1,6-Dideutero-1,3-diphenylhexane (VI), bp 137°C (2-3 mm), n_D^{20} 1.5359. IR spectrum (ν, cm^{-1}): 690, 730, 1450, 1500, 1600, 1800, 1870, 1940, 2175 (C—D), 3030, 3060. PMR spectrum (δ, ppm): 0.81 t (2H, CH_2D, J = 7 Hz), 1.1-1.7 m (6H, $3CH_2$), 2.20-2.70 m (2H, CH, CHD—Ph), 7.1-7.4 m (10H, 2Ph). Calculated: C 90.0; H 10.0%. Found: C 90.0; H 10.03%. M^+ 240.

1,1-Dimethyl-2-phenylsilacyclopentane (IX), bp 55-56°C (3 mm), n_D^{20} 1.5096. IR spectrum (ν, cm^{-1}): 715 (C-H arom.); 800 (Si CH_3); 850, 860 ($Si(CH_3)_2$); 1210, 1250 ($Si—Ch_2$); 1260 ($Si—CH_3$); 1415 ($Si—CH_2$); 1500, 1600, 1735, 1790, 1860, 1925, 3030, 3070, 3090. PMR spectrum (δ, ppm): −0.175 s (3H, $CH_3—Si$), 0.25 s (3H, $CH_3—Si$), 0.92 t (2H, $CH_2—Si$, J = 7.5 Hz), 1.25-2.00 m (4H, $2CH_2$), 2.25 t (1H, CH, J = 7.5 Hz), 7.1-7.5 m (5H, Ph). Calculated, %: C 75.79; H 9.47; Si 14.74. Found, %: C 75.4; H 9.44; Si 14.69. M^+ 190. The ^{13}C NMR spectra are given in Table 1.

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SYNTHESIS OF 1-TERT-BUTYL-2-ARYLDIAZENE-2-OXIDES BY REACTIONS OF t-BuNHMgBr WITH NITROBENZENES

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UDC 542.91:542.952.1:547.566.2:
547.546:547.233+546.46'141

A new method has been developed for the synthesis of alkylaryldiazene oxides by the reactions of t-BuNHMgBr with nitrobenzenes. The cis-azoxy compound 1-tert-butyl-2-(2-chlorophenyl)diazene-2-oxide, which irreversibly isomerizes to the trans isomer upon heating, was obtained for the first time under chemical reaction conditions.

Alkylaromatic diazene oxides are usually obtained by the reactions of aromatic nitroso compounds with dihaloamines [1-3]. Synthesis of asymmetric diaryldiazene oxides from aromatic nitro compounds under the effect of $ArN(MgBr)_2$ was described earlier [4, 5].

We have shown that aromatic nitro compounds (I) react with t-BuNHMgBr (II) fairly smoothly to give a corresponding alkylaryldiazene oxides (III)

$$\underset{(I)}{ArNO_2} \xrightarrow[2.\ H_2O+NH_4Cl]{1\text{-}\ t\text{-}BuNHMgBr\ (II)} \underset{(III)}{t\text{-}BuN{=}N(O)Ar} + \underset{(IV)}{t\text{-}BuN{=}NAr}$$

$$Ar = Ph\ (a),\ 2\text{-}Me_3SiNHC_6H_4\ (b),^{*}\ 4\text{-}ClC_6H_4\ (c),\ 2\text{-}ClC_6H_4\ (d).$$

Condensation occurs slowly at ~20°C and accelerates upon heating practically without a change of the product ratio (Table 1). Characteristics of the products are given in Tables 2-4.

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*In (IIIb) and (IVb) Ar = $2\text{-}NH_2C_6H_4$, the loss of the Me_3Si group evidently occurs in step 2.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1394-1397, June, 1991. Original article submitted September 14, 1990.

0568-5230/91/4006-1234$12.50

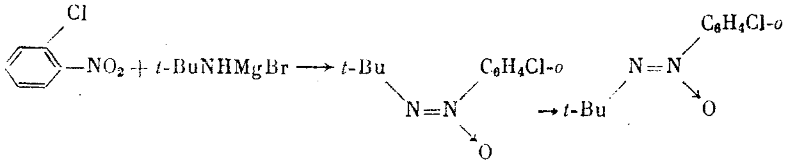
TABLE 1. Reaction Conditions and Yields of the Products of Reactions of (Ia-d) with (II)

Substrate	Mole ratio (II)/(I)	T, °C	Time, h	Substrate conversion (%)	Yield, %	
					(III)	(IV)
(Ia)	4	22	72	64	52	12
		60	3	75	60	15
(Ib)	3	22	48	86	73	13
	4	60	2,5	100	100	--
(Ic)	3,5	60	3	100	50	50
	4	22	72	78	59	19
(Id)	2,5	22	96	59	18,7 (cis) 16,3 (trans)	24
	4,5	22	96	66	28 (cis) 12 (trans)	26
	5	60	3	73	35	40

Azo compounds (IV) form as by-products, as in [4, 5], owing to reduction of either (III) or (I) to the corresponding nitroso derivative and subsequent condensation of it with (II). The latter version is evidently realized in the case of (Ia), since it was shown that (IVa) is obtained in the reaction of (II) with nitrosobenzene, but not with (IIIa). However, formation of (IVb) is most likely connected with the first version, since (II) does not react with o-nitrosoaniline.

It should be noted that (IIIb) is obtained only in reaction (II) with silylated o-nitroaniline (Ib), with unsubstituted o-nitroaniline under the same conditions giving only o-nitrosoaniline.

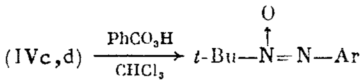
In the reaction of (II) with (Id) at ~22°C it was possible to recover the fairly stable cis isomer of (IIId), which in solution gradually and irreversibly converts to the thermodynamically more stable trans-(IIId)



cis-(IIId) trans-(IIId)

This is the first example of the formation of cis-azoxy compounds under conditions of chemical reactions. Until now the only method of obtaining them was photoisomerization of the trans derivatives [6].

It is known [7] that phenylazomethane is oxidized by perbenzoic acid to 1-methyl-2-phenyldiazene-2-oxide. Therefore, we attempted to oxidize the corresponding by-product azo compounds (IVc, d) to (IIIc, d). However, only oxygenation of the nitrogen atom bonded to the t-Bu group is accomplished in this case



$$(\text{IVc,d}) \xrightarrow[\text{CHCl}_3]{\text{PhCO}_3\text{H}} t\text{-Bu}-\overset{\overset{\text{O}}{\uparrow}}{\text{N}}=\text{N}-\text{Ar}$$

(Vc,d)

An analogous course of the reaction was observed in [1].

EXPERIMENTAL

GLC analysis was carried out on a Biokhrom 1M chromatograph (glass column 58.2 m × 0.25 mm with stationary liquid phase PEG-40M; carrier gas nitrogen). The ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer (^{1}H – 300 MHz, ^{13}C – 75.5 MHz, ^{15}N – 30.4 MHz, ^{14}N –21.7 MHz, references TMS and $MeNO_2$). All reactions with magnesium derivatives were conducted in anhydrous solvents in a dry Ar atmosphere. The starting (Ia), tert-butylamine, and o-nitroaniline of grade "pure" were used after distillation, and the o-Cl- and p-Cl-nitrobenzenes [8], EtMgBr [9], and $PhCO_3H$ [10] were obtained by well-known techniques.

TABLE 2. Parameters of ^1H, ^{14}N, and ^{15}N NMR Spectra

Compound	Sol-vent	PMR: δ, ppm						^{14}NMR: δ, ppm			Note
		H^2	H^3	H^4	H^5	H^6	Me	N → O	$\rangle$N–	N=N	
(Ib)	C_6D_6	–	6,76	7,05 t	6,40 t	8,05	0,16 s	–8,40 (NO_2)	–301,6 (NH)	–	7,71, br (NH): $^1J_{^1H,\ ^{15}N} \sim 78$ Hz
(IIIa) *	CCl_4	8,06	7,29	7,29	7,29	8,06	1,44	–	–	–	NMR ^{29}Si: 5,65 ppm
(IIIb)	$CDCl_3$	–	6,62	7,14 t	6,62	7,98	1,48 s	–47,8	–	–	5,60, br (NH_2) NMR ^{15}N: —16,8 ppm, (INEPT for t-Bu)
(IIIc)	$CDCl_3$	8,06	7,36	–	7,36	8,06	1,46 s	–54,6	–	–	
(IIId)cis	$CDCl_3$	–	7.45–7,70 m				1,16 s	–51,9	–	–	
(IIId) trans	$CDCl_3$	–	7,30–7,50 m			–	1,49 s	–51,5	–	–	
(IVb)	$CDCl_3$	–	6,68	7,12 t	6,74 t	7,62	1,32 s	–	–322,6 (NH_2)	69,8	5,30, br (NH_2)
(IVc)	$CDCl_3$	7,59	7,38	–	7,38	7,59	1,32 s	–	–	121,1 170,8	NMR ^{15}N: 170,9 ppm (INEPT for t-Bu)
(IVd)	$CDCl_3$	–	7,20–7,45 m				1,36 s	–	–	124,5 176,9	NMR ^{15}N: —29,8 ppm (INEPT for t-Bu)
(Vc)	C_6D_6	7,93	7,12	–	7,12	7,93	1,38 s	–29,8	–	–	NMR ^{15}N: —24,0 ppm (INEPT for t-Bu)
(Vd)	C_6D_6	–	7,22	6,93 t	6,77 t	7,60	1,47 s	–23,5	–	–	

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*Parameters of the PMR spectrum do not agree with those given in [2].

TABLE 3. Parameters of ^{13}C NMR Spectra of Compounds, δ, ppm

Compound	Solvent	C^1	C^2	C^3	C^4	C^5	C^6	C (*t*-Bu)	Me
(Ib)	C_6D_6	135,0	146,7	116,8	135,3	119,3	126,9	–	0,39
(IIIb)	$CDCl_3$	133,6	141,6	116,7	131,6	117,9	124,7	59,1	26,1
(IIIc)	$CDCl_3$	147,1	123,5	128,6	137,4	128,6	123,5	59,1	25,7
(IIId)cis	$CDCl_3$	147,0	124,5	131,2	127,8	130,5	124,5	60,5	28,6
(IIId)trans	$CDCl_3$	148,0	126,4	130,7	130,1	127,5	124,4	60,0	25,5
(IVb)	$CDCl_3$	136,1	142,3	116,8	131,0	117,1	125,9	67,0	27,3
(IVc)	$CDCl_3$	150,7	123,3	129,0	135,8	129,0	123,3	67,8	26,9
(IVd)	$CDCl_3$	148,9	132,9	130,2	130,4	127,2	117,9	69,0	27,0
(Vc)	C_6D_6	143,4	126,6	128,8	133,9	128,8	126,6	77,7	28,2
(Vd)	C_6D_6	142,8	129,1	130,1	128,1	127,0	123,5	78,1	28,2

TABLE 4. Properties and Results of Analysis of Products

Compound	n_D^{22}	Found/Calculated, %				Empirical formula
		C	H	N	Cl	
(IIIa) *		67.53 67,42	7,91 7,87	16.02 15,73		$C_{10}H_{14}N_2O$
(IIIb)	1,5678	62.20 62,18	7.73 7,77	22.17 21,76		$C_{10}H_{15}N_3O$
(IIIc)	1,5360	56,62 56.47	6,07 6,12	13,43 13,18	16,72 16,71	$C_{10}H_{13}N_2OCl$
trans-(IIId)†	1,5210	56,57 56,47	6,12 6,12	13,51 13,18	16,45 16,71	$C_{10}H_{13}N_2OCl$
(IVb)	1,5710	67,67 67,80	8,47 8,48	24,14 23,73		$C_{10}H_5N_3$
(IVc)	1,5310	66,98 61,07	6,65 6,62	14,60 14,25	17,99 18,07	$C_{10}H_{13}N_2Cl$
(IVd)	1,5280	60,92 61,07	6,48 6,62	14,41 14,25	18,18 18,07	$C_{10}H_{13}N_2Cl$
(Vc)	1,5370	56,51 56,47	6,15 6,12	13,47 13,18	16,51 16,71	$C_{10}H_{13}N_2OCl$
(Vd)	1,5230	56,67 56.47	6,09 6,12	13,53 13.18	16,63 16,71	$C_{10}H_{13}N_2OCl$

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*Bp 70-80°C at 0.5 mm (cf. [2]).

†cis-(IIId), bp 60-75°C.

General Technique of Conducting the Reactions of t-BuNHMgBr with $ArNO_2$. To a freshly prepared solution of EtMgBr, obtained from 65 meq Mg and 60 mmoles EtBr in 30 ml abs. THF at 0°C with stirring was added by drops an equimolar amount of tert-butylamine in 5 ml abs. THF, the mixture was held for 10 min, cooled to 0°C, the solution of (Ia-d) in 5 ml abs. THF was added, and the mixture was held under the corresponding conditions (for mole ratios of reactants and reaction time, see Table 1). The mixture was treated with saturated aqueous NH_4Cl solution, extracted with ether, and the extract was dried over $MgSO_4$ and concentrated. The products were purified and analyzed (see Tables 1-4). Product (IVa) was identified with that described in [11].

General Technique of Oxidation of (IVc-d) with Perbenzoic Acid. To a solution of 0.5 g of (IVc, d) in 10 ml $CHCl_3$ at 0°C was added 15 ml of 0.7 N solution of $PhCO_3H$ in $CHCl_3$, the mixture was held for 16 h in a refrigerator and treated with a 10% aqueous solution of KI, and then with sodium thiosulfate until the violet color disappeared. The organic layer was separated, washed with 10% $NaHCO_3$ solution, with water, and then dried over $MgSO_4$. After concentrating the solution products (Vc, d) were obtained with almost quantitative yields (see Tables 2-4).

Silylation of o-Nitroaniline. All operations were carried out in an atmosphere of dry Ar. To a three-necked flask fitted with a mechanical stirrer, thermometer, dropping funnel, and reflux condenser was added 10 g (72.5 mmoles) o-nitroaniline in 100 ml abs. C_6H_6 and 31 ml (220 mmoles) abs. Et_3N, and at ~20°C with vigorous stirring 28 ml (220 mmoles) Me_3SiCl was slowly added by drops. The mixture was boiled for 6 h with continued stirring, then cooled, filtered, and the precipitate was washed with benzene; the filtrate was concentrated by evaporation, and the residue was distilled. The yield of (IIa) was 13.2 g (87%), bp 78°C at 0.45 mm. Treating (IIa) with methanol leads to the formation of Me_3SiOMe, bp 57°C at 760 mm, n_D^{22} 1.3678 (cf. [12]), and o-nitroaniline, mp 71°C (cf. [13]).

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SYNTHESIS AND PROPERTIES OF STABLE AROMATIC BIS(NITRILE OXIDES)

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UDC 542.91:547.631.3-31

A number of stable bis(nitrile oxides) based on dimesitylmethane and didurylmethane and their analogs in which two aromatic rings are joined by various bridging groups were synthesized. The thermal isomerization of the bis(nitrile oxides) to diisocyanates and the relative reactivities of the bis(nitrile oxides) in 1,3-dipolar cycloaddition to styrene were studied.

It is known that nitrile oxides readily undergo 1,3-dipolar cycloaddition [1, 2], which makes it possible to use bis(nitrile oxides) (BNO) as effective low-temperature polymer hardeners [3]. Up until now, only a few stable aromatic BNO based on mesitylene [4, 5], durene [6], anthracene [7], and aromatic sulfonyl derivatives [8] were known. The aim of the present research was to synthesize stable compounds with two aromatic rings, each of which contains a nitrile oxide group.

In [9] we described a number of dialdehydes in which two mesitylene or durene rings were linked by various bridging bonds. These dialdehydes were converted to the corresponding oximes, which are BNO precursors. The synthesis of nitrile oxides from aldoximes can be accomplished either via halogenation with subsequent dehydrochlorination of the resulting hydroximoyl chlorides or by direct oxidative dehydrogenation [1]. Both of these possibilities were realized in our research.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1398-1403, June, 1991. Original article submitted July 24, 1990.

0568-5230/91/4006-1238$12.50