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SHORT COMMUNICATIONS

New Dipolar Spiro-σ-Complexes Derived from 4,6-Dinitrobenzofuroxan and 4,6-Dinitrobenzofurazan

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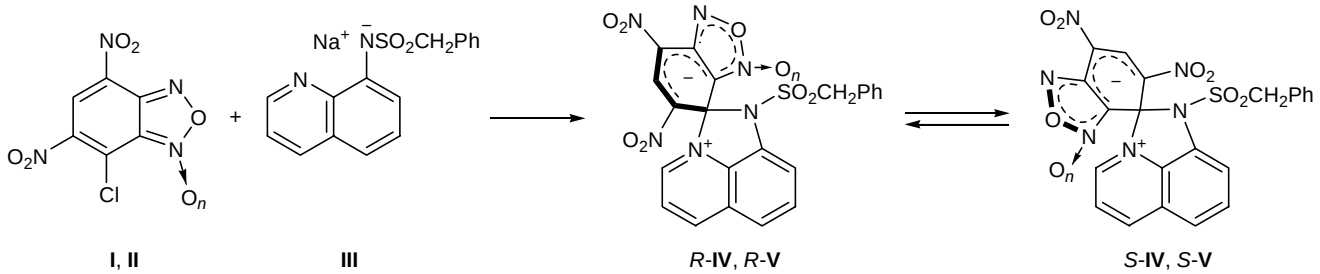
Dipolar spiro-σ-complexes on the basis of 4,6-dinitrobenzofuroxan have been reported only for derivatives of tropolone and its hetero analogs [1], while Meisenheimer anionic σ-complexes have been extensively studied [2]. The present communication reports on the first results obtained by using *N*-(8-quinolyl)-phenylmetanesulfonamide as synthon suitable for building up dipolar spiro-σ-complexes with π-deficient arenes.

σ-Complexes **IV** and **V** were synthesized by reaction of 7-chloro-4,6-dinitrobenzofuroxan (**I**) and 7-chloro-4,6-dinitrobenzofurazan (**II**) with *N*-(8-quinolyl)phenylmethanesulfonamide sodium salt (**III**). In the ^{1}H NMR spectra of compounds **IV** and **V**, signals from protons of the benzofurazan system are displaced upfield, which is typical of both anionic [2] and dipolar σ-complexes [1]. The chemical shifts of the α- and γ-protons in the quinoline ring (δ 9.8 and 9.4 ppm, respectively) are usual for *N*-alkylquinolinium salts [3]. These data suggest considerable charge distribution between the quinoline and benzofurazan fragments of **IV** and **V**. Diastereotopic methylene protons in the $PhCH_2SO_2N$ group give rise to an *AB* quartet in the ^{1}H NMR spectrum of zwitterion **IV**, indicating formation of a stereogenic carbon center. Raising the temperature leads to reversible transformation of the *AB* quartet into a singlet as a result of enantiotopomerization *R*-**IV** ↔ *S*-**IV**; $k_{298} = 1.9\times10^{-2}$ s^{-1}, $\Delta G^{\neq}_{298}$ = 19.8 kcal/mol. Replacement of the furoxan ring in **IV** by less electrophilic furazan ring (compound **V**) reduces the stability of the system, and the enantiotopomerization process *R*-**V** ↔ *S*-**V** cannot be slowed down even by cooling to –70°C.

***N*-(8-Quinolyl)phenylmethanesulfonamide sodium salt (III).** A solution of 0.05 g of sodium in 3 ml of ethanol was added to a solution of 0.7 g (2.3 mmol) of *N*-(8-quinolyl)phenylmethanesulfonamide (prepared by tosylation of 8-aminoquinoline [4]) in 10 ml of benzene. The precipitate was filtered off and washed with benzene. Yield 0.6 g (80%), mp 150°C.

Spiro complexes IV and V. A solution of 0.13 g (0.5 mmol) of 7-chloro-4,6-dinitrobenzofuroxan (**I**) or 7-chloro-4,6-dinitrobenzofurazan (**II**) in 3 ml of acetonitrile was added to a solution of 0.15 g (0.5 mmol) of sodium salt **III** in 3 ml of the same solvent. After 1 h, the precipitate was filtered off, washed in succession with ethyl acetate, acetone, water, and acetone, and dried under reduced pressure.

1-Benzylsulfonyl-5',7'-dinitro-1,2-dihydro-4'*H*-spiro[imidazo[4,5,1-*ij*]quinolin-3-ium-2,4'-[2,1,3]-benzoxadiazolate] 3'-oxide (IV). Yield 0.06 g (16.4%).



I, **II** **III** *R*-**IV**, *R*-**V** *S*-**IV**, *S*-**V**

I, **IV**, n = 1; **II**, **V**, n = 0.

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Yellow crystals, mp 230°C (decomp.). ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 4.61 d.d (2H, CH_2, J = 13.8 Hz), 7.32 br.m (5H, Ph), 7.36 d (1H, 9-H, $J_{8,9}$ = 7.8 Hz), 7.87 d.d (1H, 8-H, $J_{7,8}$ = 8.4, $J_{8,9}$ = 7.8 Hz), 7.99 d (1H, 7-H, $J_{7,8}$ = 8.4 Hz), 8.34 d.d (1H, 5-H, $J_{5,6}$ = 8.3, $J_{4,5}$ = 5.8 Hz), 9.08 s (1H, 6'-H), 9.36 d (1H, 6-H, $J_{5,6}$ = 8.3 Hz), 9.80 d (1H, 4-H, $J_{4,5}$ = 5.8 Hz). Found, %: C 50.67; H 2.83; N 16.01; S 6.03. $C_{22}H_{14}N_6O_8S$. Calculated, %: C 50.58; H 2.68; N 16.09; S 6.13.

1-Benzylsulfonyl-5',7'-dinitro-1,2-dihydro-4'*H*-spiro[imidazo[4,5,1-*ij*]quinolin-3-ium-2,4'-[2,1,3]-benzoxadiazolate] (V). Yield 0.04 g (26%). Yellow crystals, mp 225°C. ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 4.79 s (2H, CH_2), 7.46 br.m (6H, Ph, 9-H), 8.07 d.d (1H, 8-H, $J_{7,8}$ = 8.6, $J_{8,9}$ = 7.3 Hz), 8.17 d (1H, 7-H, $J_{7,8}$ = 8.6 Hz), 8.50 d.d (1H, 5-H, $J_{4,5}$ = 5.9, $J_{5,6}$ = 8.4 Hz), 9.31 s (1H, 5'-H), 9.53 d (1H, 6-H, $J_{5,6}$ = 8.4 Hz), 9.95 d (1H, 4-H, $J_{4,5}$ = 5.9 Hz). Found, %: C 52.29; H 2.84; N 16.46; S 6.18. $C_{22}H_{14}N_6O_7S$. Calculated, %: C 52.17; H 2.77; N 16.60; S 6.32.

The ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) using tetramethylsilane as internal reference.

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