REARRANGEMENT OF RADICALS WITH 1,2-MIGRATION OF CHLORINE DURING PHENYLATION OF ETHYL TRI- AND DICHLOROTHIONOACETATES

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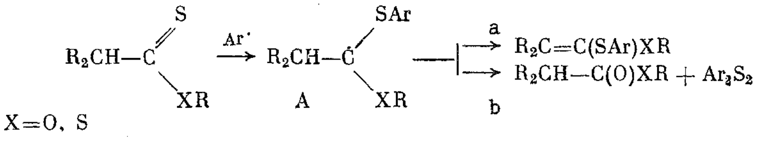
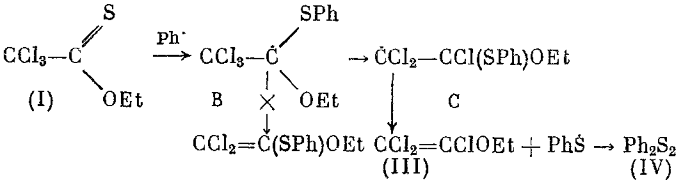
Previously [1, 2] with thiono- and dithiocarboxylic esters as examples it was established that arylation by means of N-nitrosoacetanilide (NAA) takes place in all cases at the thiono S atom to form radical adducts of type A. The latter are stabilized by cross disproportionation (route a) and oxidation (route b):



The present work is a study of the reactions of ethyl tri- and dichlorothionoacetates with materials that generate phenyl radicals. The purpose was to elucidate the effect of α-gem-polychloromethyl substituents on the radical arylation of the thiono group, and particularly on the course of the stabilization of the intermediate radical adducts.

In the reaction of ethyl trichlorothionoacetate with NAA (20°C, acetone), 1,2,2-trichloro-1-ethoxyethylene (III) and Ph_2S_2 (IV) were isolated:



According to the proposed scheme, the radical adduct B, which forms by addition of Ph˙ at the $>$C=S ester bond of I, rearranges with 1,2-migration of Cl to radical C; fragmentation of the latter gives compounds III and IV.

The possible competing routes of radical adduct B stabilization, viz., detachment of Cl and oxidation by NAA, do not take place in this case. When benzoyl peroxide (BP) is the source of phenyl radicals and the reaction is carried out at 80°C in cyclohexane solution, the main products are compounds III and IV, i.e., the same fragmentation products of radical C rearrangement. The structure of 1,1,2-trichloro-2-ethoxyethylene (III) was confirmed by ^{13}C NMR spectra, which contain signals at 107.6 ($CCl_2=$), 141.3 ($=CCl$), and 68.6 and 14.3 ppm (OCH_2CH_3).

It should be noted that in the case of ethyl trichlorothionoacetate, rearrangement with 1,2-migration of Cl goes easily already at 20°C. Rearrangements with 1,2-migration of Cl are known for chloroaliphatic radicals [3]. In the present work, rearrangement with 1,2-migration of Cl has been studied for the first time in radicals containing functional groups at the center of the radical.

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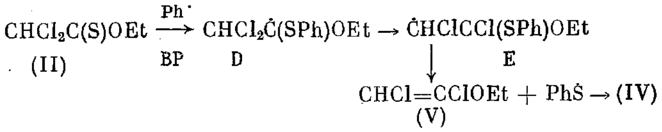
The addition of Ph· to ethyl trichlorothionoacetate (I) was also studied by EPR using the spin trap technique. The EPR spectrum obtained when I is phenylated in the presence of 2-methyl-2-nitrosopropane (MNP) shows only a triplet with $a_N = 16.6$ Oe, which is assigned to the spin adduct (SA) of thiyl radicals with MNP [4]. When the same reaction is carried out in the presence of nitrosodurene (ND) the spectrum shows signals of the SA of the rearranged (C) radicals that contain two equivalent Cl atoms at the α-C. These nitroxyl radicals have hyperfine coupling constants of $a_N = 10.6$ and $a_{Cl} = 2.2$ Oe. The rate constants of the addition of the α,α-dichloro radicals to ND are approximately an order of magnitude larger than the respective rate constants of addition to MNP [5]; therefore in the case of ND the (C) radicals add more rapidly to the spin trap (ST). As far as the unarranged (B) radicals are concerned, they cannot be fixed by means of a ST, apparently because they rearrange so easily to (C) radicals.

Study of the reaction of ethyl dichlorothionoacetate (II) with NAA or BP showed that the radical processes are more complicated than in the case of ethyl trichlorothionoacetate. The formation of 1,2-dichloro-2-ethoxyethylene (V) in the reaction of II with BP and the absence of this product in the reaction of II with NAA shows that the rearrangement of (D) radicals to (E) radicals takes place only at elevated temperature:

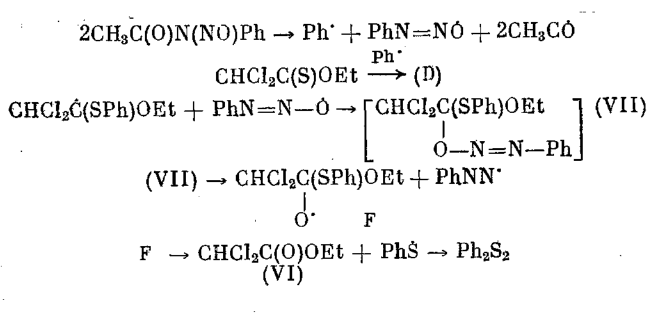


$$\begin{array}{l}\underset{(II)}{\mathrm{CHCl_2C(S)OEt}} \xrightarrow[\mathrm{BP}]{\mathrm{Ph^{\cdot}}} \underset{D}{\mathrm{CHCl_2\dot{C}(SPh)OEt}} \rightarrow \underset{E}{\mathrm{\dot{C}HClCCl(SPh)OEt}} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \underset{(V)}{\mathrm{CHCl{=}CClOEt}} + \mathrm{Ph\dot{S}} \rightarrow \mathrm{(IV)}\end{array}$$

The ^{13}C spectrum of V contains signals at 97.7 (CHCl=), 143.4 (=CCl), and 67.4 and 13.9 ppm (OCH_2CH_3).

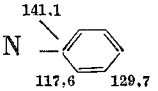
When phenyl radicals react with ethyl dichlorothionoacetate (II) in the presence of MNP, the EPR spectrum shows two triplets: $a_N = 16.6$ and 13.6 Oe. The former can be assigned to the SA of the $CHCl_2\dot{C}(SPh)OEt$ radicals (D) that form by addition of Ph radicals at the C=S bond of ester II. WHen this reaction is carried out in the presence of ND the following signals appear in the spectrum; a triplet with $a_n = 11.5$ Oe, a triplet of doublets with $a_n = 11.3$, $a_H = 9.1$ Oe, and a triplet of triplets with $a_N = 11.5$ and $a_H = 9.7$ Oe. The triplet with $a_N = 11.5$ Oe can be assigned to the SA of (D) radicals with ND. The triplet of doublets is apparently to be assigned to the SA of $CHCl_3C(S)O\dot{C}HCH_3$ radicals with ND. No assignment of the triplet of triplets has been made. In the case of ester II it was not possible to identify the SA of the rearranged $\dot{C}HClCCl(SPh)OEt$ radicals (E) with the spin traps (MNP and ND).

In the study of the reaction of ethyl dichlorothionoacetate with NAA it was established that besides phenylation a significant role is played by processes in which NAA acts as oxidant and donor of nitrogen-containing radicals. Thus ethyl dichloroacetate (VI) and diphenyl disulfide (IV) were identified in the reaction mixture by GLC. These products can form by a scheme that includes oxidation of radical adducts (D) to (F) radicals via an intermediate diazo compound (VII). This scheme is analogous to that presented in [6]:



$$\begin{array}{c}\mathrm{2CH_3C(O)N(NO)Ph \rightarrow Ph^{\cdot} + PhN{=}N\dot{O} + 2CH_3\dot{C}O} \\ \mathrm{CHCl_2C(S)OEt \xrightarrow{Ph^{\cdot}} (D)} \\ \mathrm{CHCl_2\dot{C}(SPh)OEt + PhN{=}N{-}\dot{O} \rightarrow \left[\begin{array}{l}\mathrm{CHCl_2C(SPh)OEt} \\ \quad\;| \\ \quad\;\mathrm{O{-}N{=}N{-}Ph}\end{array}\right] (VII)} \\ \mathrm{(VII) \rightarrow \underset{F}{\underset{\dot{O}}{CHCl_2\overset{}{C}(SPh)OEt}} + PhNN^{\cdot}} \\ \mathrm{F \rightarrow \underset{(VI)}{CHCl_2C(O)OEt} + Ph\dot{S} \rightarrow Ph_2S_2}\end{array}$$

Moreover in the reaction of ethyl dichlorothionoacetate with NAA, PhNH-N=C(Cl)CO_2Et (VIII) and $\mathrm{Ph\overline{N{-}N{=}C(Cl)C(O)S}}$ (IX), which contain the PhNN group, were isolated. The structure of VIII was confirmed by IR, NMR, and mass spectral data. The heterocyclic structure of IX was assigned on the basis of elemental analysis, molecular weight, and IR, NMR, and mass spectroscopy. The mass spectrum of IX contains intense peaks of the molecule ions M^+ 212 and 214, as well as the fragments M^+–C(O)S, C(O)S, PhNS, PhN, Ph, ClCCS, and ClC≡N.

The IR spectrum of IX contains the bands that are characteristic of the phenyl ring (690, 745, 755, 1480, 1500, 1600, 3025, 3060 cm^{-1}), plus two strong bands at 1660 and 1687 cm^{-1} that can be assigned to C═N and C═O valence vibrations. It also contains absorption in the 606 cm^{-1} region that is characteristic of the C–N bond. The ^{13}C NMR spectrum contains the phenyl ring signals of 

at 126.6, and two signals of C atoms without protons, viz., C(O)S (177.8 ppm) and N═C(Cl) (136.1 ppm).

Consideration of these results shows that when either NAA or BP is used, the phenylation of ethyl tri- and dichlorothionoacetates containing α-gem polychloromethyl groups takes place at the thiono S atom. But the resulting radical adducts are stabilized in various ways that depend on the reaction conditions and the structure of the thione compound. The distinguishing feature of our examples is that in the radical adducts CCl_3 and $CHCl_2$ in α-position to the radical center cause rearrangement with 1,2-migration of the Cl atom. It should be noted that when NAA is the source of phenyl radicals the $CCl_3\dot{C}(SPh)OEt$ (the (B) radicals) isomerize, whereas the $CHCl_2\dot{C}(SPh)OEt$ (the (D) radicals) are oxidized by NAA. The difference may be due to the lower efficiency of $CHCl_2$ than that of CCl_3 in reactions nvolving homolysis of the C–Cℓ bond, or to the greater stability of the rearranged $\dot{C}Cl_2CCl(SPh)OEt$ radical than that of $\dot{C}HClCCl(SPh)OEt$.

EXPERIMENTAL

EPR spectra were obtained with a RE-1306 spectrometer. Ampuls containing reaction mixtures (solution of 0.05-0.1 M $CCl_3C(S)OEt$ and 0.01 M nitrosodurene in benzene) were irradiated with a LRSh-500 lamp (Λ 366 nm) directly in the resonator of the spectrometer. Phenyl radicals were generated by photochemical decomposition of PhI in the presence of Ph_2Hg or di(m-carboran-9-yl)-mercury. When MNP was used, phenyl radicals were generated by decomposition of $PhN{=}NN(OH)C(CH_3)_3$ in the presence of PbO_2 [7].

^{13}C NMR spectra were obtained with a Bruker WP-200 spectrometer, 22.635 MHz working frequency, CCl_4 internal standard. IR spectra were obtained on a UR-20 spectrometer. Mass spectra were obtained on a MS/DS-50 instrument with direct introduction system, sample admission temperature 20°C, ionization chamber temperature 150°C, ionizing voltage 70 eV. GLC analysis was carried out on a LKhM-80 chromatograph, with katharometer, column 1 m × 3 mm with 5% SE-30 silicone and 6% PEG (20,000) on Chromatone N-AW (0.16-0.20) in He current.

Ethyl tri- (X) and dichloroacetimidate (XI). To a solution of 0.015 g · at. Na in 75 ml of abs. alcohol cooled in ice (5°C) was added gradually 0.25 mole of trichloroacetonitrile, and the reaction mixture was stirred for 2 h at ∿20°C. After the alcohol was distilled off the residue was vacuum distilled to yield 35 g (80%) of X, bp 66-67°C (25 mm), n_D^{20} 1.4625, d_4^{20} 1.3444 (cf. [8]). XI was obtained from dichloroacetonitrile analogously to X. Yield 65%, bp 55°C (25 mm), n_D^{20} 1.4600, d_4^{20} 1.2464.

Ethyl tri- (I) and dichlorothionoacetate (II). Into a reaction mixture of 48 g of X, 40 ml of glacial acetic acid, and 125 ml of ether was passed a stream of dry H_2S for 6 h at −5 to −10°C. The ether layer was washed with water and dried with $MgSO_4$. After the solvent was distilled off the residue was distilled in a column to yield 27 g (52%) of I, bp 82°C (30 mm), n_D^{20} 1.5170, d_4^{20} 1.4064. Found: C 23.67; H 2.16; Cl 51.44; S 15.43%. $C_4H_5OSCl_3$. Calculated: C 23.13; H 2.03; Cl 51.33; S 15.42%.

II was obtained analogously to XI, yield 68%, bp 87°C (45 mm), n_D^{20} 1.4990, d_4^{20} 1.2937. Found: C 27.76; H 3.38; Cl 41.20; S 18.35%. $C_4H_6Cl_2OS$. Calculated: C 27.75; H 3.47; Cl 41.04; S 18.49%.

Reactions of ethyl trichlorothionoacetate (I). (a) with NAA. A solution of 6.5 g of I and 6 g of NAA in 50 ml of acetone was stirred for 20 h at 20°C in a stream of Ar. The acetone was distilled off and the residue was chromatographed on a column of SiO_2 (L100/160). There were obtained (in order of elution by 10:1 hexane:benzene) Ph_2S_2 (IV), $CCl_3C(S)OEt$ (I), and $CCl_2{=}C(Cl)OEt$ (III) with n_D^{20} 1.4769, d_4^{20} 1.3367 (cf. [9]). Found: C 27.35; H 2.83%. $C_4H_5Cl_3O$. Calculated: C 27.35; H 2.85%. In the reaction mixture the concentrations of I (1%), III (51%), and IV (48%) were determined by GLC.

(b) with BP. A solution of 0.44 g of I and 0.42 g of BP in 3.5 g of cyclohexane was heated in an ampul for 6 h at 80°C. III (44%) and IV (40%) were identified and determined in the reaction mixture by GLC.

(c) Without initiator. A solution of 0.1 g of I in 0.6 g of cyclohexane was heated in an ampul in Ar for 6 h at 80°C. I concentration, 70%.

Reactions of ethyl dichlorothionoacetate (II). (a) With NAA. A solution of 2.4 g of II and 2.4 g of NAA in 40 ml of acetone was stirred for 20 h at 20°C in a stream of N_2. After the solvent was distilled off the residue was chromatographed on a column of silica gel (L100/160). There were separated in the following order of elution by hexane: IV, and a mixture of II and $CHCl_2C(O)OEt$ (VI); by 1:1 hexane:benzene: $PhNHN{=}C(Cl)CO_2Et$ (VIII), mp 77°C (cf. [10]). Found: C 54.10; H 5.01; Cl 15.29; N 12.58%. $C_{10}H_{11}ClN_2O_2$. Calculated: C 53.00; H 4.86; Cl 15.67; N 12.36%. IR spectrum (ν, cm^{-1}): 1725 (C=O), 1235 (COEt), 1065 (OEt), 1560 (C=N), 3280 (NH), 690, 750, 1500, 1610, 3030, 3060 (Ph). ^{13}C NMR spectrum (δ, ppm): 61.9 and 14.1 (OEt), 158.8 (C=O). 115.5 ($N^{13}C(Cl)C{=}O$). Mass spectrum: 228, 226 M^+, 198 $[M - N_2]^+$ (6%), 181 $[M - OEt]^+$ (4%), 152 $[M - CO_2Et]^+$, (42%), 105 $PhNN^+$ (3%), 91 PhN^+ (100%), 77 Ph^+ (17%); mp 119°C. Eluted by 9:1 hexane:benzene, $C_8H_5ClN_2OS$ (IX). Calculated: C 45.18; H 2.35; Cl 16.71; N 13.18; S 15.06%. The following concentrations were determined in the reactive mixture by GLC, %: II, 21; IV, 9; VI, 12; VIII, 8; IX, 22.

(b) With BP. A solution of 0.44 g of II and 0.38 g of BP in 3.0 g of cyclohexane was heated in a sealed ampul for 6 h at 80°C. The following were identified and determined quantitatively by GLC, %: II, 30; IV, 22; V, 12; VI, 6.

CONCLUSIONS

1. The addition of phenyl radicals, generated by the decomposition of nitrosoacetanilide or benzoyl peroxide, to ethyl trichlorothionoacetate proceeds with the formation of the radical adducts $CCl_3\dot{C}(SPh)OEt$ (B radicals). The latter rearrange with 1,2-migration of Cl to the $\dot{C}Cl_2C(Cl)(SPh)OEt$ radicals, which were identified by EPR using the spin trap technique.

2. Phenylation of ethyl dichlorothionoacetate followed by rearrangement of the $CHCl_2\dot{C}(SPh)OEt$ radical adducts to the $\dot{C}HClC(Cl)(SPh)OEt$ takes place only when benzoyl peroxide is the source of phenyl radicals, $Ph\cdot$. In the case of nitrosoacetanilide the primary radicals are stabilized by oxidation to form ethyl dichloroacetate and Ph_2S_2.

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