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ADDITION OF THIYL RADICALS TO THE CARBONYL GROUP

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The ability of thiyl radicals to add to the C=O group was shown by us on the examples of the S-butyl and S-phenyl thiolacetates, acetophenone, and benzophenone [1]. In the present paper: we studied the reaction of thiyl radicals with the S-phenyl (I) and S-butyl thiolbenzo-ates (II), phenyl benzoate (III), acetone (IV), and acetaldehyde (V). Below are shown the possible paths of adding thiyl radicals to the C=O group at the C and O atoms.

 $RR'C=0 + R''S \xrightarrow{O} RR'C \xrightarrow{O} (A)$   $RR'C=0 + R''S \xrightarrow{O} RR'C \xrightarrow{O} (B)$ 

Proof of the radical character of this process and identification of the intermediate radicals were accomplished mainly by the EPR method using spin traps. The photolytic addi-





UDC 542.955:541.515

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 379-382, February, 1981. Original article submitted March 26, 1980.

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TABLE 1. Parameters of EPR Spectra of Nitroxyl Radicals RN(O)C(CH<sub>3</sub>)<sub>3</sub>, Obtained by the UV Irradiation of Compounds (I)-(V) in Presence of 2-Methyl-2-nitrosopropane and (C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub>\*

Starting compound	Т., °С	R	Туре	$a_{ m N},$ Oe
(I)	25	$\begin{array}{c} C_6H_5CO\\ C_6H_5S\\ C_6H_5S\\ C_6H_5C(SC_6H_5)_2O\\ C_6H_5C(SC_6H_5)(OSC_6H_5)\end{array}$	A B	7,7 16,6 26,0 12,2
(11)	25	C <sub>6</sub> H <sub>5</sub> CO C <sub>4</sub> H <sub>9</sub> S C <sub>6</sub> H <sub>5</sub> C (SC <sub>4</sub> H <sub>9</sub> )!(OSC <sub>4</sub> H <sub>9</sub> )	В	7,7 17,6 12,2
(III)	-20	$C_{6}H_{5}S$ $C_{6}H_{5}C(OC_{6}H_{5})(SC_{6}H_{5})O$ $C_{6}H_{5}C(OC_{6}H_{5})(SC_{6}H_{5})$	A B	16,3 26,6 12,3
(IV)	$-20 \div -30$ $20 \div -20$	$\begin{array}{c} \mathrm{C_6H_5S}\\ \mathrm{(CH_3)}_{2}\mathrm{C(SC_6H_5)O}\\ \mathrm{(CH_3)}_{2}\mathrm{COSC_6H_5} \end{array}$	A B	16,3 27,1 12,3
(V) <sup>1</sup>	-15	CH <sub>3</sub> CH (OSC <sub>6</sub> H <sub>5</sub> )	В	13,1 †

 $(C_{6}H_{5}S)_{2}$  was used only in the photolysis of compounds (III)-(V).  $a_{H} = 0.3$  Oe.

tion of thiyl radicals to the C=O group of compounds (I)-(V) was studied in the range 20 to  $-30^{\circ}$ C in the presence of 2-methyl-2-nitrosopropane (MNP) as the spin trap. In the case of (I) and (II) the thiyl radicals are formed during the photolytic decomposition of these compounds, while for compounds (III)-(V) the source of C<sub>6</sub>H<sub>5</sub>S was (C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub>. The values of the UFC constants, calculated from the obtained spectra, and the assignments, are given in Table 1.

In the EPR spectrum, obtained in the photolysis of (I) in the presence of MMP (Fig. 1), based on the literature data, the triplets with the HFC constants  $a_{\rm N} = 7.7$  Oe (a lines),  $a_{\rm N} = 16.6$  Oe (b lines), and  $a_{\rm N} = 26.0$  Oe (c lines), were respectively assigned to the spin-adducts of the C<sub>6</sub>H<sub>5</sub>C = O [2], C<sub>6</sub>H<sub>5</sub>S [3], and C<sub>6</sub>H<sub>5</sub>C(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>O radicals [type (A)] [2] with MNP.\* The alkoxy radicals (A) are formed by the addition of the thiyl radical to the C atom of the C=O group of compound (I). The e lines with  $a_{\rm N} = 12.2$  Oe were assigned by us to the spin-adducts of MNP with the C<sub>6</sub>H<sub>5</sub>C(OSC<sub>6</sub>H<sub>5</sub>)SC<sub>6</sub>H<sub>5</sub> radicals [type (B)] on the basis of the data given below. It is known that in the range 12-13.5 Oe are found not only the signals of the spin-adducts of MNP with tertiary organosulfur radicals [4, 5], but also with other radicals, for example C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub> [6].<sup>+</sup> However, the signals with  $a_{\rm N} = 12.2$  Oe, recorded during the photolysis of (I), in contrast to the signals of the spin-adducts of the C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub> radicals with MNP, do not disappear after stopping the irradiation for 2 min [6], and instead decreases one half in intensity after 10 min.

Other proof for the addition of thiyl radicals to the 0 atom to give radicals of the (B) type is the photolytic reaction of acetaldehyde with  $(C_6H_5S)_2$  in the presence of MNP: Here the spin-adduct of the  $CH_3CHOSC_6H_5$  radicals were recorded as a triplet of doublets with  $a_N = 13.1$  and  $a_N = 0.3$  Oe. During the photolytic addition of the  $C_6H_5S$  radicals, generated from  $(C_6H_5S)_2$ , to acetone (IV) the (A) type radicals can be recorded as their spin-adduct with MNP only in the range 0 to -30°, and the spin-adduct of the type (B) radicals only at 0-20°.

As a result, thiyl radicals under the selected conditions can add to both the C and O atoms of the C=O group of compounds (I)-(V) to respectively give radicals of the (A) and (B) type, which were recorded as the spin-adducts with MNP (Table 1).

In the present paper the ability of thiyl radicals to add to the C atom of the C=O group was also confirmed chemically, with identification of the reaction products. For this purpose we ran the photochemical reaction of (I) with  $C_6H_5S$ , and (II) with  $C_6H_5S$ , and it was shown that exchange of the thiyl groups occurs here.

\*The triplet with an  $a_{\rm N}$  = 15.2 Oe (d lines) refers to the [(CH<sub>3</sub>)<sub>3</sub>C]<sub>2</sub>NO radicals, which are formed by the decomposition of MNP under the influence of UV irradiation. <sup>†</sup>The formation of the C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub> radicals under the conditions for the photolysis of compounds (I), (III), (IV), and (V) can be assumed to be due to the oxidation of C<sub>6</sub>H<sub>5</sub>S.



In order to exclude the alternate possibility of exchanging the thiyl groups via recombination of the acyl and thiyl radicals formed during photolysis we ran the reaction in the presence of benzoyl peroxide, i.e., under conditions that excluded the possible formation of the acyl radicals. The results, obtained when (I) is reacted with  $C_4H_9SH$  in the presence of benzoyl peroxide, proved to be analogous to those obtained in the photochemical reaction.

The possible exchange of the phenoxy group by the phenylthio group was also observed.



Evidently, this exchange goes through the intermediate formation of radicals of the (A) type, since it was shown by the EPR method that  $C_6H_5\dot{C}O$  radicals are absent in the reaction mixture, which when reacted with phenylthio radicals could give (I).

## EXPERIMENTAL

The EPR spectra were obtained on a Rubin spectrometer. The ampuls with the studied compounds were irradiated directly in the resonator with a DRSh-500 lamp. For reactions we took 0.01-0.001 mole/liter of 2-methyl-2-nitrosopropane, which was dissolved in the studied compounds. In the case of phenyl benzoate (III), acetone (IV), and acetaldehyde (V) we added 2 mmoles of  $(C_6H_5S)_2$  to the reaction mixture.

The GLC analysis was run on an LKhM-8MO chromatograph equipped with a katharometer (6% PEG-20,000 and 5% Silicone XE-60 deposited on Chromaton N-AW). As internal standards for the quantitative determination we used bis(phenylthiopropane) for compounds (I), (III), and  $(C_6H_5S)_2$ , and S-phenyl thiolbutyrate for compounds (II) and  $C_6H_5SSC_4H_9$ .

Reaction of S-Phenyl Thiolbenzoate (I) with  $(C_4H_9S)_2$ . A solution of 2.1 g of (I) and 1.8 g of  $(C_4H_9S)_2$  in 10 ml of cyclohexane was irradiated for 30 h with a PRK-4 Hg lamp at 80°. In the reaction mass, using authentic specimens, were identified C6H5COSC6H5, C6H5COS. C4H9, (C6H5S)2, and C6H5SSC4H9, and their respective yields\* were determined to be 41, 25, 8, and 19%.

Reaction of S-Butyl Thiolbenzoate (II) and Phenyl Benzoate (III) with  $(C_6H_5S)_2$ . In a similar manner, 3% of (I) and 5% of C6H5SSC4H9 are formed from (II). Phenyl benzoate (III)\* gives 3% of (I). In both cases  $\sim 90\%$  of the starting (II) or (III) was identified in the reaction mass.

## CONCLUSIONS

1. Using the EPR method, the radicals RR'C' (type (A)) and RR'C - OSR'' (type (B)),

formed via the addition of thiyl radicals to the C and O atoms of the C=O group of compounds RCOR', were identified as the spin-adducts with 2-methyl-2-nitrosopropane.

2. The stabilization products of the type (A) radicals, formed by the addition of thiyl radicals to the S-phenylthiol, S-butylthiol, and phenyl benzoates, were identified by the GLC method.

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REACTION OF PERFLUOROISOBUTYLENE WITH TRIBUTYLPHOSPHINE

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Perfluoroisobutylene (PFIB) under the influence of triphenylphosphine is converted to the cross-conjugated perfluorotriene (I) [1].\* In the present paper we studied the reaction of PFIB with tributylphosphine, which, as it proved, reacts much more sluggishly than triphenylphosphine. Here, in acetonitrile, together with triene (I), a substantial amount of perfluorotetramethylbutadiene (II) is formed, which was also detected in the reaction product of PFIB with triphenylphosphine.

 $2(CF_{3})_{2}C = CF_{2} + PBu_{3} \xrightarrow{MeCN; -30^{\circ}} (CF_{3})_{2}C = C + (CF_{3})_{2}C = CF - CF = C(CF_{3})_{2} + (CF_{3})_{2}C = CF - CF = C(CF_{3})_{2}$ (I)
(II)

The structure of the diene is confirmed by the IR, NMR, and mass spectral data, and also by counter synthesis from diol (III) and SF4 (cf. [2]). In a similar manner, the heating of diol (III) with  $PCl_5$  gave dichlorodiene (IV), which is evidently formed from allene (V) (cf. [3]). The presence of allene (V) was recorded spectrally.

 $(11) \xrightarrow{SF_{*}}_{-HF} (CF_{3})C-C \equiv C-C(CF_{3})_{2} \xrightarrow{PCl_{3}}_{-HCl} (CF_{3})_{2}C = C = C-C(CF_{3})_{2}$   $(11) \xrightarrow{OH}_{-SO_{2}F_{2}} OH OH \xrightarrow{-POCl_{3}}_{-POCl_{3}} Cl OH$  (111) (V)  $(V) \xrightarrow{PCl_{5}}_{-HCl} (CF_{3})_{2}C = C - C = C(CF_{3})_{2}$   $(V) \xrightarrow{-HCl}_{-HCl} (IV) Cl Cl$ 

As a result,  $Bu_3P$ , like  $Ph_3P$ , reacts with PFIB as a defluorinating agent, but it differs in that neither triene (I) nor perfluorodiene (II) can be obtained on a preparative scale using it. When PFIB is reacted with  $Bu_3P$  in acetonitrile, we detected, besides the triene, diene, and  $Bu_3PF_2$ , also phosphoranes (VI) (predominant) and (VII). It is interesting to mention that changing the solvent has little effect on the reaction result when using  $Ph_3P$ . In contrast to this, the reaction of PFIB with  $Bu_3P$  in ether leads only to a mixture of phosphoranes (VI) and (VII); here compounds (I) and (II) in general are not formed. The relative amounts of phosphoranes in the mixture depend on the reaction temperature and on the ratio of the reactants. Thus, with excess PFIB the main reaction product is phosphorane (VI), while with an equimolar ratio of the reactants the main product is (VII). Evidently, in this reaction, like in the reactions of other fluoroolefins with  $Bu_3P$ , the initial product is adduct (VIII) (cf. [4]), which, depending on the conditions, undergoes further transformations: a) migration of the butyl group, which leads to the isomeric phosphorane (VII),<sup>+</sup> and b) inter-

\*The assumption that the ylide  $Ph_3P = C = C(CF_3)_2$  is formed as an intermediate in the synthesis of triene (I) could be confirmed experimentally: The reaction of this ylide with PFIB gave triene (I).

<sup>†</sup>This transformation is facilitated by the high electrophilicity of the perfluoroisobutenyl group in phosphorane (VIII) [5] (cf. [6, 7]).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 383-386, February, 1981. Original article submitted March 27, 1980.

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