from alcohol). Found: C 80.96; H 6.74%. $C_{26}H_{26}O_3$. Calculated: C 80.82; H 6.74%. PMR spectrum (δ, ppm): 0.74 t ($\underline{CH_3}CH_2O$), 1.30 t ($\underline{CH_3}CH_2OCO$), 3.83 q (CH_2O), 4.10 q (CH_2OCO), 5.83 s (CH), 7.1-7.7 m (3 C_6H_5). ^{13}C NMR spectrum (δ, ppm): 14.2 and 14.7 ($2CH_3$),

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*A possible route for this reaction is homolytic decomposition of (VII) at the C–S bond with the formation of $CH_3\dot{C}(OEt)CPh_3$ and $Ph\dot{S}$ radicals. The former undergo β-fragmentation at the O–Et bond (cf. [7]), while the latter recombine with themselves and with $Ph_3\dot{C}$ radicals to give Ph_2S_2 and $PhSCPh_3$.

(CH_2OCO), 67.6 (CPh_3), 71.8 (CH_2O), 101.9 (CH=„ J_{CH} = 161 Hz), 126.0, 127.3, 130.6, 8 (p-, m-, o-, and i-arom. C), 164.3 (O–C=), 175.1 (OC=O). Mass spectrum, m/z: 86 (M^+, 1.4%), 341 (M^+ - OEt, 28.9%), 340 (M^+ - EtOH, 83.9%), 268 (M^+ - OEt - COOEt, 30.9%), 267 (M^+ - EtOH - COOEt, 100%), 244 (Ph_3CH, 21.3%), 243 (Ph_3C, 98.9%), 166 (Ph_2C, 16.4%), 165 (Ph_2C–H, 68.9%), 77 (Ph, 12%), 73 (CO_2Et, 3.2%). The crystals of (VI), $C_{26}H_{26}O_3$, grown from hexane, were triclinic, with a = 11.230 (2), b = 11.934(2), c = 10.143 (2) Å; α = 97.98(2); β = 62.20(2); γ = 72.23 (2)°; ρ_{calc} = 1.19 g/cm³; Z = 2, space group $\bar{P}1$.

A total of 2007 independent reflexions were obtained, of which 1824 with $I \geq 3\sigma(II)$ were used in the subsequent calculations. The structure was calculated directly, and refined by least squares in anisotropic (C and O) and isotropic (H) approximation. The final value of the R factor was 0.037 [R_ω = 0.039; $\omega = 1/\sigma^2(F)$].†

Reaction of $CH_3C(S)OEt$ (III) with PAT. The experiment was carried out as described above. From 2 g of (III) and 7 g of PAT there were isolated (in order of elution), eluent hexane–benzene (5:1); a) Ph_2S_2; b) Ph_3CH; c) $PhSCPh_3$, mp 106°C (from alcohol) [8]. Found: C 85.51; H 5.90; S 9.13%. $C_{25}H_{20}S$. Calculated: C 85.23; H 5.68, S 9.09%; d) starting (III); e) $CH_3CH(OEt)SPh$ [9] (0.6g). PMR spectrum (δ, ppm): 1.47 d (CH_3CH), 4.83 q ($CHCH_3$), CH_3CH_2O: ABX_3 system with multiplet centers at AB 3.43 and 3.90 (CH_2), 1.18 t (CH_3), 7.2-7.8 m (C_6H_5) (an identical spectrum was obtained for the authentic compound obtained from vinyl ethyl ether and thiophenol, as in [10]). ^{13}C NMR spectrum (δ, ppm): 14.9 (CH_3CH_2), 22.5 (CH_3CH), 62.7 (CH_2), 84.1 (CH), 127.0, 128.5, 133.4, 133.2 (p-, m-, o-, and i-arom. C), f) $Ch_3C(O)CPh_3$ (1.1 g), mp 136°C (from hexane) [11]. Found: C 88.05; H 5.96%. $C_{21}H_{18}O$. Calculated: C 88.11; H 6.20%. PMR spectrum (δ, ppm): 2.10 s (CH_3) and 7.1-7.4 m (3 C_6H_5). ^{13}C NMR spectrum (δ, ppm): 29.7 (CH_3), 126.7, 128.0, 130.3, 142.4 (p-, m-, o-, and i-arom. C), 205.7 (C=O). Mass spectrum: m/z: 286 (M^+, 1.2%), 244 (PH_3Ch, 25.7%), 243 (PH_3C, 100%), 166 (Ph_2C, 17.7%), 165 (Ph_2C–H, 60.4%), (CH_3CO, 23.5%).

CONCLUSIONS

In the reactions of thionocarboxylate esters RC(S)XR' with phenylazotriphenylmethane radical adducts $R\dot{C}(SPh)XR'$ are formed, which are stabilized by reaction with triphenylmethyl radicals.

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†The atom coordinates, temperature parameters, and tables of all the distances and angles may be obtained from the authors.