BENZENESULFONYL DERIVATIVES OF CARBOXYLIC ACID AMIDES

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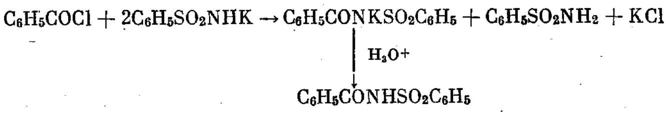
UDC 542.91:547.298.1:547.541.5

Benzenesulfonyl chloride reacts with benzenesulfonamide salts at room temperature to give the corresponding secondary amide in good yield [1].

$$C_6H_5SO_2Cl + C_6H_5SO_2NHAg \rightarrow (C_6H_5SO_2)_2NH + AgCl$$

On the assumption that secondary amides, formed by different kinds of acids (for example, carboxylic and sulfonic acids), can be obtained in a similar manner, a study was made of the reaction of carboxylic acid chlorides with the K salts of the amides of aromatic sulfonic acids. Exothermic reaction occurs when benzoyl chloride is added to an acetone solution of the K salt of benzenesulfonamide and here 2 moles of the salt are consumed per mole of acid chloride. The reaction products are benzenesulfonamide, KCl, and the K salt of N-benzenesulfonylbenzamide. Here the secondary amide is isolated in up to 90% yield when an aqueous solution of the K salt is treated with mineral acids. The reaction does not change when transition is made to other organic solvents. For example, when CH_3CN is used the yield of the secondary amide is 88%, 90% in the case of dioxane, and 85% in the case of toluene.



$$\begin{array}{l} C_6H_5COCl + 2C_6H_5SO_2NHK \rightarrow C_6H_5CONKSO_2C_6H_5 + C_6H_5SO_2NH_2 + KCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_3O^+ \\ \qquad\qquad\qquad\qquad\qquad C_6H_5CONHSO_2C_6H_5 \end{array}$$

The benzenesulfonamide salts are acylated in a similar manner by the acid chlorides of aliphatic carboxylic acids: acetic, chloroacetic, heptafluorobutyric, or methacrylic. The salts of the p-chlorobenzene-, p-methoxybenzene-, and p-toluenesulfonamides were used as the sulfonamide component in the individual reactions. In all cases the corresponding secondary amides, which represented high-melting crystalline compounds, were obtained in good yield; their structure was confirmed by the IR spectra (Table 1).

The secondary N-sulfonylamides are insoluble in H_2SO_4 and HCl solutions, they are difficultly soluble in water, and are readily soluble in dilute aqueous alkali solutions. In the last case the salts of the N-sulfonylamides are formed, which were also obtained by the reaction of secondary amides with the K salt of benzenesulfonamide.

$$RCONHSO_2C_6H_5 + C_6H_5SO_2NHK \rightarrow RCONKSO_2C_6H_5 + C_6H_5SO_2NH_2$$

This reaction makes it possible to explain the above cited reaction of acyl chlorides with the salts of sulfonamides as being a process that includes nucleophilic replacement of the Cl atom of the acid chloride and subsequent rapid neutralization.

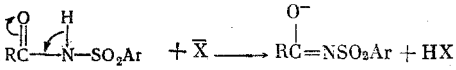
$$RCOCl \xrightarrow{ArSO_2NHK} RCONHSO_2Ar \xrightarrow{ArSO_2NHK} RCONKSO_2Ar$$

The acid properties of the secondary N-sulfonylamides are associated with the electron-acceptor effect of the CO group; apparently their salts are characterized by an imidol structure.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2272-2275, October, 1974. Original article submitted January 14, 1974.

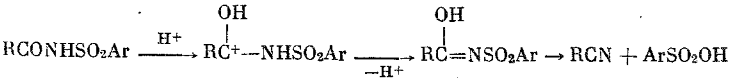
TABLE 1. Secondary Amides

Secondary amide	Yield, %	Mp, °C	cm⁻¹			Empirical formula	$\frac{\text{Found}}{\text{Calculated}}$, %					
			CO	NH	SO_2		C	H	N	F	S	Cl
$C_6H_5CONHSO_2C_6H_5$	90	139	1690	3180	1180, 1335	$C_{13}H_{11}O_3NS$	$\frac{60{,}10}{59{,}77}$	$\frac{4{,}28}{4{,}21}$	$\frac{5{,}16}{5{,}36}$	—	$\frac{12{,}48}{12{,}26}$	—
$C_6H_5CONHSO_2C_6H_4CH_3$-*p*	86	109	—	—	—	$C_{14}H_{13}O_3NS$	$\frac{61{,}43}{61{,}21}$	$\frac{4{,}98}{4{,}74}$	$\frac{5{,}33}{5{,}10}$	—	$\frac{11{,}37}{11{,}63}$	—
$CH_3CONHSO_2C_6H_5$	91	121	1670	3080	1165, 1350	$C_8H_9O_3NS$	$\frac{48{,}45}{48{,}24}$	$\frac{4{,}35}{4{,}52}$	$\frac{6{,}81}{7{,}04}$	—	$\frac{16{,}30}{16{,}08}$	—
$CH_3CONHSO_2C_6H_4OCH_3$-*p*	84	84	—	—	— —	$C_{14}H_{13}O_4NS$	$\frac{57{,}63}{57{,}83}$	$\frac{4{,}20}{4{,}48}$	$\frac{4{,}62}{4{,}82}$	—	$\frac{10{,}70}{10{,}98}$	—
$C_3H_7CONHSO_2C_6H_5$	78	101	1675	3090	1160, 1350	$C_{10}H_{13}O_3NS$	$\frac{52{,}60}{52{,}86}$	$\frac{5{,}48}{5{,}74}$	$\frac{6{,}38}{6{,}16}$	—	$\frac{14{,}30}{14{,}08}$	—
$C_3H_7CONHSO_2C_6H_4Cl$-*p*	80	99	—	—	— —	$C_{10}H_{12}O_3NClS$	$\frac{48{,}02}{47{,}78}$	$\frac{5{,}00}{4{,}78}$	$\frac{5{,}28}{5{,}57}$	—	$\frac{12{,}30}{12{,}63}$	$\frac{14{,}01}{14{,}13}$
$ClCH_2CONHSO_2C_6H_5$	86	101	1700	3105	1145, 1355	$C_8H_8O_3NClS$	$\frac{41{,}20}{41{,}19}$	$\frac{3{,}75}{3{,}43}$	$\frac{5{,}92}{5{,}99}$	—	$\frac{13{,}36}{13{,}64}$	$\frac{14{,}88}{15{,}13}$
$C_3F_7CONHSO_2C_6H_5$	70	118	1720	3120	1170, 1355	$C_{10}H_6O_3NF_7S$	$\frac{33{,}78}{34{,}04}$	$\frac{0{,}33}{0{,}17}$	$\frac{3{,}99}{3{,}97}$	$\frac{37{,}35}{37{,}70}$	$\frac{10{,}00}{9{,}60}$	—
$CH_2{=}C(CH_3)CONHSO_2C_6H_5$	98	128	1665	3090	1170, 1350	$C_{10}H_{11}O_3NS$	$\frac{53{,}66}{53{,}81}$	$\frac{5{,}21}{4{,}94}$	$\frac{6{,}53}{6{,}28}$	—	$\frac{14{,}62}{14{,}32}$	—



$$RC(=O)-NH-SO_2Ar + \overline{X} \longrightarrow R\overset{O^-}{\overset{|}{C}}=NSO_2Ar + HX$$

The formation of compounds of the imidol type can also explain the observed catalytic action of strong acids during the thermal decomposition of secondary amides. Thus, if the first indications of the decomposition of N-benzenesulfonylbenzamide and N-benzenesulfonylacetamide are observed only at 240-250°, then in the presence of either sulfuric or benzenesulfonic acid these same amides decompose at 180-200° to respectively give benzonitrile and acetonitrile.



$$RCONHSO_2Ar \xrightarrow{H^+} R\overset{OH}{\overset{|}{C}}{}^{+}-NHSO_2Ar \xrightarrow[-H^+]{} R\overset{OH}{\overset{|}{C}}=NSO_2Ar \rightarrow RCN + ArSO_2OH$$

The secondary amides from the chloroacetic, butyric, and heptafluorobutyric acids decompose in a similar manner. The obtained carbonitriles were identified by GLC and the physical properties.

The decomposition of the secondary N-sulfonyl-containing amides was also observed previously on the examples of the adducts of hexafluorodimethylketene with sulfamic acid and the benzene-, p-chlorobenzene-, and methanesulfonamides [2-4].

$$(CF_3)_2C{=}C{=}O + RSO_2NH_2 \rightarrow (CF_3)_2CHCONHSO_2R \xrightarrow{200^\circ} (CF_3)_2CHCN + RSO_2OH$$

As a result, the formation and decomposition of the N-benzenesulfonyl derivatives of carboxylic acid amides are quite general reactions. They are accomplished in good yields, and can be used to obtain secondary sulfonamides and carbonitriles.

EXPERIMENTAL METHOD

The IR spectra were taken on a Hitachi—Perkin—Elmer R-457 instrument as a Nujol mull. The values of the characteristic frequencies are given in Table 1. The NMR spectra were taken on a Hitachi—Perkin—Elmer R-20 instrument using CF_3COOH as the external standard. The GLC analysis was run on an LCM-7A instrument, using a 6-m column, packed with the stationary liquid phase 15% SE-52 deposited on the solid phase TNDTSM, a temperature of 20-180°, and a helium flow rate of 10-15 ml/min.

Benzenesulfonylbenzamide. To a stirred suspension of 39 g of the K salt of benzenesulfonamide in 150 ml of anhydrous acetone was added 14.05 g of benzoyl chloride at such a rate that the temperature of the mixture was 20-30°. The stirring was continued for 1 h, the precipitate was filtered, washed with ether, the mother liquor was combined with the ether extracts, the solvent was vacuum-distilled, and the residue was recrystallized from water. We obtained 15.1 g (96%) of benzenesulfonamide with mp 155°. The mixed melting point with an authentic sample was not depressed.

The precipitate (30.5 g) was dissolved in 120 ml of water, and to the stirred solution was added HCl solution (d 1.19) until acid to litmus. The obtained precipitate (18.2 g) was filtered and recrystallized from toluene. We obtained 16.6 g of N-benzenesulfonylbenzamide as white needle crystals.

When the reaction was run in acetonitrile, dioxane, or toluene the yield of N-benzenesulfonylbenzamide was respectively 88, 90, or 85%. The other secondary amides were obtained in a similar manner. The yields, constants, and elemental analysis data are given in Table 1.

Salts of Secondary Amides. To a stirred solution of 2.61 g of N-benzenesulfonylbenzamide in 10 ml of alcohol was added a solution of 1.95 g of the K salt of benzenesulfonamide in 10 ml of water. The mixture was diluted with 20 ml of dioxane, and the obtained precipitate was filtered and recrystallized from aqueous alcohol (1 : 1). We obtained 3.3 g (94%) of the K salt of N-benzenesulfonylbenzamide as prismatic crystals with mp 260° (decompn.). Found: C 51.87; H 3.11; N 4.88%. $C_{13}H_{10}O_3NSK$. Calculated: C 52.17; H 3.37; N 4.68%.

The K salts of N-benzenesulfonylacetamide [mp 240° (decompn.)], N-benzenesulfonylchloroacetamide [mp 220° (decompn.)], and N-benzenesulfonylheptafluorobutyramide [mp 230° (decompn.)] were obtained in a similar manner.

Thermal Decomposition of Secondary Amides. A mixture of 15-20 g of the secondary amide and 5-6 drops of conc. H_2SO_4 was placed in a distillation flask and heated in an oil bath. The obtained distillate was distilled repeatedly, and the benzonitrile, acetonitrile, butyronitrile, or chloroacetonitrile was isolated in a respective yield of 63, 73, 68, or 70%. The compounds were identified by GLC and a comparison of the constants.

Heptafluorobutyronitrile. A mixture of 17.65 g of N-benzenesulfonylheptafluorobutyramide and 5-6 drops of conc. H_2SO_4 was heated at 160°, and the distillate was collected in a trap cooled to −78°. Fractional distillation of the condensate through a low-temperature column led to the isolation of 7.6 g (78%) of heptafluorobutyronitrile with bp −10°. Found: C 24.80; N 7.38; F 67.87%. C_4NF_7. Calculated: C 24.52; N 7.19; F 68.29%. The following chemical shifts (ppm) relative to CF_3COOH were detected in the ^{19}F NMR spectrum: 3.72 t, 44.0 m, and 50.9 t.

CONCLUSIONS

1. The reaction of the acid chlorides of the benzoic, acetic, butyric, chloroacetic, heptafluorobutyric, and methacrylic acids with the salts of the amides of aromatic sulfonic acids gave the corresponding secondary amides.

2. The corresponding carbonitriles were obtained by heating the secondary amides in the presence of sulfuric acid.

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