SULFONATION OF AROMATIC AND HETEROCYCLIC COMPOUNDS WITH BIS(TRIMETHYLSILYL) SULFATE

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When bis(trimethylsilyl) sulfate (BTS) reacts with water, HCl, NH_3, alcohols, Grignard reagents, sodium acetylide, triorganylsilanes, and the salts of organic and mineral acids, it can function either as a silylating agent or as an oxidizing agent [1, 2].

We were the first to discover the ability of BTS to sulfonate aromatic and heterocyclic compounds by the scheme

$$RH + [(CH_3)_3SiO]_2SO_2 \rightarrow RSO_3H + (CH_3)_3SiOSi(CH_3)_3$$

where R = aryl, hetaryl.

Thus, toluenesulfonic acid is formed in 23% yield (the isomers were not studied) when toluene is heated with BTS (200°C, 10 h). The reaction of BTS with aniline and dimethylaniline (160-170°) leads respectively to sulfanilic acid (65%) and dimethylanilinesulfonic acid (79%). Anisolesulfonic acid (78% yield) is easily formed from anisole and BTS at 125-170°. Benzene and nitrobenzene do not react with BTS even under quite drastic conditions (200-210°, 2 h).

The sulfonation of thiophene using BTS proceeds even at 20°, but very slowly (2 months is required to complete the reaction when the reactants are taken in an equimolar ratio). At 100° the reaction time drops to 2 h, but the thiophenesulfonic acid is formed in only 20-30% yield. The yield of the latter increases to 77% if a 3-fold excess of BTS is used. Tar formation is simultaneously suppressed here. This method of sulfonating thiophene substantially expands the possibility of synthesizing thiophenesulfonic acids [3-5]. In its sulfonating ability BTS resembles pyridinesulfotrioxide [4-7] in many respects. Like the latter, it does not react with benzene, but easily sulfonates anisole, aniline, and thiophene.

EXPERIMENTAL

BTS [8, 9] was obtained by the reaction of $(CH_3)_3SiCl$ with H_2SO_4 and was purified by vacuum-distillation. The formed sulfonic acids were isolated as the Ba salts, except sulfanilic acid and dimethylanilinesulfonic acid, which were isolated and identified as the acids.

Sulfonation of toluene. A mixture of 2.0 g (0.022 mole) of toluene and 5.3 g (0.022 mole) of BTS was heated in a sealed glass tube for 10 h at 200-220°. The cooled reaction mixture was stirred with an equal volume of water, then with an aqueous suspension of 5.2 g (0.026 mole) of $BaCO_3$, heated for 30 min in a water bath, and filtered. The filtrate was evaporated and the residue was dried at 130° to give 1.2 g (23%) of barium toluenesulfonate. Found: C 35.07; H 3.02%. $C_{14}H_{14}S_2O_6Ba$. Calculated: C 35.14; H 2.93%.

Sulfonation of aniline. A mixture of 1.7 g (0.018 mole) of aniline and 4.4 g (0.018 mole) of BTS was heated to 160°. On reaching this temperature the mixture first became homogeneous and then it frothed stormily with the formation of white flocs and HMDS. After distilling off 2.3 g (80%) of HMDS the residual white solid was dissolved in 40% NaOH solution, filtered, and the filtrate was made acid with conc. HCl and then cooled to 0°. The obtained crystals were suction-filtered and dried in vacuo to give 2 g (65% yield) of sulfanilic acid, mp 279° (decompn.) Found: C 41.64; H 4.11; S 18.54; N 8.37%. $C_6H_7NO_3S$. Calculated: C 41.62; H 4.05; S 18.50; N 8.09%.

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Sulfonation of Dimethylaniline. In a similar manner, from 2 g (0.016 mole) of dimethylaniline and 3.9 g (0.016 mole) of BTS we obtained 2.2 g (85%) of HMDS and 2.6 g (79%) of dimethylanilinesulfonic as white crystals with mp 270°. Found: C 47.54; H 5.47; S 15.66; N 6.61%. $C_8H_{11}NO_3S$. Calculated: C 47.76; H 5.47; S 15.92; N 6.96%.

Sulfonation of Anisole. A mixture of 3.8 g (0.035 mole) of anisole and 8.5 g (0.035 mole) of BTS was heated at 125-170° for 2 h, and here 2.5 g (70%) of HMDS was distilled off. The cooled mixture was poured into 10 ml of water and the anisolesulfonic acid was isolated as the Ba salt. Yield 5.8 g (78%). Found: C 32.47; H 2.55%. $C_{14}H_{14}S_2O_8Ba$. Calculated: C 32.87; H 2.74%.

Sulfonation of Thiophene. A mixture of 10.9 g (0.045 mole) of BTS and 1.3 g (0.015 mole) of thiophene was heated in a sealed glass tube for 2 h at 100°. The thiophenesulfonic acid was isolated as the Ba salt. Yield 2.7 g (77%). Found: C 21.13; H 1.59%. $C_8H_6S_4O_6Ba$. Calculated: C 20.73; H 1.30%.

CONCLUSIONS

A new sulfonating agent, namely bis(trimethylsilyl) sulfate, was found, which easily sulfonates benzene derivatives that contain substituents of the first type, and also thiophene. Benzene and nitrobenzene do not react with bis(trimethylsilyl) sulfate.

LITERATURE CITED

1. S. N. Borisov, M. G. Voronkov, and É. Ya. Lukevits, Organosilicon Derivatives of Phosphorus and Sulfur [in Russian], Khimiya, Leningrad (1968), p. 182.
2. M. G. Voronkov, V. K. Roman, and E. A. Maletina, Chemistry of Heteroorganic Compounds [in Russian], Nauka, Leningrad (1976), p. 49.
3. J. A. Joule and G. F. Smith, Heterocyclic Chemistry, Van Nostrand-Reinhold (1972).
4. E. E. Gilbert, Sulfonation of Organic Compounds [Russian translation], Khimiya (1969). pp. 17, 96.
5. A. P. Terent'ev and L. A. Kazitsina, Organic Compounds: Reactions and Study Methods [in Russian], Vol. 2, Goskhimizdat, Moscow–Leningrad (1952), p. 245.
6. A. P. Terent'ev and G. M. Kadatskii, Zh. Obshch. Khim., 22, 153 (1952).
7. A. P. Terent'ev and A. V. Dombrovskii, Zh. Obshch. Khim., 19, 1467 (1949).
8. W. Patnode and F. S. Schmidt, J. Am. Chem. Soc., 67, 2272 (1945).
9. M. F. Shostakovskii, N. V. Komarov, and O. G. Yarosh, Zh. Prikl. Khim., 38, 435 (1965).

ANALYSIS OF POLARITY OF gem-DIAMINES AND α-AMINO ETHERS

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In many cases a study of the conformations of compounds with two geminal axes of internal rotation is a quite complicated problem, since a large number of conformers is possible [1], which correspond to the minimums of the potential energy of the molecule. In particular, the dipole moments (DM) of molecules with two dipoles in the 1,3 position (1,3-dihalopropanes and their analogs [2, 3]), with many conformations of the X—C—C—C—X chain, are the same due to the identity of the mutual steric orientation of the dipoles. A coinciding of the moments of the conformers also occurs for acetals and ketals [4]. In such cases it is necessary to study the substituted derivatives and (or) use a complex of physical methods, for example, a common analysis of the DM and Kerr constants [1, 2, 4]. In the case of gem-diamines, which are formal analogs of acetals and ketals, each of the heteroatoms has two substitutents, whose steric orientation changes during the internal rotation process. The following questions arise in connection with this: how does the insertion of an additional dipole affect the relative polarity of the conformers, how does this additional substituent affect the relative energies of the conformers; and finally, which methods of experimental

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