3. Theories regarding the role of the symmetry of the π orbital and the polarizability of the dipolarophile in the possibility of its mild involvement in cyclization with oxiranes and thiiranes have been advanced.

LITERATURE CITED

1. A. V. Fokin and A. F. Kolomiets, Usp. Khim., 45, 71 (1976).
2. A. V. Fokin and A. F. Kolomiets, The Chemistry of Thiiranes [in Russian], Nauka, Moscow (1978).
3. V. A. Ponomarenko, S. P. Kurkovskii, and A. Yu. Alybina, Fluorine-Containing Mixed-Chain Polymers [in Russian], Nauka, Moscow (1973).
4. A. V. Fokin, A. F. Kolomiets, and T. I. Fedyushina, Dokl. Akad. Nauk SSSR, 227, 104 (1976).
5. Yu. V. Zeifman and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 173, 354 (1967).
6. G. F. Il'in and A. F. Kolomiets, Zh. Vses. Khim. O-va D. I. Mendeleeva, 25, 705 (1980).
7. G. F. Il'in and A. F. Kolomiets, ibid., 25, 706 (1980).
8. G. F. Il'in, A. F. Kolomiets, and G. A. Sokol'skii, Zh. Org. Khim., 16, 1096 (1980).
9. G. F. Il'in, A. F. Kolomiets, and G. A. Sokol'skii, Zh. Vses. Khim. O-va D. I. Mendeleeva, 25, 109 (1980).
10. G. F. Il'in, A. F. Kolomiets, and G. A. Sokol'skii, Zh. Org. Khim., 15, 2216 (1979).

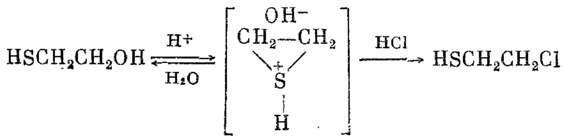
NUCLEOPHILIC SUBSTITUTION OF HYDROXYL GROUPS IN 2-ALKYL(ARYL)-THIOETHANOLS

A. V. Fokin, A. F. Kolomiets,
L. S. Rudnitskaya, M. G. Iznoskova,
and L. S. Paimulkina

UDC 542.91:547.269

The features of the reactivity of 2-alkyl(aryl)thioalkanols in the nucleophilic substitution of the hydroxyl group have practically not been revealed, and the limited information on these conversions refers predominantly to reactions involving the replacement of the OH group by a halogen atom [1].

The possibility of the occurrence of such reactions was demonstrated for the first time in the example cases of the synthesis of di(2-chloroethyl) sulfide by reacting di(2-hydroxyethyl) sulfide with hydrochloric acid saturated with HCl upon heating [2]. 2-Chloroethyl mercaptan was obtained from 2-hydroxyethyl mercaptan by the same method under pressure in [3]. The comparatively mild replacement of the OH group by a chlorine atom in the reactions just cited is attributed to the ability of the original hydroxy compounds to form episulfonium ions upon protonation, which are opened not only by a hydroxide anion, but also by a chloride ion.



The low solubility of 2-alkyl(aryl)thioethanols in hydrochloric acid presents their exhaustive substitutive halogenation by the method considered above. It is possible to carry out such conversions exclusively only under homogeneous conditions, for example, in solutions of alcohols [4]:

$$PhSCH_2CH_2OH + HCl \xrightarrow{\text{EtOH, boiling}} \underset{72\%}{PhSCH_2CH_2Cl}$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1876-1881, August, 1982. Original article submitted December 1, 1981.

0568-5230/82/3108-1667$07.50

TABLE 1. Temperature Effects and Yield of the Product of the Reaction of 2-(n-Octylthio)-ethanol with HCl

Catalyst acid	Maximum temp. for reaction, °C	Yield of product, %
HCl	27	49,4
H_3PO_4	34	63,5
H_2SO_4	37	76,4
$4\text{-}CH_3C_6H_4SO_3H$	42	83,6
HBF_4	47	88,9
$HClO_4$	49	86,4
$HOSO_2F$	49	87,4

According to the data in [5], higher 2-alkylthioethanols react exothermically with anhydrous HCl in the absence of solvents and are converted into the corresponding 2-alkylthioethyl chlorides with 65-81% yields; however, evidence of the purity of the compounds formed was not given in the patent.

Only one example of the nucleophilic substitution of an OH group in a 2-alkyl(aryl)-thioethanol by an alkoxy group is known. As was shown in [6], 2-arylthioethanols are converted extremely easily into the corresponding ethers under catalysis by strong mineral acids. 2-Alkylthioethanols undergo this reaction with somewhat greater difficulty:

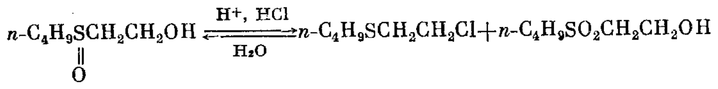
$$2RSCH_2CH_2OH \xrightarrow[-H_2O]{H_3PO_4;\ 80^\circ} (RSCH_2CH_2)_2O$$

The present communication provides new information on the reactions of 2-alkyl(aryl)-thioethanols with HCl, ethanols, and thiols. In the investigations of the reactions with HCl attempts were made to realize the exhaustive substitutive chlorination of 2-alkyl(aryl)-thioethanols in hydrochloric acid, employing catalysis of the process by strong mineral acids for these purposes. The results of the systematic study are illustrated by the data in Table 1, which presents some characteristics of the reaction of 2-octylthioethanol with HCl in hydrochloric acid with the supply of HCl to the reaction mass at the rate of 15 ml/min over the course of 4 h:

$$n\text{-}C_8H_{17}SCH_2CH_2OH \underset{H_2O}{\overset{H^+;\ HCl}{\rightleftharpoons}} n\text{-}C_8H_{17}SCH_2CH_2Cl$$

The data presented show that strong mineral acids significantly increase the rate of the substitutive chlorination of 2-octylthioethanol and simultaneously noticeably shift the equilibrium of the reaction in favor of the formation of 2-chloroethyl octyl sulfide. This compound forms with a preparative yield already in the presence of sulfuric acid.

2-Butyl- and 2-phenylthioethyl chloride were obtained with 85.6 and 72.4% yields, respectively, under the conditions for the formation of 2-octylthioethyl chloride and catalysis by p-toluenesulfonic acid. Therefore, the replacement of the OH groups in 2-alkyl(aryl)-thioethanols by chlorine atoms in hydrochloric acid catalyzed by strong mineral acids has a general character. At the same time, 2-sulfinyl- and 2-sulfonylethyl chlorides could not be obtained by this method. For example, when 2-butylsulfinylethanol is reacted with HCl in hydrochloric acid under catalysis by H_2SO_4, it is converted into a mixture of 2-butylthioethyl chloride and butyl 2-hydroxyethyl sulfone:



$$n\text{-}C_4H_9\underset{\underset{O}{\|}}{S}CH_2CH_2OH \underset{H_2O}{\overset{H^+,\ HCl}{\rightleftharpoons}} n\text{-}C_4H_9SCH_2CH_2Cl + n\text{-}C_4H_9SO_2CH_2CH_2OH$$

Acid catalysis of the reactions under consideration under anhydrous conditions proved to be less effective. For example, the reaction of 2-octylthioethanol with anhydrous HCl catalyzed by H_2SO_4 under the conditions of patent [5] produces a mixture of 2-octylthioethyl chloride and the original compound, and under similar conditions 2-phenylthioethanol also forms the corresponding ether:

$$PhSCH_2CH_2OH \xrightarrow{H^+;HCl} PhSCH_2CH_2Cl + (PhSCH_2CH_2)_2O$$

In order to reveal the features of the nucleophilic replacement of the OH groups in the compounds investigated by alkoxy groups, the reactions of 2-butyl- and 2-octylthioethanol with butanol and 1,1,5-trihydrooctafluoropentanol were studied. As it turned out, these reactions produce mixed ethers and take place under conditions similar to the conditions for the conversion of 2-alkyl(aryl)thioethanols into symmetric ethers:

$$RSCH_2CH_2OH + R'OH \xrightarrow[-H_2O]{H^+;\ 80-100^\circ} RSCH_2CH_2OR'$$

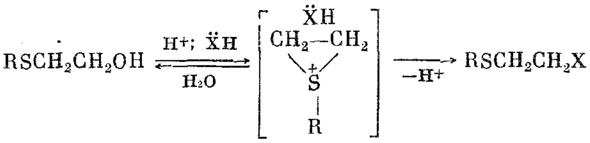
p-Toluenesulfonic acid proved to be an especially good catalyst in this case. A preparative yield of the products was obtained with a three- to fourfold excess of butanol and a five- to sixfold excess of an acidic alcohol, such as 1,1,5-trihydrooctafluoropentanol.

2-Alkyl(aryl)thioethanols undergo reactions with thiols catalyzed by mineral acids in a considerably more well-defined manner. The predominant replacement of OH groups by alkyl(aryl)thiol groups takes place even with an equimolar reactant ratio, and when there is a twofold excess of the thiol, practically pure 1,2-di[alkyl(aryl)thio]ethanes form:

$$RSCH_2CH_2OH + R'SH \xrightarrow[-H_2O]{H^+;\ 80-100^\circ} RSCH_2CH_2SR'$$

Thiophenols react somewhat more readily with 2-alkyl(aryl)thioethanols than do mercaptans, and 2-arylthioethanols have a somewhat higher reactivity than 2-alkylthioethanols (Table 2).

From the data obtained in the work it follows that the ability of hydroxyl groups to be replaced by another nucleophilic particle is a common property of 2-alkyl(aryl)thioethanols. This property is displayed only when the hydroxyl group in the compounds investigated is protonated, i.e., under conditions for the generation of a low σ^* orbital on the β carbon atom, which favor the formation of episulfonium states:



$$RSCH_2CH_2OH \underset{H_2O}{\overset{H^+;\ \ddot{X}H}{\rightleftarrows}} \left[\overset{\ddot{X}H}{CH_2-CH_2 \atop \diagdown \overset{+}{S} \diagup} \atop | \atop R \right] \xrightarrow{-H^+} RSCH_2CH_2X$$

X = Hal, OR, SR, SAr.

The selectivity of the processes studied increases with decreasing strength of the nucleophilic reagents, as was clearly manifested in the reactions with $H(CF_2CF_2)_2CH_2OH$, $p\text{-}C_4H_9OH$, HCl, RSH, and ArSH. In this respect the processes of the nucleophilic substitution of hydroxyl groups in 2-alkyl(aryl)thioethanols are somewhat reminiscent of the nucleophilic opening of thiirane rings.

EXPERIMENTAL

The purity of the products was determined by gas chromatography on a Tsvet-4-69 instrument with the use of a 3 m × 3 mm column with 5% SE-52 on TND-TSM (the carrier gas was He). The IR spectra were recorded on a Perkin–Elmer R-225 instrument in thin layers between KBr prisms, and the mass spectra were recorded on a Varian MAT CH-8 instrument.

Reaction of 2-(n-Octylthio)ethanol with HCl in Hydrochloric Acid. An emulsion of 19.2 g of 2-(n-octylthio)ethanol in 50 ml of concentrated HCl was given an addition of 0.05 of an equivalent of a mineral acid, and then HCl was bubbled in at the rate of 15-20 ml/min with intense stirring over the course of 4 h. The organic layer was separated, given an addition of chloroform extracts from the aqueous layer (two 20-ml portions), dried over $CaCl_2$, and fractionated. 2-(n-Octylthio)ethyl chloride with bp 123-124°C (4 mm), d_4^{20} 0.9644, and n_D^{20} 1.4805 was recovered. Mass spectrum (70 eV): m/z 208 (M^+), 210 (M^+), 172 (M − HCl). Found: C 57.33; H 10.02; Cl 16.85; S 14.96%. Calculated for $C_{10}H_{21}ClS$: C 57.55; H 10.07; Cl 17.03; S 15.34%.

The catalysts used in these reactions, the temperature effects of the reactions, and the yields of the products are given in Table 1.

2-(n-Butylthio)ethyl Chloride. 2-(n-Butylthio)ethyl chloride was obtained in the presence of p-toluenesulfonic acid from 13.4 g of 2-(n-butylthio)ethanol under the conditions

TABLE 2. Yield and Some Properties of the Products of the Reaction $RSCH_2CH_2OH+R'SH \xrightarrow{H^+} RSCH_2CH_2SR'$

R	R′	Time, h	Yield, %	bp, °C (p, mm Hg) mp, °C	d_4^{20}	n_D^{20}	Found/calc., %			Empirical formula
							C	H	S	
n-C_8H_{17}	n-C_8H_{17}	8	72,15	72–75 (0,01)	0,8542	1,4632	67,82/67,92	11,90/11,95	19,76/20,13	$C_{18}H_{38}S_2$
n-C_9H_{19}	n-C_8H_{17}	8	76,3	76–78 (0,01)	0,9016	1,4820	68,41/68,67	11,94/12,05	19,03/19,28	$C_{19}H_{40}S_2$
n-C_9H_{19}	n-C_9H_{19}	8	70,6	45–47	–	–	69,16/69,36	12,07/12,14	18,24/18,50	$C_{20}H_{42}S_2$
n-C_8H_{17}	4-$CH_3C_6H_4$	5	78,4	154–157 (1)	0,9821	1,5410	68,80/68,92	9.22/9,46	21,37/21,62	$C_{17}H_{28}S_2$
n-C_9H_{19}	C_6H_5	3,5	83,1	110 (0,015)	–	–	68,75/68,92	9,41/9,46	21,04/21,62	$C_{17}H_{28}S_2$
C_6H_5	n-C_9H_{19}	3	86,2	115 (0,02)	–	–	68,81/68,92	9,54/9,46	21,31/21,62	$C_{17}H_{28}S_2$
C_6H_5	C_6H_5	3	89,0	71–73	–	–	68,01/68,29	5,44/5,69	25,61/26,02	$C_{14}H_{14}S_2$

for the synthesis of 2-(n-octylthio)ethyl chloride. The yield was 13.05 g (85.6%), bp 55-57°C (2 mm), d_4^{20} 1.0149, and n_D^{20} 1.4815 (compare [7]).

2-Phenylthioethyl Chloride. This compound was obtained in the presence of fluoboric acid from 15.4 g of 2-phenylthioethanol under the conditions for the synthesis of 2-(n-octylthio)ethyl chloride. The yield was 12.32 g (72.4%), bp 94-95°C (2 mm), d_4^{20} 1.1718, n_D^{20} 1.5829. The values given in the literature [7] are: bp 90°C (1 mm), n_D^{20} 1.5818.

Reaction of 2-(n-Butylsulfinyl)ethanol with HCl. A mixture of 50 ml of concentrated hydrochloric acid and 1 ml of sulfuric acid was given a dropwise addition of 31.0 g of 2-(n-butylsulfinyl)ethanol with stirring, HCl being bubbled through the mixture at the rate of 15-20 ml/min. After 2 h the reaction was stopped, and the acid-insoluble product was extracted by chloroform (three 20-ml portions), dried over calcium chloride, and fractionated. This yielded 15.45 g (48.3%) of 2-(n-butylthio)ethyl chloride, bp 55-57°C (2 mm), n_D^{20} 1.4821.

The aqueous layer was evaporated in a vacuum, and 17.5 g (100%) of a viscous liquid, viz., 2-hydroxyethyl n-butyl sulfone, were obtained. Found: C 35.95; H 7.20; S 32.54%. Calculated for $C_6H_{14}O_3S$: C 36.37; H 7.07; S 32.32%. IR spectrum (ν, cm^{-1}): 3530-3420 (OH), 1340 and 1145 (SO_2).

Reaction of 2-(n-Octylthio)ethanol with Anhydrous HCl. Hydrogen chloride was bubbled into a mixture of 9.6 g of 2-(n-octylthio)ethanol and 0.5 g of H_2SO_4 with stirring, the temperature being maintained no higher than 65°C. After the completion of the exothermic reaction, HCl was passed for another 1 h, and the organic layer was separated, dissolved in CCl_4, washed with water, and fractionated. This yielded 8.0 g (76%) of a substance with bp 120-121°C (4 mm) and n_D^{20} 1.4721 (compare [4]). IR spectrum (cm^{-1}): 3360-3200 (OH). According to the results of the chromatographic analysis, it is a mixture of two compounds in a 76:24 ratio.

Reaction of 2-Phenylthioethanol with Anhydrous HCl. This reaction was carried out under the conditions of the preceding experiment. The products were 4.9 g (52%) of 2-phenylthioethyl chloride with bp 94-95°C (2 mm) and n_D^{20} 1.5820 and 2.9 g of 2,2-di(phenylthio)diethyl ether with bp 192-194°C (1 mm) and n_D^{20} 1.6134 (compare [6]).

1-(n-Butoxy)-2-(n-octylthio)ethane. A solution of 9.6 g (0.05 mole) of 2-(n-octylthio)ethanol, 12.0 g (0.16 mole) of n-butanol, and 0.5 g of p-toluenesulfonic acid in 25 ml of benzene was boiled in a Dean–Stark trap until the evolution of water vapor ceased. The reaction mass was cooled, washed with water to a neutral reaction, dried over Na_2SO_4, and fractionated. This yielded 9.4 g (77.7%) of a product with bp 133-135°C (4 mm), d_4^{20} 0.9138, n_D^{20} 1.4680. IR spectrum (ν, cm^{-1}): 1420 (C–O), 654 (C–S). Found: C 68.09; H 12.16; S 13.45%. Calculated for $C_{14}H_{30}OS$: C 68.29; H 12.20; S 13.01%.

1-(α,α,ω-Trihydrooctafluoropentoxy)-2-(n-butylthio)ethane. This compound was obtained under the condition of the preceding experiment from 7.2 g (0.05 mole) of 2-(n-butylthio)ethane and 62.5 g (0.27 mole) of 1,1,5-trihydrooctafluoropentanol in the presence of 0.5 g of p-toluenesulfonic acid. The yield was 14.3 g (76.1%), bp 106-109°C (3 mm), d_4^{20} 1.3183, n_D^{20} 1.3892. Found: C 37.63; H 4.52; F 43.15; S 9.04%. Calculated for $C_{11}H_{16}F_8OS$: C 37.93; H 4.60; F 43.68; S 9.20%.

1,2-Di[alkyl(aryl)thio]ethanes (Typical Experiment). A solution of a 2-alkyl(aryl)thioethanol, 0.1 mole of a thiol, and 0.5 g of p-toluenesulfonic acid in 25 ml of toluene was boiled in a Dean–Stark trap until the evolution of water vapor ceased. The mixture was cooled, washed with water (two 20-ml portions), and dried over magnesium sulfate, and the product was isolated by fractionation. The reaction time, the yield of the products obtained, and the results of their elemental analysis are given in Table 2.

CONCLUSIONS

1. The reactions of 2-alkyl(aryl)thioethanols with HCl in hydrochloric acid, alcohols, and thiols under anhydrous conditions have been studied. It has been shown that selective replacement of the hydroxyl groups in these compounds by chlorine atoms and alkoxy, alkyl, and arylthio groups occurs under certain conditions under catalysis by strong mineral acids.

2. Several laws governing the acid-catalyzed nucleophilic substitution of hydroxyl groups in 2-alkyl(aryl)thioethanols have been revealed. In particular, an increase in the selectivity of the process with decreasing strength of the nucleophilic reagent has been established.

LITERATURE CITED

1. A. V. Fokin and A. F. Kolomiets, The Chemistry of Thiiranes [in Russian], Nauka, Moscow (1978).
2. H. T. Clarke, J. Chem. Soc., 101, 1583 (1912).
3. German Patent No. 47,835 (1940); Chem. Abstr., 34, 6302 (1940).
4. W. Steinkopf, J. Herold, and J. Stohr, Ber., 53, 1006 (1920).
5. U. S. Patent No. 2,598,640 (1952); Chem. Abstr., 47, 2199 (1953).
6. A. V. Fokin, A. F. Kolomiets, and V. S. Shchennikov, Zh. Org. Khim., 7, 1406 (1971).
7. M. Kirner and H. Richter, J. Am. Chem., 51, 3413 (1929).

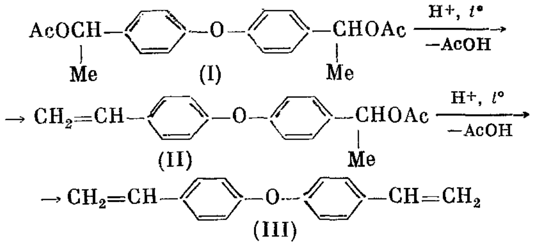
CLEAVAGE OF 4,4'-BIS(1-ACETOXYETHYL)DIPHENYL ETHER

B. A. Zaitsev, L. L. Dantsig,
I. O. Gusarova, M. B. Tennikov,
and B. G. Belen'kii

UDC 542.92:547.562.4'562.1

Cleavage of esters is often used for the synthesis of alkenes [1, 2]. However, there is no information on the use of this method to obtain vinyl- and divinylaromatic monomers, which are of significant interest for the preparation of crosslinked polymers.

In the present paper, we investigated the kinetics of thermal and catalytic cleavage of 4,4'-bis(1-acetoxyethyl)diphenyl ether (I) to 4-vinyl-4'-(1-acetoxyethyl)diphenyl ether (II) and 4,4'-divinyldiphenyl ether (III)



The reaction mixtures were analyzed by exclusion liquid chromatography and titration.

During heating in air or in an inert medium to ∿200°C, (I) retained its stability. In 3 h at 218°C, (I) underwent 7-10% cleavage, with (II) being formed (5% yield) together with a small amount of oligomeric products (IV) and (V). In 3 h at 230°C, 40% of (I) underwent conversion, being converted to (II) (4%) and (V), products of the oligomerization and co-oligomerization of ethers (II) and (III) (Fig. 1, curve 1). When the thermolysis time was increased to 5 h, the conversion of (I) increased to 50%.

If we assume that the acetate groups in (I) are independent and that their activities in (I) and (II) are identical, the rate of the reaction being investigated can be represented in the following integral form:

$$\ln \frac{C_0}{C} = kt \qquad (1)$$

where C_0 and C are the concentrations of the acetate groups, k is the rate constant, and t is the reaction time.

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1881-1883, August, 1982. Original article submitted July 28, 1981.

0568-5230/82/3108-1672$07.50