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ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Some Bisnitrosaccharins

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Abstract—Method for synthesis of previously unknown bisnitrosaccharins from 6-nitrosaccharin under the action of bishalide compounds in polar aprotic solvents in the presence of anhydrous potassium carbonate is suggested.

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Aromatic polyimides containing phenyl oxide units in the backbone are of great interest not only because of their high thermal stability and flexibility, but also owing to the improved solubility in readily available organic solvents [1].

A method for synthesis of aromatic polyesterimides via aromatic nucleophilic substitution of nitro groups of bisnitrophthalimides with dianions of bisphenols has been suggested [2].

It should b noted that the aromatic nucleophilic substitution of the nitro group of nitrophthalimides with the phenolate anion has been studied previously on model reactions [3–5].

The nucleophilic substitution reaction between activated aromatic imide-containing dinitro compounds and dianions of bisphenols has also been used to synthesize aromatic polyesterimides [6, 7]. It has been shown that the reaction products have an improved solubility in ordinary organic solvents and are easily processed.

The introduction of phenyl oxide units into the backbone of heterocyclic polymers has been used to synthesize such derivatives as poly(aryl ether phenylquinoxaline)s [8], poly(aryl ether phthalazine)s [9], and poly(aryl ether phthalazinone)s [10], which possess an improved solubility in ordinary organic solvents.

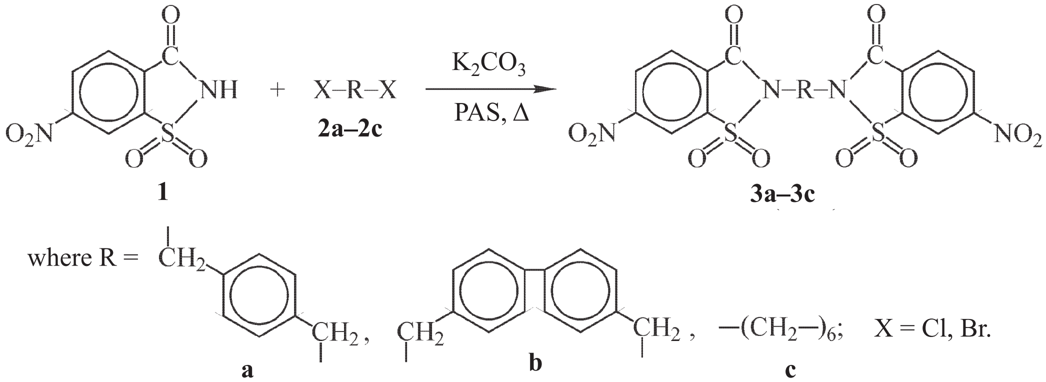
It should be noted that, in contrast to the rather extensively studied polyimides, their sulfur-containing analogs, i.e., polysaccharins, have been the subject of only several reports [11–14]. The products synthesized in these studied were for the most part difficultly soluble and insufficiently macromolecular. In the present communication, we suggest a method for synthesis of previously unreported bisnitrosaccharins, which can be used as monomers for synthesis of polyestersaccharines, i.e., polysaccharine derivatives with improved solubility. These bisnitrosaccharins were produced by the nucleophilic substitution reaction between nitrosaccharin and bishalide compounds in polar aprotic solvents (PASs) in the presence of anhydrous K_2CO_3 (Scheme 1).

The structural formulas of compounds **3a–3c** are presented in Scheme 2.

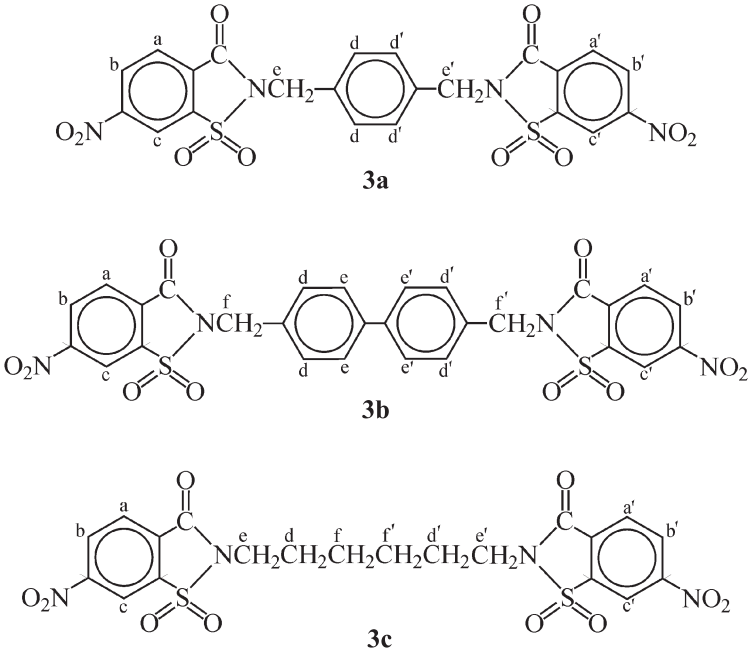
As the starting product for synthesis of 6-nitrosaccharin served *para*-nitrotoluene. By successive treatment of this compound with chlorosulfonic acid [15] and aqueous ammonia [16], we obtained, respectively, sulfochloride and sulfamide derivatives of *para*-nitrotoluene. Then, the corresponding nitrosaccharin was produced from the sulfamide derivative via oxidation by the known methods [17, 18].

Bisnitrosaccharins **3b, 3c** were synthesized in accordance with the above scheme. The reaction was performed by heating of a mixture of stoichiometric amounts of 6-nitrosaccharine (**1**) and the corresponding bishalide compound **2a–2c** in *N,N*-dimethylacetamide

Scheme 1.



Scheme 2.



(DMAc) at 130°C for 3 h in the presence of anhydrous K_2CO_3. The reaction products **3a–3c** were obtained in rather high yields (80–90%); on being purified by recrystallization from DMFA, they had the form of high-melting crystalline substances.

The composition and structure of the resulting bisnitrosaccharins **3a–3c** were characterized by elemental analysis and IR and ^{1}H NMR spectroscopies.

The IR spectra of compounds **3a–3c** contain absorption bands at 1740, 1375–1270, and 1200–1180 cm^{-1}, characteristic of, respectively, the >C=O and >SO_2 groups of the saccharine ring. The absorption band at 1540 cm^{-1} is characteristic of the NO_2 group. The absorption band at 1330 cm^{-1}, also characteristic of the NO_2 group, presumably overlaps the absorption band of the >SO_2 group. The absorption bands at 3100–3000, 2930, and 2855 cm^{-1} can be attributed to aromatic (=C–H) and aliphatic (–CH_2) bonds, respectively. The characteristic absorption bands observed in the IR spectra of compounds **3a–3c** are in good agreement with published data [16, 19].

The ^{1}H NMR spectra of bisnitrosaccharins **3a–3c** show signals with chemical shifts δ 7.35–9.40 ppm, associated with the aromatic protons. In addition, the signal observed at δ 1.22–5.08 ppm can be attributed to the aliphatic ptrotons. These characteristic chemical shifts are observed in the ^{1}H NMR spectra of compounds **3a–3c** (Figs. a–c).

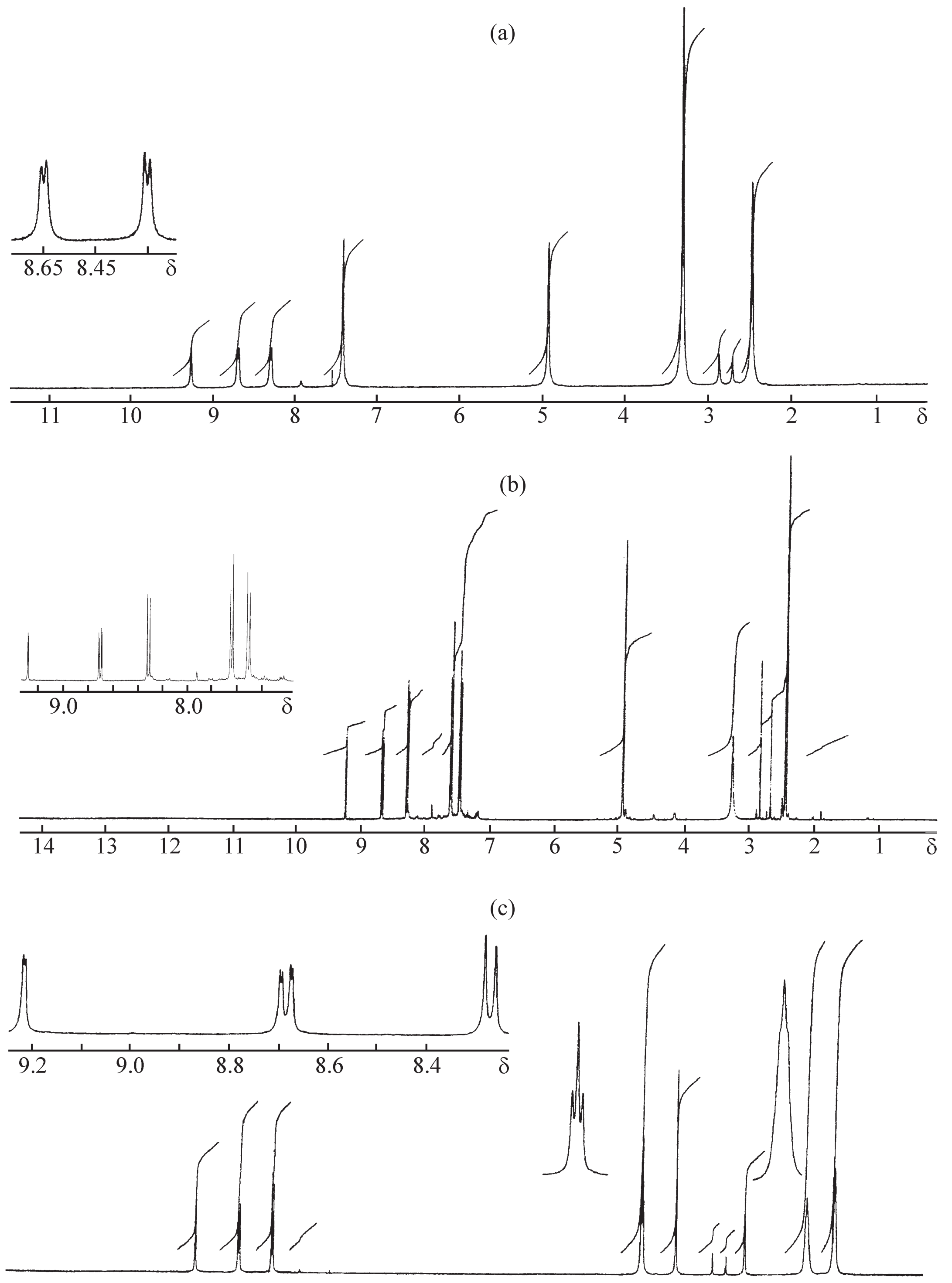


Fig. 1. ^{1}H NMR spectra of compounds (a) **3a**, (b) **3b**, and (c) **3c** in DMSO-d_6. (δ) Chemical shift.

EXPERIMENTAL

The following starting products were used in the study without additional purification (all except Na_2CO_3 from Merck): *para*-nitrotoluene, chlorosulfonic acid, ammonia (24% aqueous solution), 1,6-dibromohexane, α,α'-dichloro-*para*-xylene, 4,4'-dichloromethylbiphenyl, $K_2Cr_2O_7$, *N,N*-

dimethylformamide, *N,N*-dimethylacetamide, K_2CO_3, and Na_2CO_3 (Fluka).

4-Nitrotoluene-2-sulfo chloride was synthesized by the method previously described in the literature. The product obtained in quantitative yield was used without additional purification to synthesize the corresponding sulfamide derivative.

4-Nitrotioluene-2-sulfamide was synthesized from the corresponding sulfo chloride [16]. On being recrystallized from water, the product had the form of light gray fine needle-like crystals, yield 74%, mp 191–192°C (published value 185–187°C [16]).

6-Nitrosaccharin was synthesized from 4-nitrotoluene-2-sulfamide via oxidation by the known methods [17, 18]. The yield of an unpurified dry solid product was 90%. On being purified by precipitation from an aqueous solution of Na_2CO_3,the product had the form of a light yellow fine powder, yield 82%, mp 207–209°C (published value 209–211°C [16]).

***N,N*'-Xylinene-1,4-bis(6-nitrosaccharin) [*N,N*'-xylinene-1,4-bis(6-nitro-1,2-benzisothiazole-3-(2*H*)-OH-1,1-dioxide)] (3a).** A reaction vessel equipped with a magnetic rabble, thermometer, reflux condenser, and Dean–Stark apparatus was charged with 11.40 g of compound (1) (50 mmol), 3.59 g of anhydrous K_2CO_3 (26 mmol), and 100 mL of dimethylacetamide. The mixture was agitated for 15 min at room temperature,20 mL of toluene was added, and the resulting mixture was heated on an oil bath at 130°C until water release terminated. After water was removed, 4.37 g of compound **2** (25 mmol) and approximately 100 mg of KI were added to the reaction mass. The reaction mixture was continued to be agitated for 3 h at 130°C. In 20–25 min after the beginning of the reaction, the reaction mixture turned dark brown and remained so till the end of the reaction. After the reaction was complete, the contents of the vessel were cooled to room temperature and poured into 1 L of icy water acidified with small amounts of hydrochloric acid. The reaction product precipitated in the form of beige floccules was collected, filtered off, washed on the filter with water and then with a small amount of methanol, and dried in air and then in a vacuum. The yield of the unpurified solid product was 13.20 g (95%), mp 314–316°C. On being recrystallized from DMFA, product (3a) had the form of fine crystals with a light straw color. Yield 12.50 g (90%), mp 334.6–335.2°C. Found (%):C 46.85, 46.80; H 2.30; 2.25; N 9.75, 9.80; S 11.20, 11.26. $C_{22}H_{14}O_{10}N_4S_2$. Calculated (%): C 41.27, H 2.50, N 10.02, S 11.46. ^1H NMR spectrum (400 MHz, DMSO-d_6), δ ppm): 9.40–9.20 s ($H_c + H_{c'}$, 2H), 8.71–8.70 d (*J* = 7.0 Hz, H_a+$H_{a'}$, 2H), 8.31–8.29 d (*J* = 7.0 Hz, $H_b + H_{b'}$, 2H), 7.42 s ($2H_d + 2H_{d'}$, 4H), 3.31 s ($H_e + H_{e'}$, 4H) (Fig. 1a).

***N,N*'-Biphenylene-4,4'-dimethylenebis(6-nitrosaccharin) [*N,N*'-biphenylene-4,4'-dimethylenebis(6-nitro-1,2-benzisothiazole-3-(2H)-OH-1,1-dioxide)] (3b).** Compound **3b** was synthesized by the method described for the case of compound **3a**. The reaction of compound **1** (10 mmol) with compound **2b** (5 mmol) in DMAc (35 mL) in the presence of anhydrous K_2CO_3 (5.2 mmol) yielded compound **3b**. The yield of the unpurified dry grayish-yellow solid product was 3.00 g (94%), mp 314–316°C (with decomposition). On being recrystallized from DMFA, compound **3b** had the form of grayish-yellow finely crystalline substance. Yield 2.62 g (80%), mp 322–324°C (with decomposition). Found (%):C 52.64, 52.72; H 2.74, 2.65; N 8.58, 8.65; S 10.38, 10.46. $C_{28}H_{18}O_{10}N_4S_2$. Calculated (%): C 52.99, H 2.88, N 8.82, S 10.10. ^1H NMR spectrum (400 MHz, DMSO-d_6), δ (ppm): 9.29–9.28 s (H_c+$H_{c'}$, 2H), 8.73–8.72 d (*J* = 1.8 Hz, $H_a + H_{a'}$, 2H), 8.33–8.31 d (*J* = 1.8 Hz, $H_b + H_{b'}$, 2H), 7.66–7.64 d (*J* = 8.4 Hz, $2H_e + 2H_{e'}$, 4H), 7.50–7.25 d (*J* = 8.4 Hz, $2H_d$+$2H_{d'}$, 4H), 4.99 s ($2H_f$+ $2H_{f'}$, 4H) (Fig. 1b).

***N,N*'-Hexamethylene-1,6-bis(6-nitrosaccharin) [*N,N*'-hexamethylene-1,6-bis(6-nitro-1,2-benzisothiazole-3-(2*H*)-OH-1,1-dioxide)] (3c).** Compound 3c was also synthesized by the method described for synthesis of compound **3a**, by the reaction of compound **1** (5 mmol) with compound **2c** in DMAc (10 mL) in the presence of anhydrous K_2CO_3 (2.6 mmol).The yield of the unpurified dry product of light straw color was 1.27 g (94%), mp 210–214°C. On being recrystallized from DMFA[1], compound **3c** had the form of light yellow fine crystals. Yield 1.16 g (86%), mp 242–244°C. Found (%): C 44.34, 44.12; H 3.18, 3.27; N 10.62, 10.70; S 12.32, 12.40. $C_{20}H_{18}O_{10}N_4S_2$. Calculated (%): C 44.61, H 3.37, N 10.40, S 11.91.

^1H NMR spectrum (400 MHz, DMSO-d_6), δ (ppm): 9.22–9.2 d (*J* = 1.8 Hz, H_c+$H_{c'}$, 2H), 8.70–8.69 d (*J* = 1.8 Hz, $H_a + H_{a'}$, 2H), 8.68–8.67 d (*J* = 1–8 Hz, $H_b + H_{b'}$, 2H), 3.75–3.71 t (*J* = 6.9 Hz, $2H_e + 2H_{e'}$, 4H),

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[1] The crystallization commenced upon addition of a small amount of ethanol.

1.73 ($2H_d + 2H_{d'}$), 1.40 m ($2H_f + 2H_{f'}$, 4H) (Figure c).

CONCLUSIONS

Three bis(nitrosaccharin)s were synthesized for the first time by the reaction of 6-nitrosaccharine with bishalide compound and characterized: *N,N*'-xylinene-1,4-bis(6-nitrosaccharin), *N,N*'-biphenylene-4,4'-dimethylenebis(6-nitrosaccharin), and *N,N*'-hexamethylene-1,6-bis(6-nitrosaccharin).

REFERENCES

1. Sachirdrapal, P. and Nanjan, M.J., *Makromol. Chem. Rapid. Commun*., 1980, vol. 1, pp. 667–670.
2. White, D.M., Takekoshi, T., Williams, F.J., et al., *J. Polym. Sci. Polym. Chem. Ed*., 1981, vol. 19, pp. 1635–1658.
3. Williams, F.J. and Donahue, P.E., *J. Org. Chem*., 1977, vol. 42, no. 21, pp. 3414–3419.
4. Williams, F.J., Relles, H.F., Donahue, P.E., and Manello, J.S., *J. Org. Chem*., 1977, vol. 42, no. 21, pp. 3425–3431.
5. Williams, F.J., Relles, H.F., Manello, J.S., and Donahue, P.E., *J. Org. Chem*. 1977, vol. 42, no. 21, pp. 3419–3425.
6. Mandal, B.K. and Maiti, S., *J. Polym. Sci. Polym. Chem. Ed*., 1985, vol. 23, pp. 317–321.
7. Maiti, S. and Mandal, B.K., *Makromol. Chem. Rapid. Commun*., 1985, vol. 6, no. 12, pp. 841–846.
8. Hedrick, J.L. and Labadie, J.W., *Makromolecules*, 1990, vol. 23, pp. 1561–1569.
9. Singh, R. and Hay, A.S., *Makromolecules,* 1992, vol. 25, pp. 1033–1042.
10. Wang, S.J., Mang, Y.Z., Hlil, A.R., and Hay, A.S., *Makromolecules,* 2004, vol. 37, pp. 60–65.
11. D'Alelio, G.F., Fessler, W.A., Giza, Y., et al., *J. Macromol. Sci.-Chem*., 1971, vol. A5, no. 2, pp. 383–420.
12. D'Alelio, G.F., Fessler, W.A., Giza, Y., et al., *J. Macromol. Sci.-Chem*. 1971, vol. A5, no. 6, pp. 1097–1121.
13. *USSR Inventor's Certificate*, no. 301314.
14. Mel'nikova, E.P. and Tagiev, B.A., *Azerb. Khim. Zh*., 1974, no. 2, pp. 65–67.
15. Suter, C. M., *The Organic Chemistry of Sulfur: Tetracovalent Sulfur Compounds,* New York: Wiley, 1944.
16. D'Alelio, G.F., Fessler, W.A., and Feigl, D.M., *J. Macromol. Sci.-Chem*., 1969, vol. A3, no. 5, pp. 941–958.
17. *USSR Inventor's Certificate*, no. 213837.
18. *USSR Inventor's Certificate*, no. 1182782.
19. Tagiev, V.A., *Kafkas University Faculty of Sciences and Letters, The Journal of the Sciences*, 1996, vol. l, nos. 1–2, pp. 81–87.