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SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences V.I. Minkin on his 80th anniversary

Synthesis and [3+2]-Cycloaddition Reactions of Superelectrophilic (Dimethylaminophenyl)benzofulvene Derivatives

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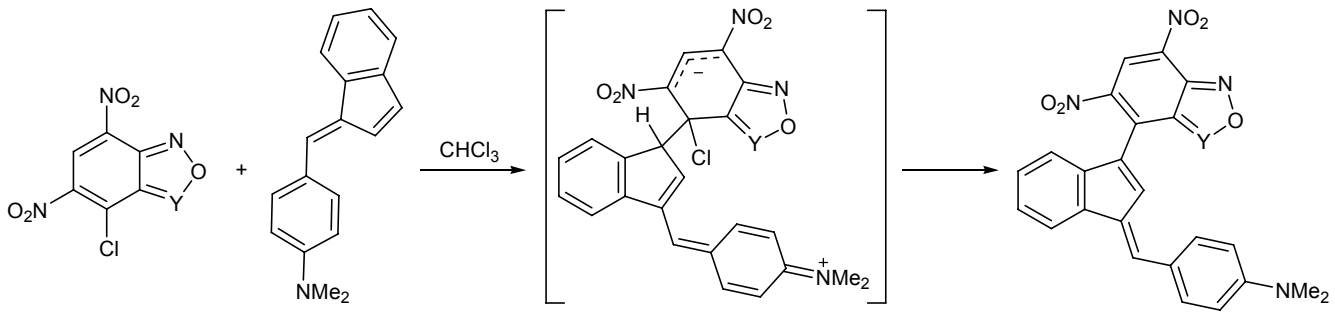
Chloro-substituted dinitrobenzofuroxan **1** and dinitrobenzofurazan **2** possess super-electrophilic properties [1, 2] which make them capable of forming highly stable dipolar spirocycles [3, 4] and intramolecular contact charge-transfer π-complexes [5], as well as of reacting with weak neutral carbon-centered nucleophiles, e.g., π-excessive nitrogen heterocycles (pyrroles, indoles, indolizines) [6–8]. We report here the reaction of super-electrophiles **1** and **2** with π-excessive benzofulfene **3** whose chemical properties have not been studied at all [according to the Chemical Abstracts data (SciFinder)].

Mixing equimolar amounts of benzofulvene **3** and chloro derivative **1** or **2** in chloroform at room temperature resulted in fast formation of deeply colored (blue–green) biaryls **4** and **5**, respectively, in high yields (Scheme 1). Presumably, this S_NAr–S_EAr reaction is mediated by dipolar Meisenheimer–Wheland σ-adduct **A** [6]. The presence in a single molecule of both donor and acceptor fragments in combination with a conjugated bond system gives rise to intramolecular charge transfer. According to DFT B3LYP/6-31G(*d*) calculations, the charge transfer from the benzofulvene fragment to nitrobenzoxadiazole amounts

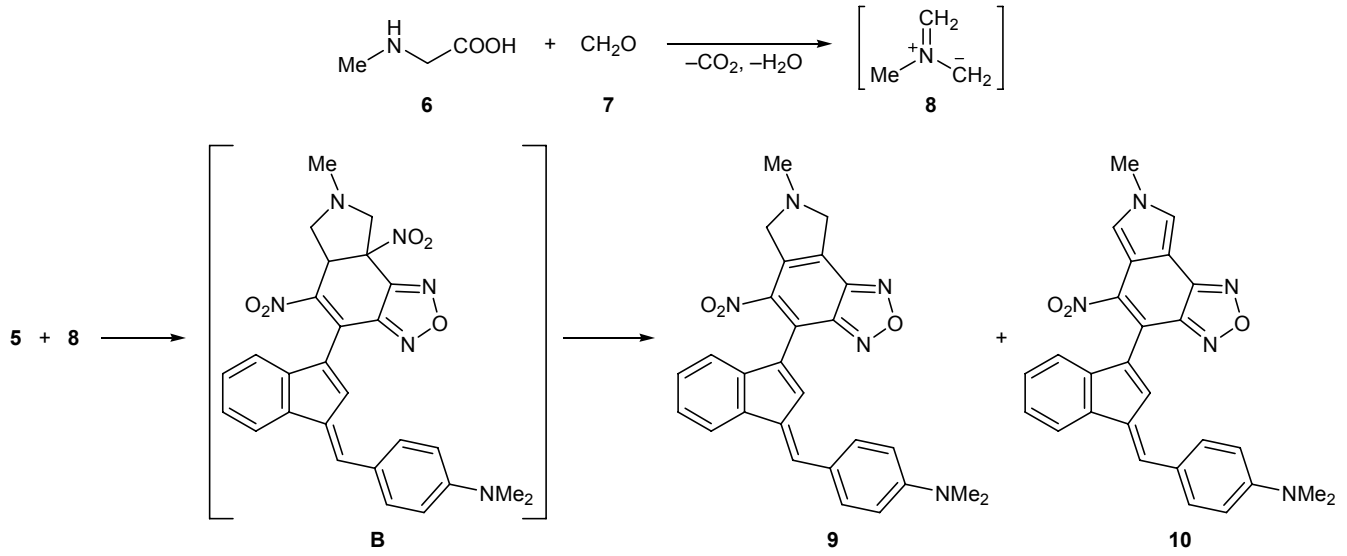
Scheme 1.



1, **2** **3** **A** **4**, **5**

1, **4**, Y = N→O; **2**, **5**, Y = N.

Scheme 2.



to 0.26 $\bar{e}$ for molecule **4** and 0.27 $\bar{e}$ for **5**, which may be related to more planar structure of the latter. The dihedral angle between the benzofulvene and dinitrobenzoxadiazole planes is 45 and 38° for molecules **4** and **5**, respectively. This may be due to the lack of *N*-oxide oxygen atom in **5**.

We have studied [3+2]-cycloaddition reaction of biaryl **5** with the simplest unstabilized azomethine ylide generated *in situ* from sarcosine (**6**) and formaldehyde (**7**) according to conventional procedure. Dinitrobenzofurazan derivative **5** rather than dinitrobenzofuroxan analog **4** was selected as substrate taking into account the known effect of a bulky substituent in position *7* of the benzofuroxan ring system [9], which favors 1,3-*N*-oxide tautomerism and thus essentially complicates product isolation and identification.

The cycloaddition process is likely to involve initial formation of cycloadduct **B** (Scheme 2); however, we failed to isolate it as pure substance. The reaction mixture contained only nitrous acid elimination product **9** and oxidative aromatization product **10** which were isolated in the pure state by column chromatography.

The relation between the spectral parameters of **5** and **10** and the empirical Brooker's solvent parameters χ_R and χ_B characterizes their polarity [12]. Compound **10** showed a good correlation between the absorption maximum frequencies and χ_B. The corresponding correlation for compound **5** was somewhat worse, whereas no correlation with χ_R was observed in both cases. The observed pattern indicated negative solvatochromism and high polarity of molecules **5** and **10** in the ground state.

***N,N*-Dimethyl-4-[(*E*)-1*H*-inden-1-ylidenemethyl]-aniline (3).** 4-(Dimethylamino)benzaldehyde, 0.745 g (5 mmol), was added under stirring to a mixture of 0.58 g (5 mmol) of indene and 0.2 g (5 mmol) of sodium hydroxide in 7 mL of ethanol. After 3 h, the precipitate was filtered off, washed with ethanol, and purified by silica gel chromatography using chloroform as eluent. Yield 0.845 g (75%), yellow crystals, mp 158–160°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.02 s [6H, $N(CH_3)_2$], 6.74 d (2H, 2-H, 6-H, J = 8.9 Hz), 6.99 d (1H, 2′-H, J = 5.5 Hz), 7.13 d (1H, 3′-H, J = 5.5 Hz) 7.17–7.22 m (2H, 5′-H, 6′-H), 7.28–7.38 m (1H, 4′-H), 7.43 s (1H, 1″-H), 7.58 d (2H, 3-H, 5-H, J = 8.9 Hz), 7.65–7.74 m (1H, 7′-H). Found, %: C 87.42; H 6.90; N 5.68. $C_{18}H_{17}N$. Calculated, %: C 87.41; H 6.93; N 5.66.

Compounds 4 and 5 (*general procedure*)**.** Compound **3**, 0.134 g (0.54 mmol), was added to a solution of 0.27 mmol of benzofuroxan **1** [10] or benzofurazan **2** [11] in 5 mL of warm chloroform. The mixture was kept for 24 h, and the precipitate was filtered off, washed with chloroform, and dried in air.

(*E*)-7-{1-[4-(Dimethylamino)benzylidene]-1*H*-inden-3-yl}-4,6-dinitro-2,1,3-benzoxadiazole 1-oxide (4). Yield 0.096 g (76%), dark blue crystals, mp 202–204°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.05 s [6H, $N(CH_3)_2$], 6.84 d (2H, 2′-H, 6′-H, J = 8.7 Hz), 7.06 d (1H, 4″-H, J = 7.5 Hz), 7.19 d.d (1H, 5″-H, J = 7.3, 7.5 Hz), 7.29 d.d (1H, 6″-H, J = 7.3, 7.4 Hz), 7.68 s (1H, 1‴-H), 7.71 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.95–8.03 m (2H, 2″-H, 7″-H), 9.06 s (1H, 5-H). Found: m/z 494.1056 $[M + Na]^+$. $C_{24}H_{17}N_5O_6$. Calculated: M + Na 494.1071.

4-{(*E*)-[3-(5,7-Dinitro-2,1,3-benzoxadiazol-4-yl)-1*H*-inden-1-ylidene]methyl}-*N*,*N*-dimethylaniline (5). Yield 0.095 g (78%), dark green crystals, mp 250–252°C. UV spectrum, λ_{max}, nm (ε, L mol^{-1} cm^{-1}): in acetonitrile: 443 (28300), 683 (10600); in acetone: 440 (27400), 668 (10200); in methylene chloride: 451 (31400), 748 (14800); in chloroform: 448 (29400), 754 (14700); in 1,4-dioxane: 438 (28800), 672 (13000); in toluene: 439 (26600), 701 (14300). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 3.12 s [6H, N(CH$_3$)$_2$], 6.90 d (2H, 2′-H, 6′-H, J = 9.0 Hz), 7.12 d (1H, 4″-H, J = 7.2 Hz), 7.23 d.d (1H, 5″-H, J = 7.2, 7.5 Hz), 7.33 d.d (1H, 6″-H, J = 7.5, 7.7 Hz), 7.81 d (2H, 3′-H, 5′-H, J = 8.9 Hz), 7.97 d (1H, 7″-H, J = 7.7 Hz), 8.00 s (1H, 1‴-H), 8.07 s (1H, 2″-H), 9.20 s (1H, 6-H). Found: m/z 478.1108 [M + Na]$^+$. $C_{24}H_{17}N_5O_5$. Calculated: M + Na 478.1122.

Compounds 9 and 10. A suspension of 0.227 g (2.55 mmol) of finely powdered sarcosine, 0.092 g (3.07 mmol) of paraformaldehyde, and 0.232 g (0.51 mmol) of benzofulvene **5** in 7 mL of anhydrous benzene was heated for 1 h under reflux. The mixture was cooled, the precipitate was filtered off, the filtrate was evaporated, and the residue was subjected to column chromatography on silica gel using chloroform–acetonitrile (5:1) as eluent.

***N*,*N*-Dimethyl-4-{(*E*)-[3-(7-methyl-5-nitro-7,8-dihydro-6*H*-[1,2,5]oxadiazolo[3,4-*e*]isoindol-4-yl)-1*H*-inden-1-ylidene]methyl}aniline (9).** Yield 0.044 g (17%), dark brown crystals, mp 130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (3H, NCH$_3$), 3.03 s [6H, N(CH$_3$)$_2$], 4.21 t (2H, 8-H, J = 3.7 Hz), 4.41 t (2H, 6-H, J = 3.7 Hz), 6.72 d (2H, 2′-H, 6′-H, J = 8.9 Hz), 7.03 d (1H, 4″-H, J = 7.3 Hz), 7.19 d.d (1H, 5″-H, J = 7.3, 7.4 Hz), 7.27 d.d (1H, 6″-H, J = 7.3, 7.4 Hz), 7.54–7.67 m (4H, 1‴-H, 2″-H, 3′-H, 5′-H), 7.77 d (1H, 7″-H, J = 7.3 Hz). Found: m/z 488.1672 [M + Na]$^+$. $C_{27}H_{23}N_5O_3$. Calculated: M + Na 488.1693.

***N*,*N*-Dimethyl-4-{(*E*)-[3-(7-methyl-5-nitro-7*H*-[1,2,5]oxadiazolo[3,4-*e*]isoindol-4-yl)-1*H*-inden-1-ylidene]methyl}aniline (10).** Yield 0.013 g (5%), blue crystals, mp 260°C. UV spectrum, λ_{max}, nm (ε, L× mol^{-1} cm^{-1}): in acetonitrile: 372 (6400), 682 (11900); in acetone: 375 (5100), 523 (2800), 689 (10100); in methylene chloride: 385 (7500), 515 (4400), 706 (15800); in chloroform: 384 (7600), 514 (4500), 707 (15900); in 1,4-dioxane: 374 (7100), 504 (3600), 727 (13800); in toluene: 375 (5800), 496 (2800), 734 (9700). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.09 s [6H, N(CH$_3$)$_2$], 4.35 s (3H, NCH$_3$), 6.87 d (2H, 2′-H, 6′-H, J = 8.5 Hz), 7.06–7.20 m (2H, 4″-H, 5″-H), 7.30–7.45 m (3H, 3′-H, 5′-H, 8-H), 7.45–7.57 m (3H, 6-H, 6″-H, 7″-H), 7.72 s (1H, 1‴-H), 9.40 s (1H, 2″-H). Found: m/z 486.1536 [M + Na]$^+$. $C_{27}H_{21}N_5O_3$. Calculated: M + Na 486.1537.

The ^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer (250 MHz). The electron absorption spectra were measured on a Varian Cary 50 spectrophotometer at 25°C ($c = 4\times10^{-5}$ M; cell path length 1 cm).

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REFERENCES

1. Terrier, F., *Modern Nucleophilic Aromatic Substitution*, Weinheim: Wiley-VCH, 2013.
2. Kurbatov, S., Lakhdar, S., Goumont, R., and Terrier, F., *Org. Prep. Proced. Int*., 2012, vol. 44, p. 289.
3. Morozov, P.G., Kurbatov, S.V., and Olekhnovich, L.P., *Chem. Heterocycl. Compd*., 2002, vol. 38, p. 1428.
4. Tkachuk, A.V., Kurbatov, S.V., Burov, O.N., Kletskii, M.E., Tavunova, Yu.P., Morozov, P.G., Voronina, V.A., and Minkin, V.I., *Russ. J. Org. Chem*., 2013, vol. 49, p. 1373.
5. Minkin, V.I., Tkachuk, A.V., Kletskii, M.E., Steglenko, D.V., Voronina, V.A., and Kurbatov, S.V., *Russ. Chem. Bull., Int. Ed*., 2013, vol. 62, p. 464.
6. Kurbatov, S., Rodriguez-Dafonte, P., Goumont, R., and Terrier, F., *Chem. Commun*., 2003, p. 2150.
7. Kurbatov, S.V., Tatarov, A.V., Minkin, V.I., Goumont, R., and Terrier, F., *Chem. Commun*., 2006, p. 4279.
8. Tatarov, A., Kurbatov, S., Borodkin, G., Goumont, R., and Terrier, F., *Tetrahedron*, 2010, vol. 66, p. 995.
9. Khmel'nitskii, L.I., Novikov, S.S., and Godovikova, T.I., *Khimiya furoksanov. Reaktsii i primenenie* (Chemistry of Furoxans. Reactions and Application), Moscow: Nauka, 1996.
10. Sharnin, G.P., Levinson, F.S., Akimova, S.A., and Khasanov, R.Kh., USSR Inventor's Certificate no. 627129, 1978; *Byull. Izobret*., 1978, no. 37.
11. Norris, W.P., Chafin, A., Spear, R.J., and Read, R.W., *Heterocycles*, 1984, vol. 22, p. 271.
12. Brooker, L.G.S., Craig, A.C., Heseltine, D.W., Jenkins, P.W., and Lincoln, L.L., *J. Am. Chem. Soc*., 1965, vol. 87, p. 2443.