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SYNTHESIS OF MESOIONIC 3-ARYL(HETARYL)-1,2,3,4-OXATRIAZOL-5-ONES BASED ON N-ARYL-AND N-HETARYLHYDRAZONES OF BROMONITROFORMALDEHYDE

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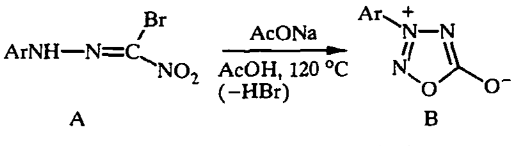
Dehydrobromination of N-arylhydrazones of bromonitroformaldehyde (at 20°C) in the presence of alkali and ammonium salts of strong mineral acids, HNO_3*, silica gel, and* Al_2O_3 *forms mesoionic 3-aryl-1,2,3,4-oxatriazol-5-ones (3-arylazasydnones). The effect of the electronic properties of the aryl substituent on the course of the reaction is evaluated. This evaluation is used to develop a general method for preparing 3-arylazasydnones with various substituents including novel 3-hetarylazasydnone derivatives of pyrazole, 1,2,4-triazole and pyridine. Aromatic electronic effects* (σ_I, σ_R, σ_m, σ_p) *of the mesionic 1,2,3,4-oxatriazol-5-on-3-yl moiety are determined by* ^{19}F *NMR. A scheme is proposed for the dehydrobromination of the bromonitroformaldehyde N-arylhydrazones that includes the intermediate N-aryl-C-(nitro)nitrilimines,* $ArN^{-}{-}N{=}C^{+}NO_2$*, with subsequent isomerization of the latter into 3-arylazasydnones.*

Mesoionic five-membered heterocyclic compounds have attracted attention [1-3] owing to their structural features and chemical reaction in addition to their valuable pharmacologic properties. The mesoionic 3-R-1,2,3,4-oxatriazol-5-ones (3-R-1,2,3,4-oxatriazolium-5-olates, 3-R-azasydnones), which exhibit antihypertensive activity [4], are especially interesting. Other types of therapeutic activity can be expected from 3-R-azasydnones [6] because they are capable to generate NO during biotransformations [5]. However, few examples of 3-R-azasydnones are known owing to their inaccessibility. Thus, 3-hetarylazasydnones were unknown until our studies.

Heating several bromonitroformaldehyde N-arylhydrazones (A) with sodium acetate in acetic acid produces compounds with an empirical formula and molecular weight consistent with the loss of HBr from the starting hydrazones A [7]. As it turned out, they are 3-arylazasydnones (B) and not 1,4-diaryl-1,4-dihydro-3,6-dinitro-1,2,4,5-tetrazines, as was reported previously [8].



Ar = 4-XC_6H_4 (X = H, Br, Cl, NO_2)

The N-aryl-C-(nitro)nitrilimine (C) should form by dehydrobromination of hydrazone A, as occurs with other hydrazonylhalogenides [9, 10] (see [7]). However, in this instance it for some reason isomerized into the azasydnone B:

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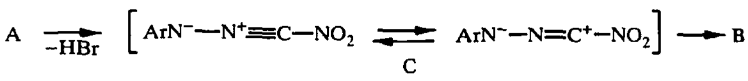
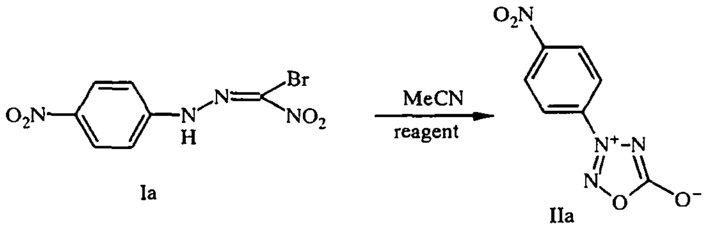


$$\mathrm{A} \xrightarrow[-\mathrm{HBr}]{} \underset{\mathrm{C}}{\left[\mathrm{ArN^{-}{-}N^{+}{\equiv}C{-}NO_2} \rightleftarrows \mathrm{ArN^{-}{-}N{=}C^{+}{-}NO_2}\right]} \longrightarrow \mathrm{B}$$

We decided to study in more detail the dehydrobromination of type A hydrazones by various reagents, as much as possible under milder conditions and using less nucleophilic reagents than NaOAc in order to avoid reaction paths for the conversion of A into B other than dehydrobromination and spontaneous rearrangement of nitrilimine C into azasydnone B. Such an arrangement has no analog in the chemistry of nitrilimines [9] and therefore should be studied separately.

In our opinion, a study of the dehydrobromination by various reagents of hydrozones A, which result from azo coupling of aryldiazonium salts with bromonitromethane [11], should enable a universal method for the preparation of 3-arylazasydnones B to be developed.

The action of various reagents on the hydrazones was studied using the 4-nitrophenylhydrazone of bromonitroformaldehyde (Ia) as an example. The hydrazone Ia (0.35 mmol) and the reagent (0.46 mmol) were stirred in CH_3CN (4 ml) at 20°C until the hydrazone had disappeared (according to TLC). In all instances where the reaction time is given, Ia was completely converted into known [7] 3-(4-nitrophenyl)azasydnone (IIa) (TLC, UV and IR data) in greater than 70% yield. Hydrazone Ia in CH_3CN solution does not spontaneously convert to IIa.



Ia

IIa

Expt. No.	Reagent	Reaction time for complete disappearance of starting hydrazone Ia and formation of azasydnone IIa
1	NH_4NO_3	15 min
2	NH_4NO_3 (10 mol. %)	1 h
3	KNO_3	1 h
4	HNO_3 (70%)	3 h
5	NH_4NO_3 + $(NH_2)_2CO$ (200 mol. %)	3 h
6	$NaNO_2$	30 min
7	CH_3COONa	15 min
8	$(NH_4)_2SO_4$	~48 h
9	$LiClO_4$	~48 h
10	$KMnO_4$*	20 min
11	$Na_2Cr_2O_7 \cdot 2H_2O$*	30 min
12	SiO_2 (silica gel)	~48 h
13	Al_2O_3 (neutr.)	~48 h
14	$NaHCO_3$	4,5 h
15	HBr (48%)	*[2]
16	NaN_3	*[3]
17	—	*[2]
18	Et_3N*[4]	3 h

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* Formation of azasydnone IIa is accompanied by its slow oxidation, which is finished after 24 h.

*[2] No reaction of hydrazone Ia is observed (after 48 h).

*[3] Extensive polymerization, azasydnone IIa is not formed.

*[4] The bromonitroformaldehyde 3-(4-chlorophenyl)hydrazone (Ib) in CH_3CN was used. The resulting 3-(4-chlorophenyl)azasydnone (IIb) was contaminated by resinous products. An analogous result (reaction finished after 3 h) was obtained under the same conditions in CH_2Cl_2.

Strong organic bases in an inert solvent promote the dehydrohalogenation of the hydrazonylhalides to generate the nitrilimides [9, 10]. For Ia, the loss of HBr with the formation of IIa occurs in the presence of anions of strong mineral acids (NO_3^-, SO_4^{2-}, ClO_4^-, MnO_4^-, $Cr_2O_7^{2-}$; Expt. Nos. 1, 3, 8-11), which have practically no basic properties and are weak nucleophiles (especially SO_4^{2-} and ClO_4^-). Moreover, the transformation of Ia into IIa occurs in the presence of HNO_3 (Expt. No. 4). This result is not due to acid catalysis because HBr has no effect on hydrazone Ia (Expt. No. 15). Such an effect of HNO_3 reveals the reason why catalytic amounts of NH_4NO_3 (Expt. No. 2) can be successfully used. During the dehydrobromination of Ia by NH_4NO_3, HNO_3 is formed along with NH_4Br and provides a source for NO_3^- ions.

The reaction in the presence of NH_4NO_3 also occurs with an excess of nitrosating agents trap, e.g., urea (Expt. No. 5), although the reaction is slower than in its absence (Expt No. 1). This may be due to formation of urea complex with NO_3^-.

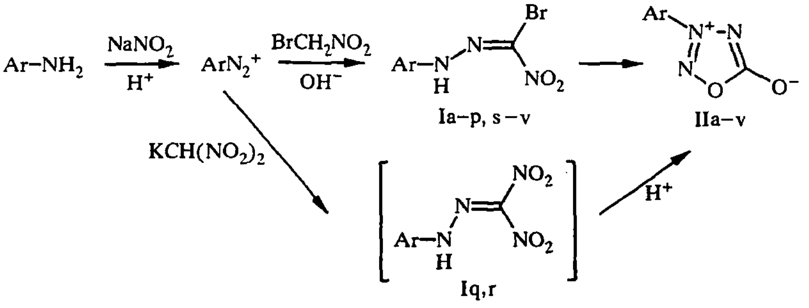
Hydrazone Ia is also dehydrobrominated by silica gel and neutral Al_2O_3 (Expt. Nos. 12 and 13) to form IIa. This apparently occurs on the surface. The reaction proceeds rather fast in the presence of moderate nucleophiles such as CH_3COO^- and NO_2^- (Expt. Nos. 6 and 7). However, IIa is not formed (Expt. No. 16) in the presence of NaN_3.

A strong acid is formed together with Br^- by the action of "nonbasic" anions on Ia. The acidity of the mixture gradually increases. However, acid is not essential for the reaction to proceed. The azasydnone Ia forms also in the presence of the weak base $NaHCO_3$ (Expt. No. 14).

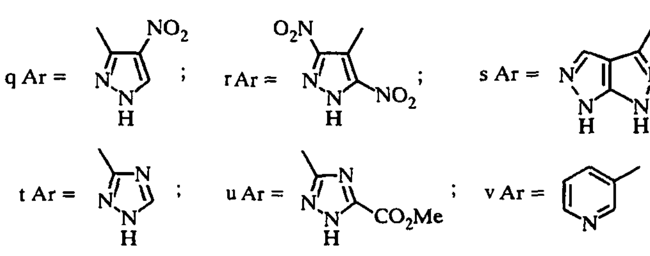
Using the bromonitroformaldehyde 3-(4-chlorophenyl)hydrazone (Ib) as an example, it was demonstrated that correspondent azasydnone IIb [7] was formed under those conditions that were used for the dehydrohalogenation of other types of hydrazonylhalides [9, 10], i.e., the use of Et_3N in CH_3CN or CH_2Cl_2 (Expt. No. 18). However, IIb in this case is contaminated with resinous products. Using Ib as an example it was also observed that IIb forms in ~70% yield by heating (100°C) a solution of Ib in dioxane–water (7:1) mixture. It was reported [12] that the nitroformic acid 4-chlorophenylhydrazide, $4\text{-}ClC_6H_4NHNHCONO_2$, was formed under similar conditions. However, we did not observe such a product. In our opinion, such a compound, if it would be formed, should be readily hydrolyzed at the $C(O)\text{–}NO_2$ bond under the reaction conditions.

Using NH_4NO_3 and alkaline nitrates as an example, the generality of the conversion of hydrazones A with various aryl substituents into the azasydnones B in the presence of "nonbasic" anions (at 20°C) was demonstrated. Instead of CH_3CN, DMF can be successfully used. The reaction also occurs in dioxane. However, the A → B

Scheme 1



I, II a Ar = $4\text{-}O_2NC_6H_4$; b Ar = $4\text{-}ClC_6H_4$; c Ar = Ph; d Ar = $4\text{-}MeOC_6H_4$;
e Ar = $3\text{-}FC_6H_4$; f Ar = $4\text{-}FC_6H_4$; g Ar = $2\text{-}CF_3C_6H_4$; h Ar = $3\text{-}CF_3C_6H_4$;
i Ar = $2\text{-}BrC_6H_4$; j Ar = $4\text{-}BrC_6H_4$; k Ar = $4\text{-}MeC_6H_4$; l Ar = $3\text{-}MeC_6H_4$;
m Ar = $3\text{-}MeOC_6H_4$; n Ar = $3\text{-}ClC_6H_4$; o Ar = $2\text{-}ClC_6H_4$; p Ar = $4\text{-}(CO_2H)C_6H_4$;



conversion is not observed (in the presence of NH_4NO_3) in acetone, ethanol and $CHCl_3$.

The electronic effect of substituents in the aryl ring on the A $\rightarrow$ B conversion rate in CH_3CN in the presence of NH_4NO_3 at 20°C was qualitatively studied. The time for complete conversion of hydrazones Ia,c,d into azasydnones IIa,c,d was used. Under identical conditions, Ia (Ar = 4-$NO_2C_6H_4$) converts in 15 min; Ic (Ar = Ph), 4 h, and Id (Ar = 4-$CH_3OC_6H_4$) - in 48 h. Thus, the rate increases with increasing electron-acceptor properties of the aryl moiety and decreases with increasing electron-donor properties.

The results enabled a general preparative synthesis of 3-aryl(hetaryl)azasydnones (IIa-v) to be developed. It consists of the reaction of bromonitroformaldehyde N-aryl(hetaryl)hydrazones (Ia-v) with NH_4NO_3 in CH_3CN or DMF or with $NaNO_3$ in DMF at 20°C (25-50% excess of salt) for several hours until the starting hydrazone Ia-v is completely reacted. It was reported [13] that hydrazones A (Ar = C_6H_5 and its derivatives) react with $NaNO_3$ in DMF (at 20°C) to give products with Br substituted on the nitrate group. However, we did not observe such products at all. The method enables the preparation of 3-arylazasydnones with various substituents on the phenyl ring. Azasydnones with hetaryl substituents, e.g., 3-hetarylazasydnones (derivatives with pyrazole, 1,2,4-triazole, pyridine, see Scheme 1, Tables 1 and 2, compounds IIq-v, and preliminary communications [14]) are synthesized for the first time.

The structures of the prepared azasydnones IIa-v were determined using multinuclear NMR, IR spectroscopy and mass spectrometry and were confirmed by elemental analysis. For known azasydnones, authentic samples were used for comparision (see Tables 1 and 2).

The spectral characteristics enabling reliable identification of IIa-v are as follows. A very strong band (often appearing as a doublet) is seen at ~1800 cm^{-1} ($C-O^-$) in the IR spectrum. The O^{17} NMR spectrum has a characteristic sharp signal with chemical shift ~215-220 ppm ($C-O^-$) and a broad signal at ~360-370 ppm (O_{ring}). The ^{13}C NMR has the $C-O^-$ signal at ~165 ppm. In the ^{14}N NMR spectrum, the $N_{(3)}$ signal appears at -80-(-95) ppm. Electron-impact mass spectra in all instances (except for Ip) exhibit a signal for $[M - NO]^+$.

The synthesis of IId (Ar = 4-$CH_3OC_6H_4$) demonstrated that in certain cases the azasydnone can be formed in the reaction mixture during the preparation of the hydrazone (Id) by azo coupling of the aryldiazonium salt with the bromonitromethane in acetic acid (see Experimental).

In addition to the bromonitroformaldehyde N-arylhydrazones, dinitroformaldehyde N-arylhydrazones, the reaction products of a diazonium salt with a dinitromethane salt (see [15]), can be used to prepare 3-arylazasydnones. We determined the conditions under which hydrazones of dinitroformaldehyde are not isolated but converted into azasydnones using IIq,r as examples (Scheme 1, Tables 1 and 2).

The chemical shifts in the ^{19}F NMR spectrum of IIe (Ar = 3-FC_6H_4) and IIf (Ar = 4-FC_6H_4) in $CDCl_3$ (Scheme 1, Table 2) in combination with the data for C_6H_5F (δ_{CFCl_3} = -117.33 ppm) in the same solvent and the literature data [16] (Eqs. 10, 22, 26 and 27 in that article) enable to determine electronic effects of the mesoionic 1,2,3,4-oxatriazo-5-on-3-yl moiety as a substituent on the aromatic ring. The aromatic induction constant $\sigma_I = 0.99$, the constant defining the resonance effect (conjugation effect) $\sigma_R = 0.13$, and the constants of the substituents in the *meta-* and *para-*positions of the benzene ring $\sigma_m = 0.98$ and $\sigma_p = 1.07$. The data suggest that this moiety has a very strong electron-accepting effect. The aromatic induction constant (σ_I) is one of the largest among neutral substituents [significantly greater than for NO_2 (0.64) and SO_2CF_3 (0.83)] and of the order of that for SO_2CN (0.99) (these σ-constants and those given later are obtained from ^{19}F NMR data and Table IV from previous work [16]). In our opinion, this indicates that $N_{(3)}$ has a marked onium character in the 3-arylazasydnones. However, the electron-accepting resonance effect of this group is not so great (by comparision σ_R for NO_2 is 0.16 and for SO_2CF_3 is 0.26) but significantly greater than for N^+Me_3 (σ_R = -0.08 [16]). To a certain extent, this is consistent with an aromatic azasydnone core.

The results obtained lead to the following conclusions.

1. The dehydrobromination of type A hydrazones in the presence of basicless anions of strong mineral acids as well as HNO_3 argue against the first step being the loss of a proton from the hydrazone NH fragment. The following dehydrobromination scheme can be proposed. The bromine atom is replaced by the "nonbasic" anion (ZO^-) during the reaction with type A hydrazones (probably through an addition-elimination mechanism). A powerful electron-acceptor on the hydrazonyl carbon atom, e.g., a nitro group, enhances this. Then, ZOH is eliminated to form the C-(nitro)nitrilimine C (Scheme 2).

TABLE 1. Properties of Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, % C	H	N	mp, °C (solvent for crystallization)	Yield, %
1	2	3	4	5	6	7
IIa	$C_7H_4N_4O_4$	—	—	—	168...169 (EtOH) (168...169 [7])	91 (A)
IIb	$C_7H_4ClN_3O_2$	—	—	—	137...138 (EtOH) (136...137 [4])	89 (B)
IIc	$C_7H_5N_3O_2$	—	—	—	86...87 (EtOH) (86...87 [7])	64 (B)
IId	$C_8H_7N_3O_3$	$\frac{49{,}69}{49{,}74}$	$\frac{3{,}58}{3{,}65}$	—	134...136 (EtOH)	48 (C)
IIe	$C_7H_4FN_3O_2$	$\frac{46{,}22}{46{,}40}$	$\frac{2{,}26}{2{,}23}$	$\frac{23{,}18}{23{,}20}$	89...90 (EtOH)	76 (A)
IIf	$C_7H_4FN_3O_2$	—	—	—	127...128 (EtOH) (122...123 [4])	74 (A)
IIg	$C_8H_4F_3N_3O_2$	$\frac{40{,}93}{41{,}56}$	$\frac{1{,}81}{1{,}74}$	—	74...76 (hexane)	53 (A)
IIh	$C_8H_4F_3N_3O_2$	$\frac{41{,}29}{41{,}56}$	$\frac{1{,}73}{1{,}74}$	—	67...68 (EtOH)	68 (A)
IIi*	$C_7H_4BrN_3O_2$	$\frac{34{,}35}{34{,}73}$	$\frac{2{,}02}{1{,}65}$	—	62...64 (hexane)	54 (A)
IIj	$C_7H_4BrN_3O_2$	—	—	—	154...155 (EtOH) (147...148 [7])	87 (B)

TABLE 1 (continued)

1	2	3	4	5	6	7
IIk	$C_8H_7N_3O_2$	—	—	—	99...100 (EtOH) (96...97 [4])	65 (B)
IIl	$C_8H_7N_3O_2$	$\frac{54,37}{54,24}$	$\frac{3,81}{3,98}$	—	70...71 (EtOH)	50 (A)
IIm	$C_8H_7N_3O_2$	$\frac{49,76}{49,74}$	$\frac{3,50}{3,65}$	—	67...68 (EtOH)	88 (B)
IIn	$C_7H_4ClN_3O_2$	$\frac{42,38}{42,55}$	$\frac{2,21}{2,04}$	—	51...52 (EtOH)	42 (A)
IIo	$C_7H_4ClN_3O_2$	$\frac{42,45}{42,55}$	$\frac{1,89}{2,04}$	—	67...68 (EtOH)	55 (A)
IIp	$C_8H_5N_3O_4$	$\frac{46,47}{46,38}$	$\frac{2,55}{2,43}$	—	200 (dec.) (EtOH)	72 (B)
IIq	$C_4H_2N_6O_4$	$\frac{24,20}{24,48}$	$\frac{1,05}{1,21}$	$\frac{42,40}{42,10}$	176...178 (dec.) (1,2-dichloroethane)	93 (A) 91 (D)
IIr	$C_4HN_7O_6$	$\frac{19,75}{20,08}$	$\frac{0,40}{0,91}$	$\frac{40,33}{40,87}$	147 (dec.)	60 (D)
IIs	$C_5H_3N_7O_2$	$\frac{31,09}{31,22}$	$\frac{1,55}{1,60}$	—	> 260	86 (A)
IIt	$C_3H_2N_6O_2$	$\frac{23,17}{23,37}$	$\frac{1,32}{1,30}$	$\frac{54,41}{54,55}$	194 (dec.)	73 (A)
IIu	$C_5H_4N_6O_4$	$\frac{28,30}{28,25}$	$\frac{1,89}{1,91}$	$\frac{39,62}{39,85}$	152...154 (dec.)	70 (A)
IIv	$C_6H_4N_4O_2$	$\frac{43,93}{43,90}$	$\frac{2,49}{2,46}$	$\frac{34,16}{34,14}$	98...99 (hexane)	72 (A)

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* Br: found 33.10%; calculated 33.06%.

TABLE 2. Properties of Synthesized Compounds

Com-pound	IR spectrum, ν, cm^{-1}	UV spectrum (in EtOH), λ$_{max}$, nm	NMR spectra, δ, ppm		
			^{1}H, DMSO-d$_6$	^{13}C* ($J_{C\text{-}F}$, Hz), CD$_3$CN	^{17}O, CD$_3$CN
1	2	3	4	5	6
IIa	1337, 1545 (NO$_2$) 1780, 1820 (C–O$^-$)	266	8,35 (2H, d); 8,55 (2H, d)	123,3 (C$_{(3,5)}$); 125,7 (C$_{(2,6)}$); 138,6 (C$_{(1)}$); 150,8 (C$_{(4)}$); 165,5 (C–O$^-$)	220,0 (C–O$^-$); 359,9 (O$_{cycl}$) 584,6 (NO$_2$)
IIb	1780, 1795 (C–O$^-$)	272	*^{2} 7,80 (2H, d); 8,15 (2H, d)		218,1 (C–O$^-$); 357,7 (O$_{cycl}$)
IIc	1775, 1795 (C–O$^-$)	267	7,75 (3H, m); 8,15 (2H, d)	121,2 (C$_{(2,6)}$); 130,2 (C$_{(3,5)}$); 133,8 (C$_{(4)}$); 165,8 (C–O$^-$)	217,3 (C–O$^-$); 355,6 (O$_{cycl}$)
IId	1775 (C–O$^-$)		3,90 (3H, m); 7,23 (2H, d) 8,05 (2H, d)	55,8 (CH$_3$); 115,2; 122,9 (C$_{(2,3,5,6)}$); 127,5 (C$_{(1)}$); 163,7 (C$_{(4)}$) 165,9 (C–O$^-$)	
IIe*^{3}	1800 (C–O$^-$)	265	*^{2} 7,45 (1H, t); 7,65 (1H, q) 7,86 (1H, d); 7,96 (1H, d)	*^{2} 109,0 (d, $^2J_{C\text{-}F}$ = 28,0, C$_{(4)}$; 116,8 (d, $^3J_{C\text{-}F}$ = 3,7, C$_{(5)}$) 121,1 (d, $^2J_{C\text{-}F}$ = 21,0, C$_{(2)}$); 131,9 (d, $^4J_{C\text{-}F}$ = 8,2, C$_{(6)}$); 135,5 (s, C$_{(1)}$) 162,7 (d, $^1J_{C\text{-}F}$ = 249, C$_{(3)}$); 165,1 (s, C–O$^-$)	*^{2} 217,8 (C–O$^-$) 360,1 (O$_{cycl}$)
IIf*^{4}	1782, 1805 (C–O$^-$)	270	7,60 (2H, d); 8,20 (2H, d)	*^{2} 117,5 (d, $^2J_{C\text{-}F}$ = 24,0, C$_{(3,5)}$; 123,5 (d, $^3J_{C\text{-}F}$ = 9,0, C$_{(2,6)}$) 130,8 (d, $^4J_{C\text{-}F}$ = 5,0, C$_{(1)}$); 164,5 (d, $^1J_{C\text{-}F}$ = 110, C$_{(4)}$); 167,2 (s, C–O$^-$)	*^{2} 216,1 (C–O$^-$) 356,2 (O$_{cycl}$)
IIg*^{5}	1800 (C–O$^-$)	270	7,80 (1H, m); 7,91 (2H, m) 8,05 (1H, m)	*^{2} 118,39 (q, $^3J_{C\text{-}F}$ = 3,9, C$_{(2)}$); 122,75 (q, $^1J_{C\text{-}F}$ = 272,9, CF$_3$) 124,25 (s, C$_{(6)}$); 130,47 (q, $^3J_{C\text{-}F}$ = 3,6, C$_{(4)}$); 131,29 (s, C$_{(5)}$) 133,18 (q, $^2J_{C\text{-}F}$ = 34,2, C$_{(3)}$); 135,13 (s, C$_{(1)}$); 164,99 (s, C–O$^-$)	*^{2} 217,8 (C–O$^-$) 364,9 (O$_{cycl}$)
IIh*^{6}	1770, 1812 (C–O$^-$)	260	8,00 (1H, t); 8,21 (1H, d) 8,43 (2H, t)	*^{2} 121,80 (q, $^1J_{C\text{-}F}$ = 273,7, CF$_3$); 125,70 (q, $^2J_{C\text{-}F}$ = 34,1, C$_{(2)}$) 127,19 (s, C$_{(6)}$); 128,46 (q, $^3J_{C\text{-}F}$ = 4,6, C$_{(3)}$); 131,77 (s, C$_{(1)}$); 133,78 133,86 (s, C$_{(4,5)}$); 165,26 (s, C–O$^-$)	*^{2} 219,2 (C–O$^-$) 359,2 (O$_{cycl}$)
IIi	1800 (C–O$^-$)	270	7,75 (2H, m); 8,05 (2H, m)		
IIj	1795 (C–O$^-$)	280	7,95 (2H, d); 8,05 (2H, d)		
IIk	1770, 1785 (C–O$^-$)	278	2,45 (3H, s); 7,55 (2H, d) 8,00 (2H, d)	20,5 (CH$_3$); 120,9 (C$_{(3,5)}$); 130,6 (C$_{(2,6)}$); 145,1 (C$_{(4)}$); 165,8 (C–O$^-$)	*^{2} 215,7 (C–O$^-$) 358,5 (O$_{cycl}$)
IIl	1785 (C–O$^-$)	275	2,47 (3H, s); 7,65 (2H, t) 7,90 (2H, t)		
IIm	1790 (C–O$^-$)	275	3,90 (3H, s); 7,40 (3H, m) 7,70 (1H, m)		
IIn		270	7,80 (1H, t); 7,90 (1H, d) 8,10 (1H, d); 8,15 (1H, s)		
IIo		275	7,75 (1H, t); 7,85 (2H, m) 8,08 (1H, d)		

TABLE 2 (continued)

1	2	3	4	5	6
IIp	1770, 1795 ($C{-}O^-$) 1690 ($C{=}O$)	268	8,20 (2H, d); 8,30 (2H, d)		
IIq*[7]	1790 ($C{-}O^-$), 1345 1540 (NO_2)		*[8] 9,15 (1H, s)	*[8] 129,2 ($C_{(4)}$); 133,2 ($C_{(5)}$); 136,3 ($C_{(3)}$); 165,9 ($C{-}O^-$)	225,2 ($C{-}O^-$); 369,6 (O_{cycl}) 597,9 (NO_2)
IIr*[9]	1770 ($C{-}O^-$), 1340 1560 (NO_2)			*[8] 106,4 ($C_{(4)}$); 146,0 ($C_{(3,5)}$); 165,4 ($C{-}O^-$)	225,2 ($C{-}O^-$); 370,6 (O_{cycl}) 595,8 (NO_2)
IIs	1780 ($C{-}O^-$)	290		110,6 ($C_{(3a)}$); 134,1 ($C_{(4)}$); 159,3 ($C_{(3)}$); 165,5 ($C{-}O^-$)	220,3 ($C{-}O^-$)
IIt	1785, 1815 ($C{-}O^-$)	263	9,00 (1H, s)	146,4 (C(5)); 165,7 ($C{-}O^-$)	221,0 ($C{-}O^-$); 363,9 (O_{cycl})
IIu*[10]	1790 ($C{-}O^-$) 1720 ($C{=}O$)	282	*[8] 4,05 (3H, s)	*[11] 53,4 (CH_3);148,2 ($C_{(5)}$); 152,6 ($C_{(3)}$); 156,4 ($\underline{C}OOCH_3$) 165,0 ($C{-}O^-$)	143,7 ($C\underline{O}OCH_3$) 219,3 ($C{-}O^-$); 365,2 (O_{cycl})
IIv	1780, 1807 ($C{-}O^-$)	265	*[12] 7,70 (1H, m); 8,42 (1H, d) 8,94 (1H, d); 9,28 (1H, s)	124,8 ($C_{(4)}$); 124,3 ($C_{(5)}$); 132,1 ($C_{(3)}$); 142,3 ($C_{(2)}$); 154,5 ($C_{(6)}$) 165,6 ($C{-}O^-$)	*[12] 218,8 ($C{-}O^-$) 361,4 (O_{cycl})

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* Spectra recorded with ^1H suppression.

*[2] In $CDCl_3$.

*[3] ^{19}F NMR spectrum ($CDCl_3$), -111.3 ppm.

*[4] ^{19}F NMR spectrum ($CDCl_3$), -106.8 ppm.

*[5] ^{19}F NMR spectrum ($CDCl_3$), -63.6 ppm.

*[6] ^{19}F NMR spectrum ($CDCl_3$), -60.7 ppm.

*[7] ^{14}N NMR spectrum [$(CD_3)_2CO$], -27.0 (NO_2), -87.0 ($N_{(3)}$sydnone).

*[8] In $(CD_3)_2CO$.

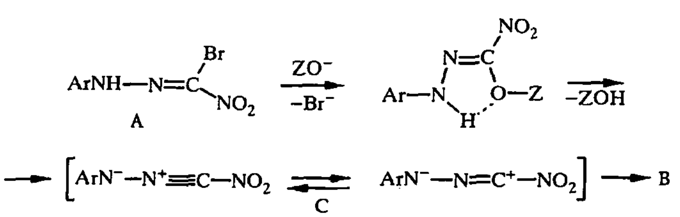
*[9] ^{15}N NMR spectrum [$(CD_3)_2CO$] -32.0 (NO_2), -93.2 ($N_{(3)}$sydnone), 8.22 ($N_{(2)}$sydnone), -113.5, -143.2.

*[10] ^{14}N NMR spectrum [$(CD_3)_2CO$] -83.2 ($N_{(3)}$sidnone).

*[11] In $(CD_3)_2CO$.

*[12] In CD_2Cl_2.

Scheme 2

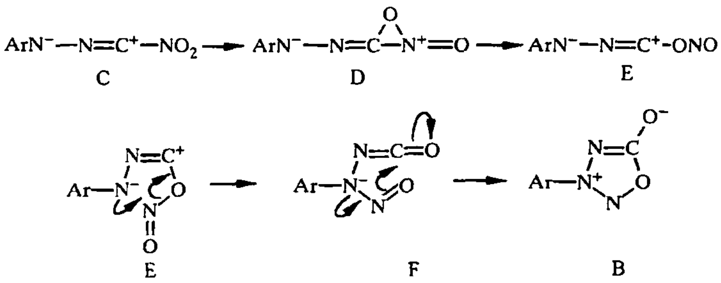


The difficulty of eliminating HN_3 during the dehydrobromination reaction in the presence of NaN_3 (Expt. No. 16) may possibly hinder the formation of IIa.

2. The fact that azasydnones B form from hydrazones A in the presence of various reagents with various acid-base properties, including "neutral" ones, and with very low nucleophilicity, is somewhat indicative of the dehydrobromination of A to form the N-aryl-C-(nitro)nitrilimine (C) (Scheme 2). This isomerizes directly into the 3-arylazasydnone (B). Other pathways for the destruction of A with subsequent cyclization of the cleavage products seems less probable in view of the results, especially with the use of "nonbasic" anions.

We propose that the N-aryl-C-(nitro)nitrileimines (C) isomerize into the 3-arylazasydnones (B) by the following scheme:

Scheme 3

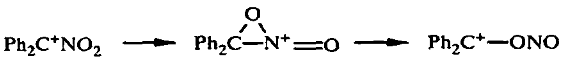


This scheme is based on the following literature analogies. The formation of 3-R-azasydnones from hydrazone derivatives requires N-nitrosation of the latter at the terminal N. The N-nitroso derivative formed is readily cyclized into a 3-R-azasydnone by nucleophilic addition of the oxygen atom of the N-nitroso group to the carbon atom of the C=N bond, for example [4]:

$$ArNH{-}N{=}C(SO_3H)_2 \xrightarrow{HNO_3} ArN(NO){-}N{=}C(SO_3H)_2 \xrightarrow[-2H_2SO_3]{H_2O} B$$

In our instance (Scheme 3), intramolecular nitrosation of the nucleophilic nitrogen atom in the zwitter ion E with formation of intermediate F is proposed. This then cyclizes by the known path into azasydnone B.

The nitro group must isomerize into a nitrite group (C → E) in order to form the zwitter ion E. This process is very facile if the nitro group is located on the carbonium center. For example, the isomerization



occurs rapidly even at -40°C, despite the stabilization of the carbonium ion by the two phenyl substituents. The reaction is proposed [17] to go through a three-membered intermediate that corresponds to intermediate D in Scheme 3. A quantum-chemical calculation indicates that the $(CH_3)_2C^+{-}NO_2 \rightarrow (CH_3)_2C^+{-}ONO$ isomerization proceeds unhindered through the three-membered intermediate [18]. A nonempirical quantum-chemical calculation of each step of the proposed scheme for the C → B isomerization (Scheme 3) confirms that it is valid. These data will be published separately.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument; ^{13}C, ^{14}N, ^{15}N, and ^{17}O NMR spectra, on a Bruker AM-300 instrument. Chemical shifts are given relative to TMS (^{13}C and ^1H), CH_3NO_2 (^{14}N and ^{15}N), $CFCl_3$ (^{19}F), and H_2O (^{17}O). Strong-field shifts are assigned a minus value. IR spectra were taken on a Specord-M-80 instrument in KBr pellets. UV spectra were recorded on a Specord UV-Vis instrument. The course of the reactions and the purity of the compounds were monitored using TLC on Silufol UV-254 plates. Bromonitromethane [19], the potassium salt of dinitromethane [20], 3-amino-4-nitropyrazole [21], 4-amino-3,5-dinitropyrazole [22], and 3-aminopyrazolo[3,4-*c*]pyrazole [23] were synthesized by the literature methods. The remaining starting materials are commercially available. The arylhydrazones of bromonitroformaldehyde were prepared by the literature procedure [12]. They were used further without purification.

A. General Method of Synthesis of 3-Arylazasydnones in CH_3CN (IIa,e-i,l,n,o,q,s-v). Solution or suspension of hydrazone Ia,e-i,l,n,o,q, or Is-v (2.5 mmol) in CH_3CN (10 ml) was treated with NH_4NO_3 (3.5 mmol) under stirring at 20°C. Stirring was continued until the starting hydrazone completely disappeared (3-10 h). The precipitate was filtered off. The filtrate was evaporated to dryness. The solid was recrystallized from the appropriate solvent (Table 1).

B. General Method of Synthesis of 3-Arylazasydnones in DMF (IIc,j,k,m,p). Solution or suspension of hydrazone Ic,j,k,m or Ip (4 mmol) in DMF (20 ml) was treated with $NaNO_3$ (6 mmol) under stirring at 20°C. Stirring was continued until the starting hydrazone completely disappeared (3-10 h). Water was added. The precipitate was filtered off, washed with water, dried in a vacuum desiccator over P_2O_5, and recrystallized from the appropriate solvent (Table 1).

C. Synthesis of 3-(4-Methoxyphenyl)azasydnone IId. Solution of *p*-anisidine (0.62 g, 5 mmol) in AcOH (10 ml) was treated with portions of $NaNO_2$ (0.38 g, 5.5 mmol) at 15°C. After all $NaNO_2$ was added, the mixture was stirred for 15 min. Then, CH_2BrNO_2 (0.7 g, 5 mmol) was added. Stirring was continued for 3 h at 20°C. The mixture was poured into cold water (30 ml). The precipitate was filtered off, washed with water, dried in air and recrystallized from EtOH. Yield 0.46 g (48%) of IId.

D. Synthesis of 3-Hetarylazasydnones IIq and IIr Using Potassium Salt of Dinitromethane. $KC(NO_2)_2H$ (2 mmol) was added by small portions to stirred solution of diazopyrazole [22, 24] (1 mmol) in water (15 ml) at 3-5°C. Stirring was continued for 1 h. The mixture was acidified with 20% H_2SO_4 until pH = 1. The precipitate (IIq) was filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. Azasydnone IIr was isolated by acidifying the reaction mixture and extracting with ether (3×10 ml). The ether extracts were dried over $MgSO_4$. The solvent was evaporated. The solid was recrystallized from the appropriate solvent (Table 1).

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REFERENCES

1. W. D. Ollis and C. A. Ramsden, *Advances in Heterocyclic Chemistry*, Academic Press, New York and London (1976), Vol. 19, p. 3.
2. V. G. Yashunskii and L. E. Kholodov, *Usp. Khim.*, **49**, 54 (1980).
3. V. G. Yashunskii and V. V. Ogorodnikova, *Khim. Geterotsikl. Soedin.*, No. 3, 291 (1981).
4. M. O. Lund, L. B. Kier, R. A. Glennor, and J. L. Egle, *J. Med. Chem.*, **25**, 1503 (1982).
5. K. L. Rehse and P. Koenig, *Arch. Pharm.*, **328**, 137 (1995).
6. V.G. Granik, S. Yu. Ryabov, and N. B. Grigor'ev, *Usp. Khim.*, **66**, 792 (1997).
7. M. N. Martynov, M. S. Pevzner, N. A. Smorygo, and N. M. Serebryakova, *Khim. Geterotsikl. Soedin.*, No. 12, 1682 (1981).
8. L. S. Pupko, A. I. Dychenko, and P. S. Pel'kis, *Khim. Geterotsikl. Soedin.*, No. 4, 759 (1969).
9. A. Padwa (ed.), *1.3-Dipolar Cycloaddition Chemistry*, Wiley, New York (1984), Vols. 1 and 2.
10. A. S. Shavali and C. Parkanyi, *J. Heterocycl. Chem.*, **17**, 833 (1980).
11. L. S. Pupko, G. A. Lanchuk, and A. I. Dychenko, *Ukr. Khim. Zh.*, **29**, 610 (1963).

12. A. I. Dychenko, L. S. Pupko, and P. S. Pel'kis, *Zh. Org. Khim.*, **10**, 2229 (1974).
13. A. I. Dychenko and P. S. Pel'kis, *Ukr. Khim. Zh.*, **45**, 451 (1979).
14. S. A. Shevelev, I. L. Dalinger, V. I. Gulevskaya, and T. I. Cherkasova, *Khim. Geterotsikl. Soedin.*, No. 7, 1002 (1997).
15. S. Hünig and O. Boes, *Liebigs Ann. Chem.*, **579**, 28 (1953).
16. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91**, 165 (1991).
17. G. A. Olah, G. K. S. Prakash, M. Arvanghi, V. V. Krishnamurty, and S. C. Narang, *J. Am. Chem. Soc.*, **106**, 2378 (1984).
18. O. S. Chizhov, V. I. Kadentsev, G. G. Palmbach, K. Ia. Burstein, and S. A. Shevelev, *Org. Mass Spectrom.*, **13**, 611 (1978).
19. B. R. Fishwick, D. K. Rowles, and C. J. M. Stirling, *J. Chem. Soc. Perkin Trans. I*, No. 7, 1171 (1986).
20. I. V. Tselinskii, and V. K. Krylov, *Zh. Org. Khim.*, **9**, 2474 (1973).
21. S. A. Shevelev, V. M. Vinogradov, I. L. Dalinger, and T. I. Cherkasova, *Izv. Akad. Nauk, Ser. Khim.*, No. 11, 1949 (1993).
22. I. L. Dalinger, T. I. Cherkasova, and S. A. Shevelev, *Mendeleev Commun.*, No. 2, 58 (1997).
23. A. Deeb, M. El-Mobayed, A. N. Essawy, A. A. El-Hamid, and A. M. A. El-Hamid, *Collect. Czech. Chem. Commun.*, **55**, 728 (1990).
24. N. V. Latypov, V. A. Silevich, P. A. Ivanov, and M. S. Pevzner, *Khim. Geterotsikl. Soedin.*, No. 12, 1649 (1976).