∆ <i>P</i> /atm	Oil yellow	Sudan red	
0.5	6.2	4.2	
1	5.8	4.6	
1.5	6.3	6.1	
2.0	6.8	6.5	
(0-1)*	5.2	4.0	

Table	3.	Longitudina	l size	of	chroma	tographic	zones	(mm)
with v	aric	ous pressure	drops	(siz	e of the	starting s	pot is 3	mm)

* Linear pressure increase with time.

It should be noted in conclusion that the use of the TLC variant on plates with the sorption layer enclosed by the polymeric film and with forced flow of the mobile phase (when the pressure at the beginning of the plate is higher than atmospheric pressure) makes it possible to substantially accelerate the process of chromatographic separation in thin-layer chromatography.

References

- Thin-Layer Chromatography, Wiley-Interscience Publications, New York, 1978.
- Modern Thin-Layer Chromatography, Ed. Nely Grinberg, M. Dekker, New York, 1990.

- 3. M. P. Volynets, Kolichestvennayay tonkosloinaya khromatografiya v neorganicheskom analyze [Quantitative Thin-Layer Chromatography in Inorganic Analysis], Nauka, Moscow, 1993 (in Russian).
- K. I. Sakodynskii, V. V. Brazhnikov, S. V. Volkov, V. Yu. Zel'venskii, E. S. Gankina, and E. S. Shatts, *Analiticheskaya khromatografiya* [*Analytical Chromatography*], Moscow, Khimiya, 1993 (in Russian).
- 5. High Performance Thin-Layer Chromatography, Eds. A. Zlatkis and R. E. Kaiser, Elsevier, Amsterdam, 1977.
- V. G. Berezkin and A. S. Bochkov, Kolichestvennaya tonkosloinaya khromatografiya [Quantitative Thin-Layer Chromatography], Nauka, Moscow, 1980 (in Russian).
- 7. V. G. Berezkin and V. V. Buzaev, *Usp. Khim.*, 1987, 56, 656 [*Russ. Chem. Rev.*, 1987, 56 (Engl. Transl.)].
- E. Tyihak, H. Kalasz, E. Mincsovisc, and G. Nagy, Proc. XVII Hung. Ann. Meet. Biochem., 1977, 17, 183.
- E. Mincsovisc and E. Tyihak, J. Chromatogr., 1980, 191, 293.
- V. G. Berezkin and V. V. Buzaev, Tonkosloinaya plastinka i sposob ee izgotovleniya [Thin-Layer Plate and Procedure of Its Preparation], Russ. Pat. 1, 347, 704, Byull. Izobr., 1995, No. 25 (in Russian).
- 11. V. V. Buzaev, V. G. Berezkin, and M. A. Koshevnik, Tonkosloinaya plastinka i sposob ee izgotovleniya [Thin-Layer Plate and Procedure of Its Preparation], Russ. Pat. 1394916, Byull. Izobret., 1995, No. 25 (in Russian).
- 12. V. G. Berezkin and E. B. Guglya, Ustroistvo dlya khromatograficheskogo razdeleniya smesi veshchestv v tonkom sloe sorbenta [Device for Chromatographic Separation of a Mixture of Substances in a Thin Sorbent Layer], Russ. Pat. 1800361, Byull. Izobr., 1993, No. 9 (in Russian).

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Reactions of α -halonitrosoalkanes with resorcinol

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 α -Halonitrosoalkanes react with resorcinol as nitrosylating agents to form 3-hydroxy-N-(2,4-dihydroxyphenyl)-1,4-quinone imine.

Key words: α -halonitrosoalkanes, resorcinol, 3-hydroxy-N-(2,4-dihydroxyphenyl)-1,4-quinone imine.

It is known that in the presence of strong mineral acids aromatic nitroso compounds C-aminate phenols at the *para*-position to the hydroxyl group to form N, N-diarylhydroxylamines, which after elimination of water

transform to indophenols or cyclize to phenoxazine derivatives.¹⁻²

We have found that 1,2-dichloro-1,2,2-trifluoronitrosoethane **la** readily reacts with resorcinol in the

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 $R = CCIF_2CCIF(\mathbf{a}), C_3H_7CCI_2(\mathbf{b})$

absence of a catalyst at 20°C. The reaction reaches completion immediately after mixing the reagents to eliminate 1,2-dichloro-1,2,2-trifluoroethane and to form 3-hydroxy-N-(2,4-dihydroxyphenyl)-1,4-quinone imine 2 (isolated in a yield of 35%) and oligomeric substances. It is likely that the primary product of this reaction is N-(2,4-dihydroxyphenyl)-N-(1,2-dichloro-1,2,2-trifluoroethyl)hydroxylamine, which undergoes "haloform" decomposition to form nitroresorcinol, whose condensation with resorcinol results in the formation of indophenol 2.

1,1-Dichloro-1-nitrosobutane reacts with resorcinol similarly but considerably more slowly. The reaction is accompanied by elimination of 1,1-dichlorobutane, and the resorcinol transforms predominantly to resin-like oligomeric substances. Trifluoronitrosomethane does not react with resorcinol under the same conditions.

The ability of nitroso compounds 1a,b to act as nitrosylating agents in reactions with resorcinol is likely caused by the electron-deficient character of the nitrogen atom of these compounds, the presence of easily leaving group R in the primary adduct, and the high rate of formation of thermodynamically stable indophenol 2. The absence of a reaction in the case of trifluoronitrosomethane can be explained by the considerably lower tendency of its primary product for "haloform" decomposition and the reverse character of the reactions. In fact, in the presence of organic bases promoting haloform decomposition, trifluoronitrosomethane reacts vigorously with resorcinol to give only a mixture of oligomeric products.

The structure of indophenol 2 was determined by spectral methods. 1,2-Dichloro-1,2,2-trifluoroethane and 1,1-dichlorobutane were identified by GLC by comparison with the known samples.

Experimental

¹HNMR spectra were recorded on a Bruker WP-200SY spectrometer relative to SiMe₄ (external standard). IR spectra were recorded on a UR-20 instrument in KBr pellets. Chromatographic analyses were performed on a gas chromatograph (model 3700), column of stainless steel 2000×3mm in

size, 15% Carbowax 20M on Chromaton N-super 0.2-0.25 as stationary phase, temperature of the column 120°C, helium as carrier gas, and pressure of 1.3 bar.

3-Hydroxy-N-(2,4-dihydroxyphenyl)-1,4-quinone imine (2). a. A solution of 1,2-dichloro-1,2,2-trifluoro-1-nitrosoethane (1.2g, 6.6mmol) in 5mL of ether was added with stirring to a solution of resorcinol (0.7g, 6.4mmol) in 14mL of ether. The mixture was left to stand for 12h for sedimentation of a suspension that had formed. Then the solvent was decanted, and the precipitate was washed with ether (5×3mL). Indophenol (2) was extracted with EtOH and precipitated with ether to obtain dark crystals (0.52g, 2.2mmol, 35%) withm.p. > 380°C. ¹HNMR, (DMSO- d_6), δ : 6.92 (s, 1 H,OH); 7.58 (s, 1 H,C₆H₃), 7.83 (s, 1 H, C_6H_3), 8.08 (s, 1 H, C_6H_3). IR, v/cm⁻¹: 1600– 1630 (C=O; N=Č). Found (%): Č,56.94; H,11.79; N,5.33. C12H9NO4 H2O. Calculated (%): C,57.34; H,11.63; N,5.57. The GLC method showed that the reaction mass contained 1,2-dichloro-1,1,2-trifluoroethane, identified by comparison with a known sample that was obtained by chlorination of trifluoroethylene in the presence of FeCl₁.³

b. A solution of 1,1-dichloro-1-nitrosobutane (0.66g, 4.2mmol) and resorcinol (0.46g, 4.2mmol) in SmL of ether was kept for 10 days. The solution was decanted, and a product (0.1g, 0.8mmol, 19%) with b.p. 112–115°C was isolated by distillation. The product was identified as 1,1-dichlorobutane by the GLC method by comparison with a known sample obtained by the action of PCl₅ on butyric aldehyde. Indophenol 2 (0.1g, 0.4mmol, 9%) withm.p. >380°C was obtained similarly to the previous experiment.

Attempt to perform the reaction of trifluoronitrosomethane and resorcinol. A solution of trifluoronitrosomethane (0.5 g) in 15mL of ether was added to a solution of resorcinol (0.5g,4.5mmol) and Et₃N (two droplets) in 5mL of ether. After decolorization of a mixture, the solvent was evaporated to obtain nonidentified insoluble residue (0.52 g).

References

- A. Silberg, Z. Frenkel, and E. Bauer, Stud. Univ. Babes-Bolyai, Ser. Chem., 10, 31 (1965); Chem. Abstr., 1966, 65, 545.
- 2. M. Kotoucek, M. Martinek, and E. Ruzicka, *Monatsh.*, 1965, 96, 1433.
- J. D.Park, W. R. Lycan, and J. R. Lacher, J. Am. Chem. Soc., 1951, 73, 74.

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