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A Novel Reaction of 1-Aryl-2-(α,β-unsaturated)diazene 1-Oxides with Hydrogen Chloride

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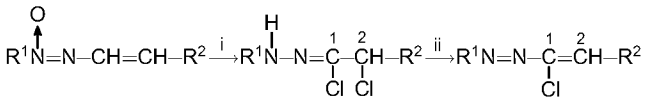
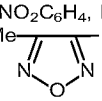
Treatment of 1-aryl-2-(2-R-ethenyl)diazene 1-oxides **1** with hydrogen chloride gives arylhydrazones of 2-chloro-2-R-acetylchloride, which yield 1-aryldiazenyl-1-chloro-2-phenylethenes after HCl elimination.

Recently[1] we described a facile synthesis of 1-aryl-2-(1-alkenyl)diazene 1-oxides **1** by reaction of 1-aryl-2-bromodiazene 1-oxides with alkenes followed by treatment with triethylamine. Some compounds of this class had been obtained previously[2] but their chemical behaviour had not been investigated. Here we wish to report that reaction of **1** with an ethereal solution of HCl gives chlorohydrazones **2** in practically quantitative yield (Table 1, Scheme 1).

Table 1 Preparation of chlorohydrazones **2** (Scheme 1).

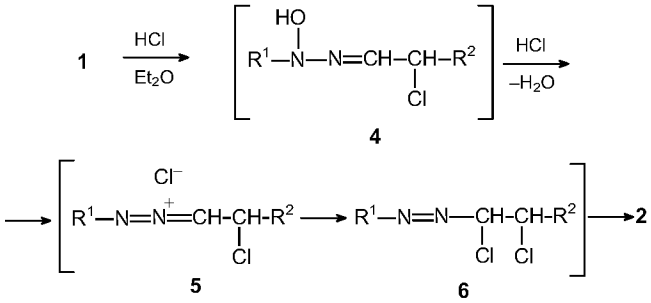
Compound **2**	Time of reaction/h	Yield (%)	M.p./°C
a	1	100	84–87 (decomp.)
b	1	100	72–74
c	3	95	95–96
d	1	95	100–108 (decomp.)
e	1	100	oil



a R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Ph
b R^1 = 2,4,6-$Cl_3C_6H_2$, R^2 = Ph
c R^1 = 4-$NO_2C_6H_4$, R^2 = Ph
d R^1 =  ; R^2 = Ph
e R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Bu^n

Scheme 1 *Reagents and conditions:* i, HCl, ether, 24 °C; ii, H_2O, MeCN, **3a**, m.p. 111–116 °C (1:2 mixture of *E*:*Z* isomers), after heating in MeCN for 15 h, m.p. 126–128 °C (one isomer); **3c**, m.p. 165–167 °C (one isomer).

The formation of **2** can be explained by assuming that in the first stage HCl adds to azoxyalkene **1** at the 1–5 position to give an intermediate **4** (Scheme 2). Protonation of **4** on oxygen then takes place and a molecule of water is eliminated to give cation **5** followed by addition of chlorine anion to yield azo compound **6**. Chlorohydrazones **2** are formed after



Scheme 2

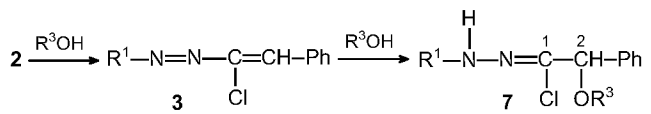
proton migration. The reason for the ready cleavage of the N–O bond is probably the stability of cation **5** in which the positive charge is located on the N atom. Some similar reactions exist in the literature. For example,[3] diazene oxides, which contain an active methylene fragment connected with the N atom, also give chlorohydrazones on treatment with HCl.

The structure of **2** was confirmed by ^1H and ^{13}C NMR spectroscopy (Table 2). The hydrazone fragment shows an NH signal in the ^{15}N NMR spectrum ($\delta \sim -250$ ppm, $^1J_{^{15}N-^1H} \sim 90$ Hz).

Chlorohydrazones **2** open up a new route to hitherto practically unknown azochloroalkenes **3**. When an acetonitrile solution was treated with water, **3** was precipitated as red (**3a**) or yellow (**3c**) crystals (Scheme 1).

Compound **3c** was formed as one isomer and **3a** as two isomers, but after heating (MeCN, 15 h) we obtained only one isomer. We suppose it to be the thermodynamically stable *E*-isomer in which the bulky substituents – Ph and Cl groups – are *trans* to each other.

Chlorohydrazones **2** are the precursors for chlorohydrazones which contain various functional groups at the α-position, *e.g.* compound **2** readily reacts with alcohols and carboxylic acids to give **7** in good yield (Scheme 3, Table 3).



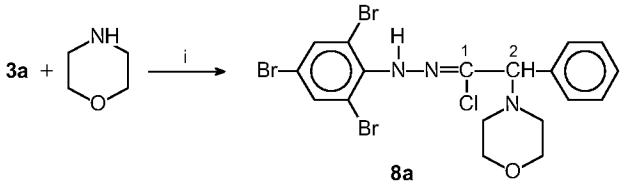
Scheme 3

Table 2 Selected NMR data for some new compounds (δ, ppm).

Substance	^{1}H NMR		^{13}C NMR		^{15}N NMR ($^1J_{^{15}N-^1H}$/Hz) (standard $MeNO_2$)
	C^2H	N–H wide	C^1	C^2	
2a	5.90	7.91	128.35	63.95	−246.80 (^{15}N–H, $J = 89$)
2b	5.86	7.90	128.50	63.85	−253.15 (^{15}N–H, $J = 90$)
2c	5.95	8.35	129.28	64.17	−241.97 (^{15}N–H, $J = 95$)
2d	5.83	8.70	128.35	63.90	−262.94 (^{15}N–H, $J = 94$)
2e	4.69(t)	7.90	129.11	62.99	
Z-**3a**[a]	7.57	–	136.57	136.86	
E-**3a**[a]	8.01	–	137.61	140.94	
3c	8.05	–	133.10	144.81	
7a	5.14	7.88	130.71	84.40	−247.35 (^{15}N–H, $J = 88.2$)
7b	5.26	7.88	131.34	82.60	−247.47 (^{15}N–H, $J = 88$)
7c	5.11	8.51	133.39	84.68	
7d	5.22	8.55	133.89	83.0	
7e	6.53	7.88	127.20	76.21	−246.85 (^{15}N–H, $J = 88.5$)
8a	4.30	7.85	130.93	76.20	

[a] A 1:2 mixture of *E*/*Z* isomers.

We suppose the reaction to proceed *via* intermediate azoalkene **3**. In any case, the isolated compound **3a** gave the same product as that formed from chlorohydrazone **2a**.



8a

Scheme 4 *Reagents and conditions:* i, 1,4-dioxane, 2 h, yield 55%, m.p. 144.5–146 °C.

To obtain chlorohydrazones containing an amino group at the α-position, it is best to carry out a reaction of amine with the preliminary isolated azoalkene **3** (Scheme 4).

All new compounds were characterized by ^{1}H NMR (300 MHz), ^{13}C NMR (75.43 MHz), IR and MS spectroscopy and elemental analysis; some of them additionally by ^{15}N NMR (30.42 MHz) spectroscopy (Table 2).

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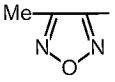
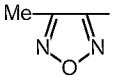
3 O. A. Luk'yanov, Yu. B. Salamonov, A. G. Bass, Yu. A. Strelenko and N. A. Karpenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 352 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, 294).

Table 3 Preparation of chlorohydrazones **7** (Scheme 3).

Substance	Reagent	Hydrazone **7**	R^1	R^3	Time of reaction/h	Yield (%)	M.p./°C
2a	MeOH	**7a**	$Br_3C_6H_2$	Me	0.5	90	81–82
3a	MeOH	**7a**	$Br_3C_6H_2$	Me	2.5	95	80–82
2a	EtOH	**7b**	$Br_3C_6H_2$	Et	4	95	79–80
3a	EtOH	**7b**	$Br_3C_6H_2$	Et	1	95	79–80
2d	MeOH	**7c**		Me	4	90	136–138
2d	EtOH	**7d**		Et	24	90	85–86
3a	AcOH	**7e**	$Br_3C_6H_2$	Ac	1	89	78–79

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