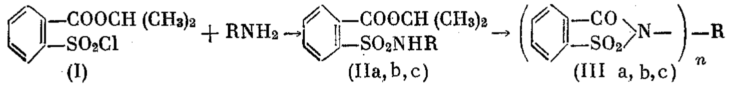
SYNTHESIS OF ISOPROPYL o-SULFAMOLYBENZOATES AND PREPARATION OF IMIDES FROM THEM

B. A. Tagiev and E. P. Mel'nikova

UDC 542.91:547.541.521

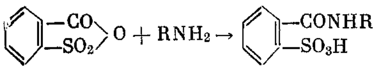
Our study consisted in finding a method for the synthesis of some isopropyl o-sulfamoylbenzoates and ascertaining the conditions for their conversion to the corresponding imides



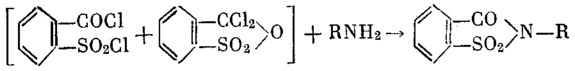
a R=H, $n=1$; b R=C_6H_5, $n=1$; c R= $-(CH_2)_6-$, $n=2$

The indicated reaction can be a model for the two-step synthesis (with the intermediate formation of polysulfamoyl esters) of some new polyimides containing SO_2 and CO groups in the imide ring.

The reaction of o-sulfobenzoic anhydride with amines proceeds with the formation of the benzamide of the o-sulfonic acid, a compound from which the imide derivative could not be obtained even under very drastic conditions [1, 2]



Intermediate compounds of an amide character cannot be isolated when the dichlorides of o-sulfobenzoic acid are reacted with amines, and instead the formation of the imides occurs immediately [3]



Consequently, in order to obtain the indicated model compounds, we selected the reaction of o-(chlorosulfonyl)benzoates with amines. The starting compound, isopropyl o-(chlorosulfonyl)benzoate (I), was synthesized in known manner [2]. The reaction of compound (I) with amines of variable basicity led to obtaining some new o-sulfamoylbenzoates, which were then converted to known compounds of imide character. The conditions for running the indicated reactions were studied on the example of the synthesis (see [2]) of isopropyl o-sulfamoylbenzoates (IIa), and of saccharin (IIIa) from it. The new compound, isopropyl o-(N-phenylsulfamoyl)benzoate (IIb), was obtained by us reacting compound (I) with aniline. The known imide N-phenylsaccharin [4] was formed when compound (IIb) was heated at 300°C.

The reaction of compound (I) with hexamethylenediamine (HMDA) also led to a previously unknown compound, namely hexamethylenedi(isopropyl o-sulfamoylbenzoate) (IIc). As was to be expected, when (IIc) was heated it was converted to the diimide, namely hexamethylenedisaccharin (IIIc). The synthesis of this compound by a different route in one step was described in [5] and was checked by us.

The obtained compounds were characterized by the physical constants and by analysis. Their structure was corroborated by the IR spectra (Fig. 1a). In the IR spectra of compounds (IIa-b) are present absorption bands at 1300-1260 and 1100 cm^{-1}, which correspond to the stretching vibrations of the ester group $-COO$, and also an absorption band at 1720 cm^{-1}, which is characteristic for the $>C=O$ group in esters. In addition, absorption bands are present in the 1350-1310 and 1180-1140 cm^{-1} regions, which correspond to the stretching vibrations of the $-SO_2N<$ bond in the sulfamoyl group [6], and also in the 3400-3200 cm^{-1}

Institute of High-Molecular Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2562-2564, November, 1971. Original article submitted December 16, 1969.

region, which correspond to the $-NH_2$ and $>$NH groups. Absorption bands characteristic for the indicated groups are absent in the IR spectra of compounds obtained by heating the corresponding benzoates (IIIa) and (IIIc). The absorption band of the $>$C=O group is shifted toward higher frequencies and corresponds to the position of this band in the imides of o-sulfobenzoic acid.

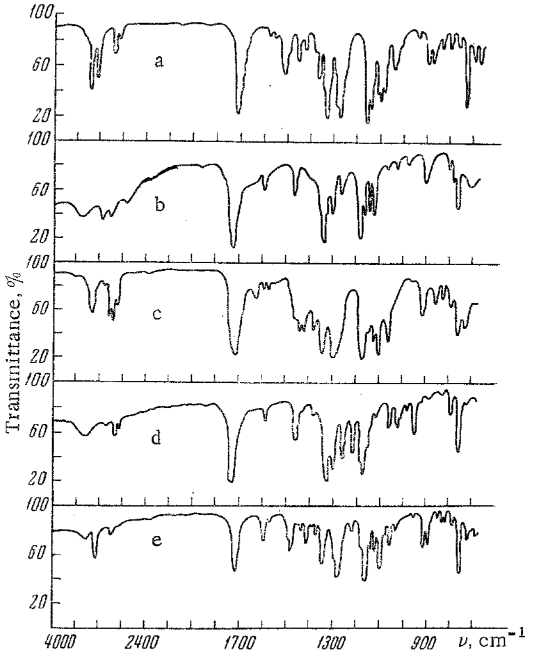


Fig. 1. Infrared spectra of model compounds: a) isopropyl o-sulfamoylbenzoate; b) imide of o-sulfobenzoic acid (saccharin); c) hexamethylenedi(isopropyl o-sulfamoylbenzoate); d) hexamethylenedisaccharin; e) isopropyl o-(N-phenylsulfamoyl)-benzoate.

EXPERIMENTAL METHOD

Isopropyl o-(chlorosulfonyl)benzoate (I) was obtained as in [2] and was used for reaction without additional purification. Isopropyl o-sulfamoylbenzoate (IIa) was obtained by a modification of the method given in [2]. A solution of 5.49 g of (I) in 50 ml of ether, cooled to −45 to −50°, was mixed with an equal volume of a saturated ether solution of ammonia. The reaction mass was allowed to stand overnight at room temperature. The obtained precipitate was filtered, and the ether was distilled from the filtrate. An oily substance was obtained that gradually crystallized. The yield of (IIa) after recrystallization from water was 2.97 g (58.5% of theory), mp 73-74.5°. From [2]: mp 72-75°.

Imide of o-Sulfobenzoic Acid (IIIa). Compound (IIa) (0.4 g) was heated in an argon atmosphere for 45-50 min, in which connection the temperature was gradually raised up to 205-210°. After the evolution of volatile substances had ceased we obtained 0.3 g (~100% of theory) of a crude product with mp 140-192°. The yield of compound (IIIa) after recrystallization from water was 0.15 g (50% of theory), mp 218-219°. From [7]: mp 224-225°. The IR spectrum of the obtained substance was identical with that of authentic saccharin.

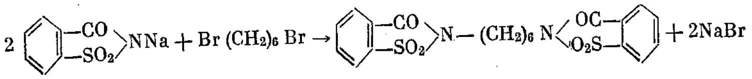
Isopropyl o-(N-Phenylsulfamoyl)benzoate (IIb). Equal volumes (40 ml each) of ether solutions of 9.7 g of (I) and 6.7 g of aniline, cooled to −5°, were mixed. The cooling was maintained for 15 min, and then the reaction mass was allowed to stand at room temperature for 4 h. The obtained precipitate of aniline hydrochloride was filtered, and the ether was distilled from the filtrate. The dry residue was recrystallized from ether. The yield of (IIb) was 3.57 g (29% of theory); the compound is new. Found: C 61.09, 60.91; H 5.67, 5.72; N 4.24, 4.56%. $C_{16}H_{17}NS$. Calculated: C 60.8; H 5.96; N 4.38%.

N-Phenylsaccharin (IIIb). A solution of 0.2 g of compound (IIb) in 5 ml of dibenzyl ether was heated at reflux for 1 h. After cooling the solution, the reaction product was extracted with a mixture of 1 ml of water, 4 ml of acetone and 5 ml of alcohol. After distilling off the solvents we obtained a crystalline substance, which was washed with ether and dried in vacuo. The yield of (IIIb) was 5%, mp 186°. From [7]: mp 189-190°.

Hexamethylenedi(isopropyl o-Sulfamoylbenzoate) (IIc). Solutions of 5.49 g of compound (I) in 30 ml of ether and 2.42 g of HMDA in 45 ml of ether, cooled to −45 to −50°, were mixed. The reaction mass was allowed to stand at room temperature overnight. The precipitate of HMDA hydrochloride was filtered. The residue from distilling off the ether was washed with chilled ether and dried in vacuo to give crystals of (IIc) with mp 52-54°; yield 3.34 g of (53% of theory). Compound (IIc) is not reported in the literature and its structure was corroborated by the IR spectrum (see Fig. 1d), and also by preparing the known (IIIc) from it.

Hexamethylenedisaccharin (IIIc). Compound (IIc) (0.59 g) was gradually heated in an argon atmosphere up to 180° in approximately 45 min. Heating at this temperature was continued until the evolution of volatile materials ceased (~5 min). The yield of crystalline product after recrystallization from ethyl acetate was 0.18 g (40% of theory); mp 178-180°. From [5]: mp 183°.

For additional confirmation of the structure of (IIIc) we obtained hexamethylenedisaccharin in known manner (from sodium saccharin and hexamethylene dibromide) [5].



A study of samples synthesized by the two indicated method, gave analogous results.

CONCLUSIONS

1. Isopropyl o-(N-phenylsulfamoyl)benzoate and hexamethylenedi(isopropyl o-sulfamoyl benzoate) were synthesized for the first time.

2. A study was made of the conditions for the formation of the imide derivatives from the corresponding isopropyl o-sulfamoylbenzoates.

LITERATURE CITED

1. C. M. Suter, The Chemistry of Organic Sulfur Compounds [Russian translation], Part 2, IL (1951), p. 392.
2. B. Loev and M. Kormendy, J. Org. Chem., 27, 1703 (1962).
3. Beilstein, 27, 171 (1944).
4. I. Remsen and C. E. Coates, Jr., Am. Chem. J., 17, 311 (1895).
5. E. E. Reid, L. M. Rice, and C. H. Grogan, J. Am. Chem. Soc., 77, 5628 (1955).
6. K. Nakanishi, Infrared Absorption Spectroscopy and Structure of Organic Compounds [Russian translation] Mir (1965).
7. W. A. Noyes, Am. Chem. J., 8, 180 (1886).