

# Synthesis of thermostable aliphatic alkylene-bis(*N*-phenyl aldonitrones)

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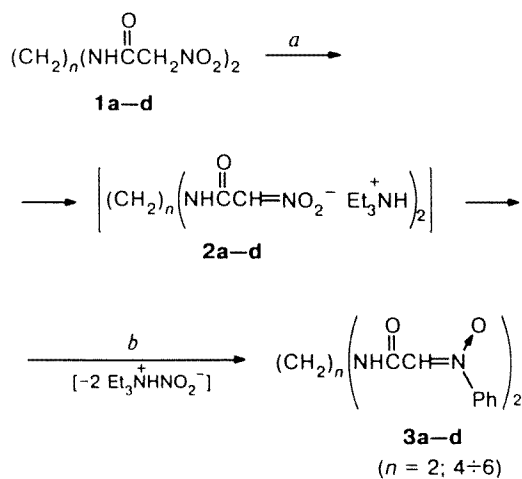
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A general method for the synthesis of alkylene-bis(*N*-phenyl aldonitrones) (bisnitrones) by reaction of dianions of *N,N'*-bisnitroacetyldiamines with nitrobenzene in DMF was proposed.

**Key words:** alkylene-bis(*N*-phenyl aldonitrones), salts of nitro compounds, *N,N'*-bisnitroacetyldiamines, nitrosobenzene.

Earlier, we proposed a novel general method for the synthesis of nitrones using the reaction of salts of nitro compounds with nitroso compounds.<sup>1</sup> In this communication, we demonstrate the applicability of this method for the synthesis of alkylene-bisnitrones, which were obtained by the reaction of *N,N'*-bisnitroacetyldiamines (**1a–d**)<sup>2</sup> with nitrosobenzene in the presence of Et<sub>3</sub>N as a base (Scheme 1, Table 1).

Scheme 1

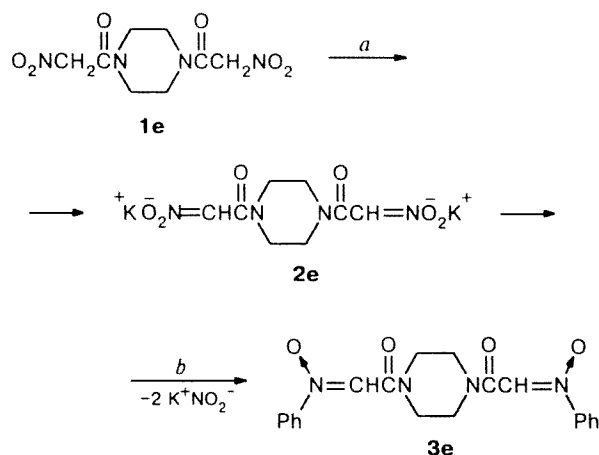


**Reagents and conditions:** *a.* 2 Et<sub>3</sub>N, DMF, 0 °C; *b.* 2 PhNO, DMF–MeCN, –20 °C → 0 °C.

The target products are formed, obviously, as a result of interaction of bistriethylammonium salts **2a–d** generated *in situ* with PhNO and crystallized in high yields from the reaction mixtures as they were obtained. The alkylene-bisnitrones **3a–d** were isolated by filtration followed by washing with MeOH and did not require additional purification.

The attempts to obtain product **3e** by this method failed. It was synthesized by a two-step scheme involving isolation of dipotassium salt **2e** followed by its reaction with two equivalents of PhNO in DMF (Scheme 2).

Scheme 2



**Reagents and conditions:** *a.* 2 KOH, H<sub>2</sub>O–MeOH, 0 °C → 20 °C; *b.* 2 PhNO, DMF, –10 °C → 20 °C.

**Table 1.** Physicochemical characteristics of alkylene-bis(*N*-phenyl aldonitrones) (**3b–e**)

Compound	<i>n</i>	Yield (%)	M.p. /°C	Found / Calculated (%)		
				C	H	N
<b>3b</b>	4	78	208–212	62.96	5.75	14.52
				62.82	5.80	14.65
<b>3c</b>	5	74	207–209	63.70	5.93	14.04
				63.62	6.10	14.13
<b>3d</b>	6	85	202–204	64.44	6.30	13.58
				64.38	6.38	13.65
<b>3e</b>	—	72	215–218	63.38	5.17	14.80
				63.15	5.30	14.73

Таблица 2.  $^1\text{H}$  and  $^{14}\text{N}$  NMR data for compounds **3b–e**

Compound	$\delta$ $^1\text{H}$ (J/Hz)					$\delta$ $^{14}\text{N}$ ( $\Delta\nu_{1/2}/\text{Hz}$ ) = $\text{N}(\text{O})$
	$\text{CH}_2\text{N}$	$\text{CH}=\text{N}$	$\text{NH}$	$\text{H}_{\text{Ar}}$ (m)	Other signals	
<b>3b</b>	3.39 (m, 4 H)	7.92 (s, 2 H)	10.02 (br.m., 2 H)	7.59 (4 $\text{H}_m$ + 2 $\text{H}_p$ ); 7.89 (4 $\text{H}_o$ )	1.65 (br.m., $(\text{CH}_2)_2$ )	–84 ( $J = 500$ )
<b>3c</b>	3.35 (m, 4 H)	7.97 (s, 2 H)	10.06 (br.m., 2 H)	7.59 (4 $\text{H}_m$ + 2 $\text{H}_p$ ); 7.88 (4 $\text{H}_o$ )	1.40 (m, $\text{CH}_2$ ); 1.60 (m, $(\text{CH}_2)_2$ )	–83 ( $J = 500$ )
<b>3d</b>	3.35 (m, 4 H)	7.92 (s, 2 H)	10.02 (br.m., 2 H)	7.60 (4 $\text{H}_m$ + 2 $\text{H}_p$ ); 7.90 (4 $\text{H}_o$ )	1.41 (m, $(\text{CH}_2)_2$ ); 1.60 (m, $(\text{CH}_2)_2$ )	–83 ( $J = 250$ ) <sup>a</sup> ; –277 ( $J = 260$ ) <sup>b</sup>
<b>3e<sup>c</sup></b>	3.60 (m, 8 H)	8.20 (s, 2 H); 8.23 (s, 2 H)	—	7.57 (4 $\text{H}_m$ + 2 $\text{H}_p$ ); 7.88 (4 $\text{H}_o$ )	—	–84 ( $J = 700$ )

<sup>a</sup> At 60 °C. <sup>b</sup>  $\delta$   $^{14}\text{N}$  ( $\Delta\nu_{1/2}/\text{Hz}$ ) for  $\text{NHC}(\text{O})$  at 60 °C. <sup>c</sup> A mixture of two rotamers (~1.3 : 1) due to the hindered rotation around the amide bond  $\text{C}(\text{O})\text{N}$ .

Table 3.  $^{13}\text{C}$  NMR data for compounds **3b–e**

Compound	$\delta$ $^{13}\text{C}$				
	$\text{CH}_2\text{N}$	$\text{CH}=\text{N}$	$\text{C}=\text{O}$	$\text{C}_{\text{Ar}}$	Other signals
<b>3b</b>	37.86	130.11	160.08	121.58 ( $\text{C}_o$ ); 129.23 ( $\text{C}_m$ ); 131.20 ( $\text{C}_p$ ); 146.83 ( $\text{C}-\text{N}$ )	26.47 ( $(\text{CH}_2)_2$ )
<b>3c</b>	38.10	130.22	160.12	121.64 ( $\text{C}_o$ ); 129.30 ( $\text{C}_m$ ); 131.27 ( $\text{C}_p$ ); 146.87 ( $\text{C}-\text{N}$ )	23.87 ( $\text{CH}_2$ ); 28.53 ( $(\text{CH}_2)_2$ )
<b>3d</b>	38.37	130.32	160.28	121.73 ( $\text{C}_o$ ); 129.41 ( $\text{C}_m$ ); 131.30 ( $\text{C}_p$ ); 147.11 ( $\text{C}-\text{N}$ )	26.23 ( $(\text{CH}_2)_2$ ); 28.91 ( $(\text{CH}_2)_2$ )
<b>3e<sup>*</sup></b>	40.65; 41.62; 44.84; 45.87	128.08	159.95	121.29 ( $\text{C}_o$ ); 129.07 ( $\text{C}_m$ ); 130.73 ( $\text{C}_p$ ); 146.42 ( $\text{C}-\text{N}$ )	—

\* A mixture of two rotamers (~1.3 : 1) due to the hindered rotation around the amide  $\text{C}(\text{O})\text{N}$ .

Alkylene-bisnitrones **3a–e** are thermostable materials, and the pure compounds are white crystalline solids. At ~20 °C they are insoluble in water and organic solvents except for DMF and DMSO; compound **3e** is much better soluble than the acyclic analogs. The structure of the products was confirmed by a heteronuclear NMR method\* (Tables 2 and 3) and the elemental analysis data.

The possible application of bisnitrones as curing agents for polymeric compositions has been reported earlier.<sup>3</sup> Preliminary experiments with alkylene-bisnitrones **3a–e** carried out at FCDT "Soyuz" showed that these compounds favor hardening of butadiene rubber and some unsaturated compositions at 150 °C.

### Experimental

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  NMR spectra were recorded on a Bruker AM-300 (300.13, 75.5, and 21.5 MHz, respectively) in  $\text{DMSO}-d_6$ .

The synthesis of nitrones were carried out in absolute solvents; the reactions were performed under an atmosphere of dry argon.

\* Alkylene-bisnitrone **3a** is poorly soluble in DMSO; for this reason, we failed to record its NMR spectra. However, the structure of compound **3a** was confirmed by its IR- and mass-spectra, and the elemental analysis data (see Experimental).

**Synthesis of bisnitrones 3a–d.** Triethylamine (2 equivalents) was added to a solution of the corresponding alkylene-bis-*N*-nitroacetyldiamine in DMF (~0.4 mol  $\text{L}^{-1}$ ) at 0 °C, the resulting mixture was stirred for 10–15 min, the solution was cooled to –20 °C, and a solution of 2 equiv. of  $\text{PhNO}$  in  $\text{MeCN}$  (~1.5 mol  $\text{L}^{-1}$ ) was added dropwise for 0.5–0.75 h with vigorous stirring at a temperature not above –15 °C. Products **3a–d** precipitated from the reaction mixtures in the course of the addition as they formed. After completion of the addition, the reaction mixture was stirred for an additional 0.5 h at about –15 °C, then for 2 h at 0–5 °C. The product precipitated was filtered off, washed with  $\text{MeOH}$ , and dried.

**3a** ( $n = 2$ ). Yield 96%, m.p. 228–232 °C (decomp.). IR,  $\nu/\text{cm}^{-1}$ : 1073 ( $\text{N}\rightarrow\text{O}$ ); 1525 ( $\text{C}=\text{N}$ ); 1650 ( $\text{C}=\text{O}$ ); 3280 ( $\text{N}-\text{H}$ ). MS,  $m/z$ : 354  $[\text{M}]^{+}$ , 338  $[\text{M}-\text{O}]^{+}$ , 337  $[\text{M}-\text{OH}]^{+}$ , 247  $[\text{M}-\text{PhNO}]^{+}$ , 246  $[\text{M}-\text{PhNOH}]^{+}$ . Found (%): C, 61.11; H, 4.94; N, 15.73.  $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_4$ . Calculated (%): C, 61.01; H, 5.12; N, 15.81.

**Synthesis of dipotassium salt 2e.** A solution of  $\text{KOH}$  (1.04 g, 18.6 mmol) in 2 mL of distilled water was added to a suspension of *N,N'*-bisnitroacetyl piperazine<sup>2</sup> (**1e**) (2.10 g, 8.1 mmol) in 4 mL of distilled water with stirring and cooling (0–5 °C), and the temperature was elevated to 20 °C. The minimum amount of  $\text{H}_2\text{O}$  needed for the formation of a homogenous solution was then added to the reaction mixture, and it was kept for 0.25 h. The resulting solution was then diluted with fivefold amount (by volume) of  $\text{MeOH}$  and cooled. The salt **2e** that formed was filtered off, washed 2–3 times with small portions of chilled  $\text{MeOH}$ , and dried to give product **2e** (2.18 g, 80%).

**Synthesis of bisnitro 3e.** A solution of PhNO (0.95 g, 8.92 mmol) in 6.5 mL of DMF was added to a suspension of salt **2e** (1.50 g, 4.46 mmol) in 9 mL of DMF for 10 min with stirring and cooling ( $-10^{\circ}\text{C}$ ), and the resulting mixture was stirred for 30 min at  $-10^{\circ}\text{C}$ , for 1 h at  $(0-5^{\circ}\text{C})$ , and for 3 h at  $20^{\circ}\text{C}$ . Potassium nitrite was separated by filtration and washed with a small amount of DMF. The solvent from the combined filtrate was evaporated *in vacuo*, and the solid residue was washed on a filter with ice water and small portions of chilled MeOH, and dried to yield product **3e** (1.22 g, 72%).

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