Reaction of $FO_2SOCF_2CF_2I$ (If) with $Fe(CO)_5$. A mixture of 0.652 g (2 mmoles) of compound (If) and 0.392 g (2 mmoles) of $Fe(CO)_5$ was heated for 15 min at 140°C. There was obtained 0.5 g (89%) of $IFeOSO_2F$ as solid brown substance, infusible to 250°C and insoluble in organic solvents. Found: Fe 19,27; S 10.98; F 6.51%. $FFeIO_3S$. Calculated: Fe 19.82; S 11.38; F 6.74%.

CONCLUSIONS

1. Fluoroaliphatic iodides containing electron-accepting substituents in the α-position homolytically add to double bonds with cleavage of the C–I bond upon thermal, peroxide, or metallocomplex initiation.

2. Di-tert-butylperoxide and the $Fe(CO)_5$–DMF system initiate effectively addition of $(CF_3)_2CFCF{=}CFCF_2I$, ICF_2CN, ICF_2COOCH_3, $CF_3CF_2CF_2I$, $CF_3(CF_2)_4CF_2I$, $ICF_2CF_2OSO_2F$, and $(CF_3)_2CFOCF_2CF_2I$ to 1-hexene.

3. Addition to methyl acrylate takes place only with the most reactive addends, $(CF_3)_2CFCF{=}CFCF_2I$ and ICF_2CN.

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POLAR CONTROL IN THE REMOTE OXIDATIVE FUNCTIONALIZATION OF SULFONES

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UDC 542.943.7:547.279.53

By rearrangement with 1,5- and 1,6-migration of the hydrogen of oxygen- and nitrogen-centered radicals and cation-radicals, generated by one-electron oxidation, we have developed a general method for the single-step remote oxidative functionalization of organic compounds at the unreactive γ- or δ-carbon atoms [1]. Using this method in systems containing sodium peroxydisulfate, remote functionalization of carboxylic acids and their amides [2], ketones [3, 4], and various types of sulfonamides [1, 5, 6] has been achieved. The possibility of effecting remote functionalization in these reactions is governed by the presence of unpaired electrons in the groups $C(O)O^{\cdot}$, $C(O)\dot{N}H$, $C{=}O^{+}$, and $SO_2\dot{N}R^1$.

We have now examined the oxidation of dialkyl sulfones in systems containing $Na_2S_2O_8$, with a view to the possible use of the sulfonyl group SO_2 as an activator of remote functionalization. We have found that the dialkyl sulfones (I) on oxidation with an excess of $Na_2S_2O_8$ [(I):$Na_2S_2O_8$ = 1:2-4] are selectively converted into the 3-oxosulfones (II). When the amount of oxidant is reduced, in addition to (II) the 3-hydroxysulfones (IIIa, c) are formed. The use of large amounts of $Na_2S_2O_8$ also clearly results in side reactions involving more extensive oxidation, which are in part responsible for the low yield of (IIb) from

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2138-2144, September, 1988. Original article submitted March 26, 1987.

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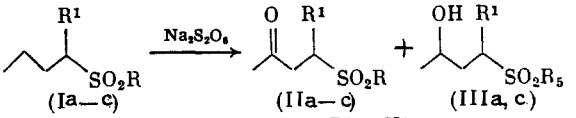
TABLE 1. Oxidation of Sulfones (I) by Treatment with $Na_2S_2O_8$*

Substrate	(I) : $Na_2S_2O_8$	Conversion, %	Products, yield as % conversion of (I)
(Ia)	1:1	84	(IIa), 13; (IIIa), 20
(Ia)	1:2	100	(IIa), 37; (IIIa), –
(Ib)	1:4	88	(IIb), 23; (IIIb), –
(Ic)	1:2†	36	(IIc), 28; (IIIc), 56
(Ic)	1:4	58	(IIc), 48; (IIIc), –

*85-90°C, 5 h.
†Reaction in the presence of 15 mole % [from (Ic)] $FeSO_4$.

(Ib). Oxidation of (Ic) in the system $Na_2S_2O_8$–$FeSO_4$, which converts alkanones into γ- and β-diketones [3], gives a mixture of 3-oxo- and 3-hydroxysulfones (IIc) and (IIIc) (Table 1).



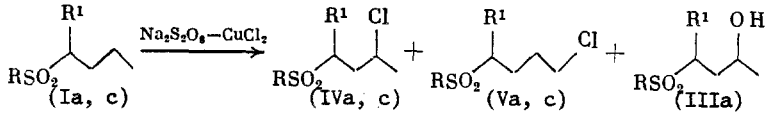
R = Me, R^1 = H(a), R = R^1 = Me(b), R = Bu, R^1 = H(c).

According to PMR spectroscopy, the reaction mixtures obtained on oxidizing (Ia-c) did not contain products of the functionalization of (I) at the α-, β-, or δ-carbon atoms; i.e., oxidation of sulfones by treatment with $Na_2S_2O_8$ occurs selectively at the nonactivated atom C^3, as in the regiospecific γ-oxygenation of butanesulfonamide to 3-oxobutanesulfonamide in the system $Na_2S_2O_8$–$AgNO_3$–$CuSO_4$ [6].

Since oxidation of (I) with excess $Na_2S_2O_8$ gave high conversions of the substrate [in the case of (Ia) and (Ib) nearly complete] to give a single product, the 3-oxosulfone (II), its preparative isolation was simplified. In the case of (IIa), all that was required was extraction of the reaction mixture with an organic solvent (ether or chloroform), the purity of the product thus obtained being satisfactory (by GC and PMR). Compound (IIb) was further purified by TLC, and (IIc) was separated from unreacted (Ic) by TLC.

This reaction therefore provides a simple method for the synthesis of the 3-oxosulfones (II), which is fully competitive with the method involving addition of alkyl sulfinates to α,β-enones [7].

Methyl butyl sulfone (Ia) in the system $Na_2S_2O_8$–$CuCl_2$ [(Ia):$Na_2S_2O_8$:$CuCl_2$=1:1:1] is chlorinated at C^3 and C^4, γ-chlorination predominating (as in the chlorination of butanesulfonamides $BuSO_2NHR^1$ by this system [5]). In addition to the chlorosulfones (IVa) and (Va), the hydroxysulfone (IIIa) is formed, the yields of (IVa), (Va), and (IIIa) being 48, 33, and 6% on (Ia) reacting, conversion 88%. Oxidative chlorination of dibutyl sulfone (Ic) under similar conditions affords the γ- and δ-chlorosulfones (IVc) and (Vc) in yields of 60 and 35% on (Ic) reacted respectively, conversion 90%.



The course and regioselectivity of the remote oxidative functionalization of sulfones (Ia-c) with a maximum chain length of four carbon atoms [butyl in (Ia) and (Ic) and 1-methylbutyl in (Ib)] are thus similar to those found for the oxidation of butanesulfonamides under similar conditions.

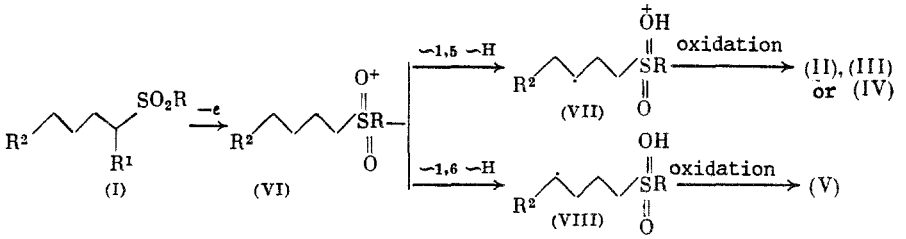
The remote functionalization of sulfonamides has previously been shown [1, 5, 6] to involve the generation of sulfonylamidyl radicals, followed by rearrangement with 1,5(1,6)-hydrogen migration to give 3(4)-aminosulfonylalkyl radicals, which are precursors of the functionalization of alkanesulfonamides at C^3 and C^4. Since the orientation and regioselectivity of the oxidative functionalization (chlorination and oxygenation) of butyl alkyl sulfones and butanesulfonamides are similar for these substrates, it is reasonable to suppose that the remote functionalization of sulfones involves one-electron oxidation to the oxygen-cen-

TABLE 2. Oxidation of Methyl Hexyl Sulfone (IX) by $Na_2S_2O_8$*

(IX) : $Na_2S_2O_8$	Conversion of (IX), %	Yields of products, as % of (IX) reacting
1:2	85	(X), 20; (XI), 30
1:4	100	(X), 28; (XI), 28

*85-90°C, 5 h.

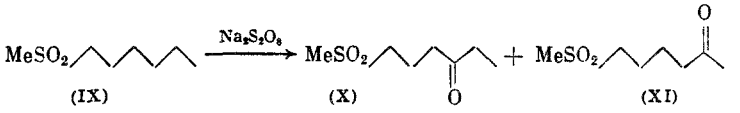
tered cation-radicals (VI), which rearrange with 1,5- or 1,6-hydrogen migration to 3- and 4-sulfonylalkyl radicals (VII) and (VIII), which are then oxidized to (III), then to (II), or to (IV), then (V). This theoretically possible mechanism was confirmed by the observa-



$R^2 = H$

tion of the rearrangement (VI) → (VII) when the cation radicals (VI) were generated by electron impact [8].

However, the similarity to sulfonamides is completely lost when the sulfones have longer hydrocarbon chains. Oxidation of methyl hexyl sulfone (IX) with $Na_2S_2O_8$ gives 4-oxohexyl and 5-oxohexyl methyl ketones (X) and (XI) (Table 2).



The expected γ-oxidation product, 3-oxohexyl methyl sulfone, which is isomeric with (X) and (XI), was totally absent, to judge from the absence in the PMR spectrum of signals for the moiety $SO_2CH_2CH_2C(O)$ (two triplets at 2.95-3.00 and 3.25-3.35 ppm).

According to the mechanism discussed above, (X) and (XI) could be formed by rearrangement of (VI) (R = Me, R^1 = H, R^2 = Et) with 1,6- and 1,7-migration of hydrogen. However, preference for 1,6- and especially 1,7-hydrogen migration over 1,5-hydrogen transfer in cation radicals and radicals has been observed previously only in a few special cases, when such shifts are favored energetically or conformationally [9, 10]. We therefore assume that such a route to (X) and (XI) is unlikely. The results obtained discount the possibility in the case of sulfones of single-step remote functionalization with the initial formation of cation radicals (VI), followed by rearrangement with hydrogen migration.

In our view, the observed orientation in the functionalization of sulfones (Ia-c) at the γ-carbon, and of the sulfone (IX) in the δ- and ε-positions, results from polar control [11]. The strongly electron-accepting SO_2 group inhibits cleavage by the electrophilic $SO_4^{-\cdot}$ anion radicals (or of $Cl^\cdot$ and $Cl_2^{-\cdot}$ in the system $Na_2S_2O_8$–$CuCl_2$) of hydrogen atoms from the α- and β-carbons in all of these sulfones. The γ-carbons also experience deactivation by the SO_2 group, as is shown by the absence of γ-functionalization when (IX) is oxidized. In the butyl sulfones (Ia-c), the γ-carbon bears a CH_3 group, which facilitates to a certain extent the fission of the γ-hydrogen. The γ-CH_3 group itself is a comparatively weak hydrogen donor (as compared with the neighboring CH_2 group) with respect to the $SO_4^{-\cdot}$ anion radical [12]. The combination of these factors determines the selectivity of oxidation of (Ia-c) virtually at the γ-position alone.

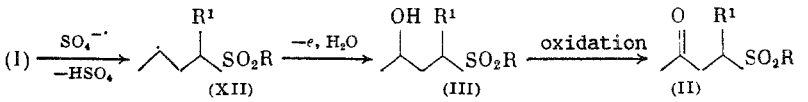


TABLE 3. Properties of Starting Materials and Reaction Products

Compound	Mp, °C, or Bp, °C (p, mm Hg)	PMR spectrum, δ, ppm, J, Hz	Mass spectrum, m/z (rel. intensity, %)
(Ia)	30	0,98 t (3H, CH_3CH_2), 1,20–2,00 m (4H, $CH_3CH_2CH_2$), 2,83 s (3H, CH_3SO_2), 2,98 t (2H, CH_2SO_2)	As in [8]
(Ib)	131–134(17)	1,07 t (3H, CH_3CH_2), 1,32 d (3H, CH_3CH), 1,40–2,00 m (4H, $CH_3CH_2CH_2$), 2,72 s (3H, CH_3SO_2), 3,10 m (1H, $CHSO_2$)	151(M^{++}1, 16), 135(4), 121(70), 108(15), 107(14), 81(75), 80(60), 72(82), 71(100), 55(80), 43(100)
(Ic)	44–45	0,98 t (6H, 2-CH_3), 1,20–1,90 m (8H, 2-CH_2CH_2), 2,90 t (4H, 2-CH_2SO_2)	As in [8]
(IIa)	87–88 *	2,22 s (3H, $CH_3C(O)$), 2,90s (CH_3SO_2), 2,98 t ($CH_2C(O)$), 3,27 t(2H, CH_2SO_2)	
(IIb) †	58.5–59,5	1,40 d (3H, CH_3CH, J=6,9), 2,23 s (3H, $CH_3C(O)$), 2,62 dd (1H_b, J_{ab}=8,3, J_{bc}=17,9) ‡, 2,87 s (3H, CH_3SO_2), 3,23 dd (1H, J_{ac}=3,5, J_{cb}=17,9), 3,60 m (1H, $CHCH_3$)	122(40), 107(12), 85(20), 84(11), 81(64), 71(7), 69(39), 55(61), 43(100), 41(31)
(IIc)	55–56 *	0.91 t (3H, CH_3CH_2), 1,35–1,83 m (4H, $CH_3CH_2CH_2$), 2,18 s (3H, $CH_3C(O)$), 2,88 t($CH_2C(O)$), 3,15 t (2H, CH_2SO_2)	–
(IIIa)	–	1,18 d (3H, CH_3CH), 1,85–1,95m (2H, CH_2CH), 2,89 s(3H, CH_3SO_2), 3,10 t(2H, CH_2SO_2), 3,89 m (1H, CHOH)	–
(IIIc)	–	0,91 t (H, CH_3CH_2), 1,21 d (1H, CH_3CH), 1,35–1,70 m (4H, $CH_3CH_2CH_2$), 1,80–2,05 m (1H, CH_2CH), 2,88 t (2H, CH_2SO_2), 3,84 m(1H, CHOH)	–
(IVa)	–	1,50 d (3H, CH_3CHCl), 2,00–2,33m (2H, CH_2CH_2Cl), 2.95–3,05 m (2H, CH_2SO_2), 4,11 m (1H, CHCl)	–
(IVc)	–	0,94 t (3H, CH_3CH_2), 1,45–1,77m (4H, $CH_3CH_2CH_2$), 1,55 t (3H, CH_3CH), 2,05–2,30 m (2H, CH_2CHCl), 2,85–3,00 m (2H, $C_3H_7CH_2SO_2$), 3,00–3,20m (2H, $ClCHCH_2CH_2SO_2$), 4,14 m (1H, CHCl)	–
(Va)	–	1.70–1,90 m (4H, $ClCH_2CH_2CH_2$), 2,86 s (3H, CH_3SO_2), 2,95–3,05 m (CH_2SO_2), 3,52 t (2H, $ClCH_2$)	–
(Vc)	–	0.94 t (3H, CH_3CH_2), 1,45–1,77 m (4H, $CH_3CH_2CH_2$), 1,80–2,05 m (4H, $ClCH_2CH_2CH_2$), 2.85–3,00 m (2H, $C_3H_7CH_2SO_2$), 3,00–3,20 m (2H, $Cl(CH_2)_3CH_2$), 3,55t (2H, CH_2Cl)	–
(IX)	90–94(0.1), 48,5	0,90t (3H, CH_3CH_2), 1,10–2,10 m (8H, $CH_3(CH_2)_4$), 2,90s (3H, CH_3SO_2), 3,04 t (2H, CH_2SO_2)	164(M^+, 1), 149(12), 147(7), 107(6), 94(12), 85(46), 84(13), 81(100), 80(21)

TABLE 3 (continued)

Compound	Mp, °C, or Bp, °C (p, mm Hg)	PMR spectrum, δ, ppm, J, Hz	Mass spectrum, m/z (rel. intensity, %)
(X)	–	1,05 t (3H, CH_3CH_2), 1,70–1,90 m (2H, $CH_2CH_2C(O)$), 2,43 q (2H, CH_3CH_2), 2,67 t(2H, $CH_2CH_2C(O)$), 2,90 s (3H, CH_3SO_2), 3,05 t (2H, CH_2SO_2)	–
(XI)	–	1,70–1,90 m (4H, $CH_3C(O)CH_2CH_2CH_2$), 2,15 s (3H, $CH_3C(O)$), 2,50 t (2H, $CH_2C(O)$), 2,92 s (3H, CH_3SO_2), 3,02 t (2H, CH_2SO_2)	–
(XIIIa)	118–120(760)	0,97 t(3H, CH_3CH_2), 1,20–1,90 m (4H, $CH_3CH_2CH_2$), 2,00 s (3H, CH_3S), 2,45 t (2H, CH_2S)	–
(XIIIb)	135–137(760)	0,95 t (3H, CH_3CH_2), 1,21 t (3H, CH_3CH), 1,30–2,10 m ($CH_3CH_2CH_2$), 2,97 s (3H, CH_3S), 2,10–2,60 m (1H, CHS)	–
(XIV)	66(20)	0,87 t (3H, CH_3CH_2), 1,10–1,60 m (8H, $CH_3(CH_2)_4$), 2,00 s (3H, CH_3S), 2,40 t (2H, CH_2S)	–

*cf. [7].

†Found: C 43.96; H 7.35; S 19.17%. $C_6H_{12}O_3S$. Calculated: C 43.90; H 7.31; S 19.51%.

‡Data for double resonance of $MeSO_2CH_aMeCH_bH_cC(O)Me$: irradiation at the frequency of the signal at 3.60 ppm resulted in the signal at 2.62 ppm (d.d) reducing to a doublet with J = 17.9 Hz, the signal at 3.23 ppm (d.d) to a doublet with J = 17.9 Hz, and the doublet at 1.40 ppm to a singlet.

Oxidation of (Ia) by treatment with $Na_2S_2O_8$ in the presence of a spin trap (2-methyl-2-nitrosopropane, MNP) gave, as shown by EPR spectroscopy, the adduct of radical (XIIa, R = Me, R^1 = H) with MNP (triplet of doublets, a_N = 15.8, a_H^β = 1.8 Oe).

In the sulfone (IX), there is no hindrance whatsoever to the detachment of hydrogen atoms from the δ- and ε-CH_2 groups by the sulfate anion radicals, whereas the γ-CH_2 group is somewhat deactivated by the SO_2 substituent, and in this case cleavage of the γ-hydrogen is less favored, which also determines the oxidative functionalization of (IX) at the δ- and ε-carbons.

In accordance with this explanation, (Ia) and (Ic) are inert towards the system $Na_2S_2O_8$–$AgNO_3$–$CuSO_4$, in which the oxidant is strictly speaking Ag^{2+} (or Cu^{3+}), which are unlikely to detach hydrogen from an alkyl chain.

Hence, the sulfonyl (SO_2) group cannot give rise on oxidation to the $-S(O^{+\cdot})O-$ cation radical followed by intramolecular hydrogen migration as an activator of remote functionalization, and consequently the general method of single-step remote functionalization is not applicable to sulfones [1-6]. The orientation in the remote functionalization of sulfones is under polar control.

This dependence of the orientation of remote oxidation functionalization of sulfones on chain length provides further confirmation of the mechanism of the remote functionalization of sulfonamides involving rearrangement of sulfonylamidyl radicals with hydrogen migration, which occurs at the γ- or γ- and δ-positions of the sulfonyl fragment irrespective of its length [5, 6].

EXPERIMENTAL

GLC analyses were carried out on an LKhM-8MD chromatograph with a flame ionization detector, in nitrogen. Columns (stainless steel) 1000 × 3 mm, 5% XE-60 on Chromatone N-AW (0.125-0.160 mm) and 1000 × 3 mm, 5% SE-30 on Chromatone N-AW DMCS (0.160-0.200 mm). PMR spectra of solutions in $CDCl_3$ were obtained on a Bruker M-250 (250 MHz). Chemical shifts are given on the δ scale, with TMS as internal standard. The EPR spectrum was obtained on an RE-1307 spectrometer, and mass spectra on a Varian MAT-CH-6 with direct introduction of

the sample into the ion source, source temperature 100°C, pressure of the gas reagent (isobutane) 0.2 mm Hg.

$Na_2S_2O_8$, $CuCl_2$, $CuSO_4 \cdot 5H_2O$, $AgNO_3$, and dibutyl sulfone (Ic) (chemically pure) were used without further purification. Water was once distilled.

Synthesis of Methyl Alkyl Sulfones (Ia, b) and (IX). The syntheses were carried out in two stages. The properties of the products are given in Table 3.

a) Synthesis of Methyl Alkyl Sulfides [13] (General Method). In a flask containing a solution of 3 g of sodium hydroxide in 50 ml of water were placed 4.1 g (0.046 mole) of RSH, 40 ml of benzene, 6.53 g (0.046 mole) of MeI, and 100 mg of tetraoctylammonium chloride. The mixture was stirred vigorously for 15 min at ~20°C, then the organic layer was separated, washed with water, dried over Na_2SO_4, and the benzene distilled off. Redistillation gave the sulfides: methyl butyl sulfide (XIIIa), 1-methylbutyl methyl sulfide (XIIIb), and methyl hexyl sulfide (XIV), yields 47, 58, and 80% respectively.

b) Oxidation of Methyl Alkyl Sulfides to Methyl Alkyl Sulfones [14] (General Method). To a solution of 0.1 mole of the sulfide (XIIIa), (XIIIb), or (XIV) in 30 ml of acetic acid was added with cooling 22.8 g (0.2 mole) of 30% hydrogen peroxide. The mixture was heated at 80-90°C for 3 h, cooled, neutralized with a solution of 20 g of sodium hydroxide in 30 ml of water, and extracted with ether (2 × 25 ml) and chloroform (2 × 25 ml). The extracts were combined, dried over Na_2SO_4, and evaporated. The sulfones (Ia, b) and (IX) were purified by vacuum distillation. (Ia) and (IX) crystallized on standing.

Oxidation of Sulfones (Ia-c) and (IX) with $Na_2S_2O_8$, and Oxidation of Sulfones (Ia, c) with $Na_2S_2O_8$–$CuCl_2$. To 0.01 mole of the sulfone in 20 ml of water was added dropwise at 85-90°C a solution of $Na_2S_2O_8$ in water (the substrate:$Na_2S_2O_8$ ratios are given in Tables 1 and 2), or to a mixture of 0.01 mole of the sulfone and 1.71 g (0.01 mole) of $CuCl_2 \cdot 2H_2O$ in 30 ml of water was added dropwise at 85-90°C a solution of 2.38 g (0.01 mole) of $Na_2S_2O_8$ in 20 ml of water. The mixture was then stirred for 5 h at 80-90°C, cooled, and extracted with ether (3 × 30 ml) [in chlorinations, also with chloroform (2 × 30 ml)]. The extracts were dried over Na_2SO_4 and evaporated. The organic residues were examined by GLC and PMR. Data on the conversion of sulfones (I) and (IX), and the compositions and yields of the products are given in Tables 1 and 2, and in the text. The oxosulfone (IIa) crystallized on standing without further purification. (IIb) and (IIc) were isolated from their mixtures with unreacted (Ib) and (Ic) by preparative TLC on silica gel L (eluent, dichloromethane–2% MeOH).

Behavior of Sulfones (Ia) and (Ic) in the System $Na_2S_2O_8$–$AgNO_3$–$CuSO_4$. To 0.01 mole of (Ia) or (Ic) in 20 ml of water was added 0.5 g (0.002 mole) of $CuSO_4 \cdot 5H_2O$ and 0.255 g (0.0015 mole) of $AgNO_3$, the mixture heated to 85°C, and a solution of 2.38 g (0.01 mole) of $Na_2S_2O_8$ in 20 ml of water added dropwise. The mixture was stirred at this temperature for 5 h, cooled, and extracted with ether (3 × 30 ml) and chloroform (3 × 30 ml). The extracts were combined, dried over Na_2SO_4, and evaporated. According to GLC and NMR, the organic residue contained the starting materials (Ia) or (Ic) only, conversion <5%.

The authors thank V. E. Zubarev for obtaining and interpreting the EPR spectra.

CONCLUSIONS

1. Oxidation of dialkyl sulfones with systems containing sodium peroxydisulfate results in remote functionalization, the site of which is dependent on the length of the alkyl chain, in agreement with polar control of this reaction by the electron-acceptor sulfonyl group.

2. Butyl alkyl sulfones are selectively oxidized by $Na_2S_2O_8$ to 3-oxobutyl alkyl sulfones, and oxidative chlorination in the system $Na_2S_2O_8$–$CuCl_2$ gives 3- and 4-chlorobutyl alkyl sulfones, the γ-chlorination products predominating.

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STUDY OF THE MECHANISM OF ISOMERIZATION OF 2-BROMOPROPYL BENZOATE USING AN ^{18}O ISOTOPIC LABEL

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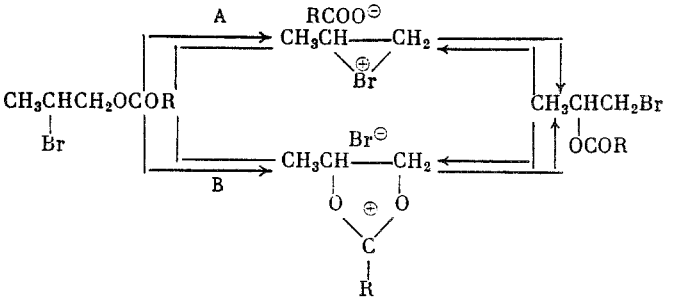
UDC 541.124:542.952.1:
547.581.2'263'141

We report here an examination of the isomerization of 1(2)-bromoprop-2(1)-yl esters, discovered previously by us [1, 2], by the labeled atom method, using the ^{18}O oxygen isotope and the model compound 2-bromopropyl benzoate bearing ^{18}O in the acyl group. It has previously been suggested that two routes are possible for this reaction:



In the case of the bromonium mechanism (A), a statistical distribution of the ^{18}O label in the RCOO group of the isomerization product would be expected, whereas in the acyloxonium route (B) the isomerization product should contain ^{18}O exclusively bonded to the secondary carbon ($CH_3CH(^{18}OCOC_6H_5)CH_2Br$).

The starting material (I) was obtained using commercial $H_2{}^{18}O$:

$$C_6H_5CCl_3 \xrightarrow{H_2{}^{18}O} C_6H_5C^{18}O^{18}OH \xrightarrow{SOCl_2} C_6H_5C^{18}OCl \xrightarrow{CH_3CHBrCH_2OH} CH_3CHBrCH_2OC(=\overset{18}{O})C_6H_5 \quad (I)$$

The mass spectrum of (I) showed a strong peak for an ion with m/z 107 ($C_6H_5C^{18}O^+$), which in the case of the ^{16}O analog was shifted to m/z 105 ($C_6H_5CO^+$).

Isomerization of the ester (I) was effected in nitrobenzene, CCl_4, or CD_2Cl_2, as described in [3]. When equilibrium was attained, the mixture was examined by GC-MS. In the mass spectrum of 1-bromoprop-2-yl benzoate, the isomerization product of (I), a peak was seen for an ion with m/z 105, no peak with m/z 107 being present. This result unambiguously confirms that the isomerization takes place by route (B), via the acyloxonium ion:

M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2144-2145, September, 1988. Original article submitted January 29, 1987.

0568-5230/88/3709-1925$12.50