## Reactions of polyhalonitrosoarenes with phenylacetylene

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Phenylacetylene reacts with polyhalonitrosoarenes to give two isomers of 1-phenyl-1,2-bis(2,4,6-trihalophenylnitrono)ethane.

**Key words:** polyhalonitrosoarenes, phenylacetylene, 1-phenyl-1,2-bis(2,4,6-trihalo-phenylnitrono)ethanes, addition.

It is known that the pathway of reactions of nitrosoarenes with alkynes depends on the structure of the latter. For instance, a reaction of nitrosobenzene 1a with tolan gives bisnitrone 2a (see Ref. 1) (Scheme 1). With other internal alkynes, the reaction proceeds similarly.

Scheme 1



A reaction of nitrosobenzene with phenylacetylene passes through the formation of unstable 1-hydroxy-3-phenylindole **3**, its O-methylation leading to more stable 1-methoxy-3-phenylindole **4** (see Ref. 2), and oxidative cyclodimerization into *cis*-1,10-diaza-9,20-dioxadibenzo-[b,g]tetracyclo[7.2.1.0<sup>4,11</sup>0<sup>6,10</sup>]dodecane **5** (see Ref. 3) (Scheme 2).

A single-step synthesis of *N*-methoxyindoles from alkynes and nitrosoarenes (PhH,  $K_2CO_3$ ,  $Me_2SO_4$ ) is simpler than the previous methods.<sup>2</sup>

In our continued systematic investigations of reactions of 2,6-dihalonitrosobenzenes with unsaturated compounds,<sup>4</sup> we studied reactions of polyhalonitrosoarenes 1b-e with phenylacetylene. It should be noted that the reactions in various solvents (PhH, PhMe, and AcOH) yield the same products. It proved preparatively conve5 nient to carry out these reactions in benzene at 45-50 °C. After nitrosoarenes were completely consumed, the reaction mixtures were cooled to 10-15 °C, which resulted in crystallization of pale yellow products **6b**—**e**. The filtrates contained compounds **6b**—**e** and **7b**—**e** (TLC data); products **7b,c** were isolated by column chromatography (Scheme 3). In boiling toluene, products **7b,c** were transformed into compounds **6b,c**, respectively.

Structures **6** and **7** were determined by physicochemical methods. According to <sup>1</sup>H NMR data, products **6b**—**e** and **7b,c** are formed from two moles of nitrosoarene and one mole of phenylacetylene (Table 1). Interestingly, the singlet signals of one proton in all the four compounds **6b**—**e** appear in the same range ( $\delta$  8.25–8.35). At the

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same time, in the spectra of compounds **7b,c**, the singlet signals of one proton are shifted upfield compared to the signals for compounds **6b,c** by ~0.6 ppm. Structures **6c** and **7c** were ultimately identified by X-ray diffraction (Figs 1, 2; Tables 2–4).

Compounds 6 and 7 are configurational isomers belonging to a rare type of structures with the acyclic fragment (O)N=C-C=N(O). According to the Cambridge Crystallographic Data (version 2007), no structurally characterized compounds containing such a fragment have been documented. Isomers 6c and 7c differ in the relative positions of the aromatic substituent C(3)-C(8) and the O(1) atom about the C(1)=N(1) bond. The torsion angle O(1)-N(1)-C(1)-C(2) is 7.4° in 6c and 174.4° in 7c.

Table 1. <sup>1</sup>H NMR spectra of 1-phenyl-1,2-bis(2,4,6-trihalo-phenylnitrono)ethanes **6b**—e and **7b**,c

Com-	δ (J/Hz)					
pound	CH=N	H(3´), H(5´), H(3''), H(5'')	${{\rm H}_{{\rm Ph}}(3),{\rm H}_{{\rm Ph}}(4),}\ {{\rm H}_{{\rm Ph}}(5)}$	H <sub>Ph</sub> (2), H <sub>Ph</sub> (6)		
6b	8.25 (s)	7.56 (d), 7.39 (d), $J = 8^*$	7.24—7.27 (m)	7.18—7.20 (m)		
6c	8.35 (s)	7.96 (s), 8.11 (s)	7.30—7.31 (m)	7.49—7.51 (m)		
6d	8.36 (s)	7.86 (s), 8.01 (s)	7.29—7.34 (m)	7.50—7.51 (m)		
6e	8.24 (s)	7.43 (s), 7.45 (s)	7.27—7.30 (m)	7.23—7.25 (m)		
7b	7.71 (s)	7.77 (d), 7.89 (d), $J = 8^*$	7.45—7.51 (m)	7.74—7.76 (m)		
7c	7.79 (s)	8.02(s), 8.13 (s)	7.46—7.49 (m)	7.73—7.75 (m)		

\* The coupling constant of the protons is due to the *ortho*-F atoms.

Both compounds show torsion about the single C(1)-C(2)bond; the dihedral angles between two planar fragments N(1)O(1)C(3)C(1)C(15) and N(2)O(2)C(9)C(2) are 24.5°



**Fig. 1.** Molecular structure of compound **6c** with atomic thermal displacement ellipsoids (50% probability).



**Fig. 2.** Molecular structure of compound **7c** with atomic thermal displacement ellipsoids (50% probability).

Bond	d/l	Å
	6c	7c
O(1)-N(1)	1.299(5)	1.282(5)
O(2) - N(2)	1.274(5)	1.277(5)
N(1) - C(1)	1.332(6)	1.331(6)
N(1) - C(3)	1.449(6)	1.454(6)
N(2) - C(2)	1.316(6)	1.299(6)
N(2) - C(9)	1.447(6)	1.452(6)
C(1) - C(2)	1.421(6)	1.438(7)

**Table 2.** Selected bond lengths (d) in compounds **6c** and **7c** 

and  $35.4^{\circ}$  in **6c** and **7c**, respectively. In both structures, the brominated aromatic rings are nearly perpendicular to the corresponding planar fragments (the dihedral angles are  $80.9^{\circ}-86.9^{\circ}$ ). At the same time, the angles between the plane of the phenyl substituent at the C(1) atom and the plane N(1)C(1)C(2) noticeably differ in compounds **6c** and **7c** (46.1° and 77.3°, respectively), which is probably due to the different positions of the bulky 2,4,6-tribromophenyl substituent at the N(1) atom.

Thus, isomers **6c** and **7c** differ in the positions of the phenyl substituent and the O atom relative to the C=N bond. Note that the *N*-oxide fragment in isomer **6c** approaches the aliphatic H atom. Apparently, the anisotropic effect of the *N*-oxide fragment is responsible for the downfield shifts of the signals for the aliphatic proton in 1-phenyl-1,2-bis(2,4,6-trihalophenylnitrono)ethanes **6b**—e.

The mass spectra of compounds **6b,c** and **7b,c** show no molecular ion peaks because of their high molecular masses. The only fundamental difference between the mass spectra of these compounds is that the spectra of com-

**Table 3.** Selected bond angles ( $\omega$ ) in compounds **6c** and **7c** 

Bond angle	ω/deg		
	6c	7c	
O(1) - N(1) - C(1)	124.4(4)	125.6(4)	
O(1) - N(1) - C(3)	113.9(4)	113.3(4)	
C(1) - N(1) - C(3)	121.5(4)	121.1(4)	
O(2) - N(2) - C(2)	126.7(4)	124.7(4)	
O(2) - N(2) - C(9)	114.4(4)	114.2(4)	
C(2) - N(2) - C(9)	118.8(4)	121.1(4)	
N(1) - C(1) - C(2)	115.5(4)	118.5(4)	
N(1)-C(1)-C(15)	120.3(4)	118.5(4)	
C(2)-C(1)-C(15)	123.8(4)	122.9(5)	
N(2)-C(2)-C(1)	123.5(5)	123.8(5)	

pounds **7b,c** contain intense peaks with m/z 105, probably due to the phenacylium ion. The formation of phenacylium ions in the fragmentation of the molecular ions of compounds **7b,c** can result from a possible migration of the O atom to the aliphatic C atom because of a shorter distance between the *N*-oxide and phenyl fragments in these products.

The formation of hydroxyindole derivatives in reactions of nitrosoarenes with phenylacetylene seems to involve [3+2] cycloaddition; this is possible when at least one *ortho*-position in nitrosoarene is not substituted<sup>2,5</sup> (see Scheme 2).

In nitrosoarenes 1b-e, both *ortho*-positions are occupied by halogen atoms and the formation of 1-phenyl-1,2bis(2,4,6-trihalophenylnitrono)ethanes **6** and **7** probably results from a sequence of reactions (Scheme 4) passing through intermediate carbene **8** or carbocation **9**.

Scheme 4



Torsion angle	φ/deg		
	6c	7c	
O(1) - N(1) - C(1) - C(2)	7.4(6)	-174.4(4)	
C(3) - N(1) - C(1) - C(2)	-167.0(4)	7.2(7)	
O(1) - N(1) - C(1) - C(15)	-179.7(4)	2.3(7)	
C(3) - N(1) - C(1) - C(15)	5.8(7)	-176.1(4)	
O(2) - N(2) - C(2) - C(1)	6.9(8)	4.2(8)	
C(9) - N(2) - C(2) - C(1)	-169.3(4)	-176.1(5)	
N(1)-C(1)-C(2)-N(2)	-170.0(4)	-150.3(5)	
C(15)-C(1)-C(2)-N(2)	17.4(7)	33.1(8)	
O(1) - N(1) - C(3) - C(4)	-89.4(5)	79.1(5)	
C(1) - N(1) - C(3) - C(4)	85.6(6)	-102.3(6)	
O(2) - N(2) - C(9) - C(10)	84.3(6)	95.9(6)	
C(2)-N(2)-C(9)-C(10)	-99.0(6)	-83.8(7)	
N(1)-C(1)-C(15)-C(16)	-101.0(6)	-132.4(5)	
C(2)-C(1)-C(15)-C(16)	71.3(7)	44.1(7)	

Table 4. Selected torsion angles ( $\phi)$  in compounds 6c and 7c

Hence, we discovered a novel pathway in reactions of nitrosoarenes with phenylacetylene.

## **Experimental**

<sup>1</sup>H NMR spectra were recorded on a Bruker DRX instrument (500 MHz) in DMSO-d<sub>6</sub> with Me<sub>4</sub>Si as the internal standard. The course of the reactions was monitored, and the purity of the compounds obtained was checked, by TLC on Silufol UV-254 plates. Melting points were measured on a Boetius hotstage microscope.

The starting nitrosoarenes 1b-e were prepared according to known procedures.<sup>6,7</sup>

1-Phenyl-1,2-bis(2,4,6-trihalophenylnitrono)ethanes (6b—e). Phenylacetylene (0.55 mL, 0.005 mol) was added to a solution of 2,4,6-trihalonitrosobenzene 1b-e (0.01 mol) in benzene (20 mL). The reaction mixture was heated at 50 °C for 3 h. The reaction products began to crystallize even in the hot solution. On cooling to 10-15 °C, compounds 6b-e were filtered off and recrystallized from benzene.

1-Phenyl-1,2-bis(2,4,6-trihalophenylnitrono)ethanes (7b,c). After the isolation of products 6b,c, the filtrates were chromatographed on alumina (Brockmann activity II) in benzene. The first and second yellow fractions were collected. An additional crop (3–5%) of compounds 6b,c was obtained from the first fraction. Compounds 7b,c were isolated from the second fraction. Compounds 6b,c and 7b,c were recrystallized from benzene and benzene—heptane (1 : 1), respectively.

Isomerization of product 7c into product 6c. A solution of compound 7c (0.3 g) in toluene (15 mL) was refluxed until the starting compound was completely consumed. On cooling, product 6c was isolated as described above. The yield was 0.16 g (53%).

Yields and physicochemical constants of compounds 6b-e and 7b,c are given in Table 5.

 
 Table 5. Yields and physicochemical properties of the 1-phenyl-1,2-bis(2,4,6-trihalophenylnitrono)ethanes obtained

Con pour	n- <i>T</i> <sub>m</sub> /°C nd	<u>Four</u> Calci	nd ulated	- (%)	Molecular Yi formula (!	eld %)
		С	Ν	Н		
6b	216-217	35.90 35.90	4.21 4.20	1.53 1.30	$C_{20}H_{10}N_2O_2Br_4F_2$	60
6c	205-207	30.38 30.40	3.54 3.50	1.27 1.10	$C_{20}H_{10}N_2O_2Br_6$	54
6d	216-217	34.68 34.23	4.07	1.70 1.42	$C_{20}H_{10}N_2O_2Br_4Cl_2$	50
6e	202-203	45.52 45.89	4.80 5.35	1.85 1.91	$C_{20}H_{10}N_2O_2Cl_6$	61
7b	188—190	35.80 35.90	4.47 4.20	1.59 1.30	$C_{20}H_{10}N_{2}O_{2}Br_{4}F_{2}$	9
7c	178—180	30.30 30.40	3.74 3.50	1.49 1.10	$C_{20}H_{10}N_2O_2Br_6$	7

X-ray diffraction analysis of compounds 6c and 7c. Selected crystallographic parameters and the data collection and refinement statistics for compounds 6c and 7c are given in Table 6. Reflection intensities were collected on Bruker SMART 1000 CCD<sup>8</sup> and Bruker SMART APEX II<sup>9</sup> diffractometers for com-

 Table 6. Crystallographic parameters and the data collection and refinement statistics for compounds 6c and 7c

Parameter	6с	7c	
Molecular formula	$C_{20}H_{10}Br_6N_2O_2$	$C_{20}H_{10}Br_6N_2O_2$	
Molecular mass	789.76	789.76	
Crystal system	Triclinic	Monoclinic	
Space group	$P\overline{1}$	$P2_{1/c}$	
a/Å	8.731(1)	8.8167(6)	
$b/\text{\AA}$	11.899(1)	12.0317(9)	
c/Å	12.099(1)	21.693(2)	
α/deg	110.197(2)	90	
β/deg	94.847(2)	97.238(2)	
γ/deg	96.915(2)	90	
$V/Å^3$	1160.3(2)	2282.8(3)	
Ż	2	4	
$d_{\rm calc}/{\rm g~cm^{-3}}$	2.261	2.298	
$2\theta_{\text{max}}/\text{deg}$	56	56	
$\mu/cm^{-1}$	104.01	105.73	
$T_{\rm min}/T_{\rm max}$	0.223/0.624	0.202/0.661	
Number of independent	5509 (0.0500)	5500 (0.0840)	
reflections $(R_{int})$			
$R_1$ (on F for reflections with $I \ge 2\sigma(I)$ )	0.0388 (3069)	0.0434 (3136)	
$wR_2$ (on $F^2$ for all	0.0936	0.0952	
reflections)			
Number of parameters refined	271	271	
GOOF	0.953	1.004	

pounds **6c** and **7c**, respectively (graphite monochromator,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\omega$  scan mode, T = 296 K). An absorption correction was applied semiempirically with the SADABS program.<sup>10</sup> The structures were solved by the direct methods and refined by the full-matrix least-squares method on  $F_{hkl}^2$  in the anisotropic approximation for all non-hydrogen atoms. All hydrogen atoms were located geometrically and refined using a riding model. All calculations were performed with the SHELXTL program package.<sup>11</sup> The comprehensive tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Center.

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## References

- 1. L. Alessandri, Gazz. Chim. Ital., 1922, 52, 194; 1924, 54, 438.
- 2. A. Penoni, G. Palmisano, G. Broggini, A. Kadowaki, K. M.
- Nicholas, J. Org. Chem., 2006, 71, 823.

- J. Iball, W. D. S. Motherwell, J. J. S. Pollock, J. M. Tedder, *Chem. Commun.*, 1968, 365.
- 4. L. M. Gornostaev, N. V. Geets, E. A. Bocharova, G. A. Stashina, S. I. Firgang, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 130 [*Russ. Chem. Bull., Int. Ed.*, 2007, 56, 137].
- 5. A. Penoni, J. Volkmann, K. M. Nicholas, *Org. Lett.*, 2002, **4**, 699.
- 6. R. R. Holmes, R. P. Bayer, J. Am. Chem. Soc., 1960, 82, 3454.
- L. M. Gornostaev, E. A. Bocharova, N. V. Geets, *Zh. Org. Khim.*, 2006, **42**, 1310 [*Russ. J. Org. Chem. (Engl. Transl.*), 2006, **42**].
- 8. SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software, 1998, Bruker AXS Inc., Madison, WI-53719, USA.
- 9. APEX II Software Package, 2005, Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI-53719, USA.
- G. M. Sheldrick, SADABS, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
- G. M. Sheldrick, *SHELXTL-97, Version 5.10*, 1997, Bruker AXS Inc., Madison, WI-53719, USA.

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