Tandem pseudopericyclic processes in the cyclization of α-diazonitriles to 5-Halo-1,2,3-triazoles. Scope and limitations†

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Dedicated to Professor Albert Padwa on the occasion of his 65th birthday
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Abstract
A series of α-carbonyl diazoacetonitriles has been synthesized and subjected to reaction with hydrogen halides. The scope and limitations of this reaction for preparing 5-halo-1,2,3-triazoles have been determined. The experimental energy of this cyclization is 15–20 Kcal mol^{-1}. A mechanism of this reaction consists of two steps—addition of HHal to α-carbonyl diazonitriles via a pseudopericyclic group transfer reaction leads to formation of intermediate α-diazo-haloimines which in subsequent hetero-electrocyclic reactions afford 5-halo-1,2,3-triazoles. Indeed, the cyclization of α-carbonyl diazonitriles is a series of tandem pseudopericyclic processes.

Keywords: α-Carbonyl diazoacetonitriles, 5-halo-1,2,3-triazoles, tandem pseudopericyclic processes

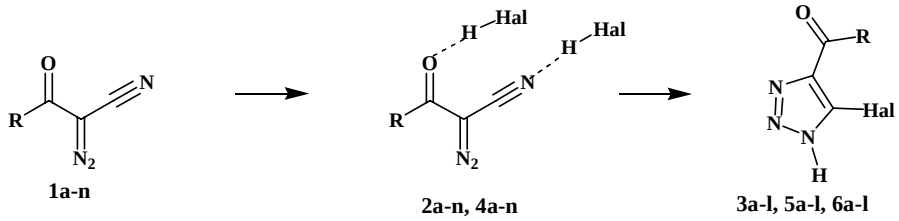
Introduction

The reaction of α-diazonitriles with hydrogen halides [2] is a good alternative to the method of synthesis of 5-halo-1,2,3-triazoles based on the Sandmeyer reaction of 5-diazo-1,2,3-triazoles with copper halides in hydrochloric acid.[3] The 5-halo-1,2,3-triazoles were then used in the synthesis of riboside derivatives that are of great interest as potential biologically active compounds, owing to their similarity to components of nucleic acid metabolism. Despite of the synthetic value of the reaction of diazonitriles with hydrogen halides it has been described for very few examples.[4–6] The mechanism, scope and limitations of this reaction have not been determined so far.

To extend these reactions to the synthesis of new 5-halo-1,2,3-triazoles, we have carried out a systematic study of the reactions of a series of diazo-acetonitriles (DAN) having a variety of substituents at the α- position, in various conditions.

Results and Discussion

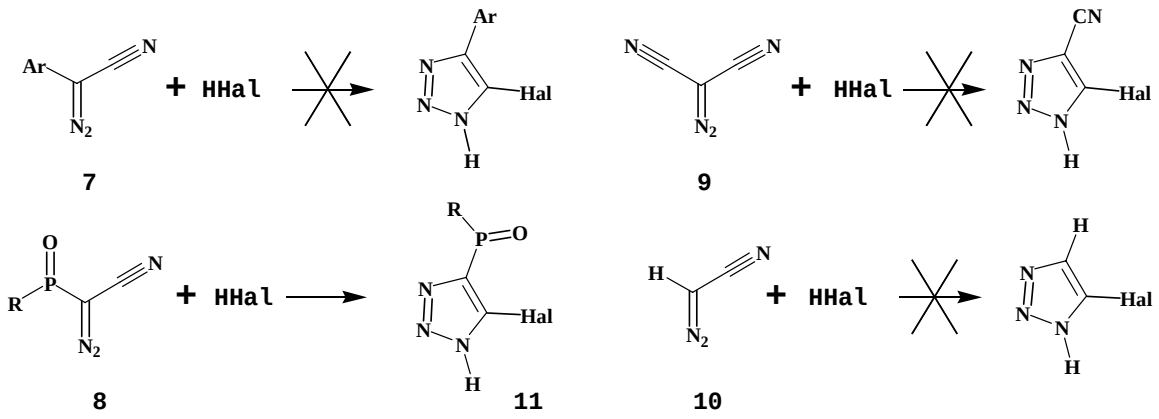
The reaction of DAN with hydrogen chloride, hydrogen bromide, or hydrogen iodide in various organic solvents leads to 5-halo-1,2,3-triazoles in very good yields.[5] We now show that the use of a non-polar solvent leads initially to formation of adducts **2a–n,** and **4a–n**, of DAN and hydrogen halides in the ratio of 1:2, which could be isolated as solid substances. These adducts have been found to be very sensitive to moisture. The treatment of the adducts **2- and 4a–n** with water leads easily to the starting DAN. We have found that the adducts **2-, and 4a–n** could be transformed into the 5-halo-1,2,3-triazoles **3, 5, 6** under heating in the solid state. The structures of the 5-halo-1,2,3-triazoles were confirmed by the synthesis of 5-chloro-1,2,3-triazole-4-carboxamide by the Sandmeyer reaction from 5-diazo-1,2,3-triazole-4-carboxamide and copper chloride.[3]



R = NH_2 (a); NHMe (b); NHC_6H_{11}-cyclo (c); NHPh (d); NHC_6H_4OMe-4 (e); NHC6H4Me-4 (f); NHC_6H_4Br-4 (g); Oet(h); Me (i); Ph (j); C_6H_4Ome-4 (k); C_6H_4Me-4 (l); CF_3(m); quinolinyl-2 (n)
Hal = Cl (2,3), Br(4,5), I (6)

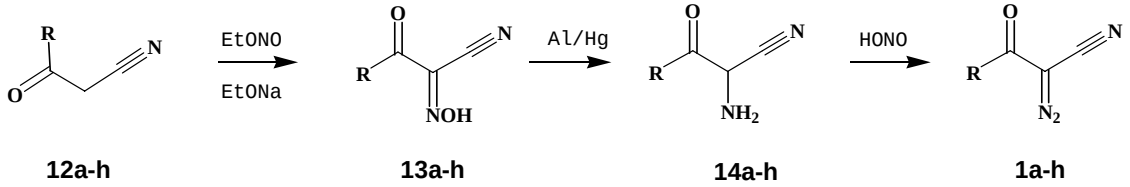
Scheme 1

To expand the scope of this reaction for the preparation of a series of 5-halo-1,2,3-triazoles we have carefully studied the behavior in this reaction of amides and esters of the 2-diazo-2-cyanoacetic acid derivatives **1a**–**h**, diazoketones **1j**–**n**, the 2-aryl-2-diazoacetonitriles **7**, 2-phosphonyl-2-diazoacetonitrile **8**, diazomalononitrile **9,** and the parent DAN **10**.



Scheme 2

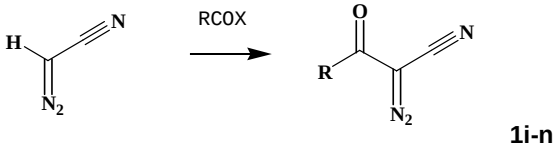
The compounds **1a–h** were prepared by a three-step process from the active methylene compounds **12** by nitrosation, either in water with sodium nitrite and hydrochloric acid or in alcohol with ethyl nitrite followed by reduction of the 2-oxyimino derivatives, **13**, formed with aluminum amalgam and treatment of the 2-aminoacetonitriles, **14,** with sodium nitrite in dilute hydrochloric acid. The final products **1a–h** were prepared in 20–30% overall yields (Scheme 3).



R = NH_2 (a); NHMe (b); NHC_6H_{11}-cyclo (c); NHPh (d); NHC_6H_4OMe-4 (e); NHC_6H_4OMe-4 (f); NHC_6H_4Br-4 (g); OEt(h)

Scheme 3

Compounds **1j–n** were prepared in one step from DAN by acylation with acyl chlorides or anhydrides (Scheme 4).



X = Cl or RCO

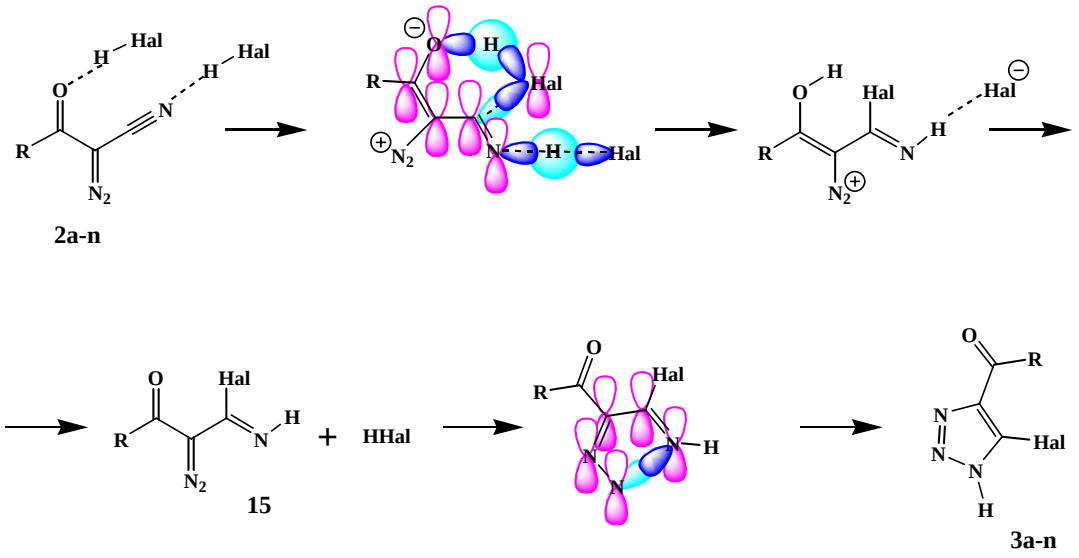
R = Me (i); Ph (j); C_6H_4OMe-4 (k); C_6H_4Me-4 (l); CF_3 (m); quino linyl1-2 (n)

Scheme 4

We have found that diazomalononitrile, **9,** and DAN, **10,** as well as its α-aryl derivatives, **7,** do not react with hydrogen halides under these conditions. Instead, the amides and ester of 2-diazo-2-cyanoacetic acid **1a**–**h**, diazoketones **1j**–**l**, and 2-phosphonyl-2-diazoacetonitrile **8** react easily with hydrogen halides to form the 5-halo-1,2,3-triazoles **3-, 5-,** and **6-a**–**l** and the 5-halo-4-phosphonyl-1,2,3-triazoles **11** in 90–99% yield. Thus, this reaction is limited to diazo compounds bearing carbonyl or phosphonyl groups at the α-position.

It is interesting to note that all of the diazo compounds that were transformed to 5-halo-triazoles were able to form solid adducts with hydrogen halides which subsequently underwent heterocylization in the solid state. The appearance of hydroxy bond-stretching at 2500–3100cm-1, the reduction in intensity of valence stretching of the cyano group, and the long-wave shift of the carbonyl band by about 50–90 cm^{-1} in the IR spectra of adducts **2a**–**l** in comparison with the parent diazonitriles indicate that the molecules of hydrogen halides are bound to the oxygen atom of the carbonyl-, and the nitrogen atom of cyano groups. We have found for diazoketones that if the shift of the carbonyl band in the IR of adducts is less than 50 cm^{-1} then the reaction would not occur. Thus, adducts of the diazoketones 2-, and 4-m and –n, in contrast to the other compounds **2-, and 4a-l,** could not be transformed into the 5-halo-1,2,3-triazoles, **3-**, and **5-m** and **-n**.

Using all these facts we can conclude that intramolecular assistance of the carbonyl (or phosphonyl) group to the addition of H-Hal to the cyano group is necessary for the reaction to take place of DAN with hydrogen halides leading to 5-halo-1,2,3-triazoles.



Scheme 5

We have studied the kinetics of cyclization of the diazonitriles 1a–l in a solution of hydrogen chloride in ethanol into the 5-chloro-1,2,3-triazoles 3a–l, and the solid-phase cyclization of adducts 4 into the 5-bromo-1,2,3-triazoles, **5**. We found that the cyclization in solution is a first-order reaction for the diazo compounds 1, and second-order for HCl. The activation energy for

the transformation of DAN into 5-halo-1,2,3-triazoles has been determined by kinetic study as 18–24 Kcal mol^{-1} in EtOH solution, and 15–18 Kcal mol^{-1} in the solid state (Table 1). It has also been shown that the introduction of electron- donating substituents in the phenyl ring of the diazoketones increases the rate of this heterocyclization.

Table 1. Kinetic data on cyclization of diazo compounds **1** and adducts **4** to triazoles **3**

Comp.	$k*10^3$, M^{-1} c^{-1}			$\Delta H^{\neq}$, Kcal mol^{-1}	$\Delta S^{\neq}$, cal mol^{-1} K^{-1}
	At 303 K	At 313 K	At 323 K		
1a	0.082±0.002	1.07±0.02	12.7±0.10	20.8±0.2	53.7±0.3
1b	0.014±0.002	0.214±0.008	2.55±0.08	21.8±0.2	55.5±0.3
1c	0.0018±0.0003	0.029±0.003	0.398±0.009	22.5±0.3	56.0±0.4
1d	0.523±0.004	6.87±0.04	8.02±0.05	20.8±0.2	55.3±0.4
1e	0.189±0.003	2.36±0.03	24.4±0.03	20.4±0.2	53.1±0.3
1f	0.128±0.005	1.63±0.02	17.8±0.02	20.5±0.2	53.1±0.5
1g	0.018±0.001	0.24±0.01	2.80±0.05	20.7±0.2	52.1±0.5
1h	0.329±0.003	3.82±0.04	38.1±0.03	19.8±0.2	51.6±0.5
1i	0.512±0.006	4.89±0.06	42.1±0.2	18.2±0.3	46.7±0.5
1j	0.387±0.003	4.08±0.05	35.2±0.5	19.0±0.2	49.1±0.4
1k	0.814±0.008	6.88±0.08	52.6±0.8	17.2±0.5	43.8±0.5
1l	0.491±0.007	4.57±0.05	38.9±0.8	18.0±0.3	47.9±0.2
4a	0.061±0.005	0.568±0.005	4.5±0.3	18.0±0.8	46.1±0.4
4b	0.033±0.003	0.327±0.006	2.8±0.2	18.4±0.5	46.9±0.2
4h	0.094±0.003	0.727±0.011	5.1±0.2	16.4±0.8	41.2±0.3
4i	0.111±0.006	0.775±0.006	4.8±0.1	15.6±0.5	38.7±0.2
4j	0.139±0.006	0.932±0.008	5.8±0.2	15.3±0.8	37.9±0.2
4k	0.122±0.005	0.791±0.005	4.6±0.3	15.0±0.6	36.8±0.8
4l	0.118±0.006	0.773±0.005	4.6±0.5	15.1±0.5	37.1±0.2

It was proposed that diazoimidoyl chlorides **9** are intermediates in the transformation of DAN derivatives upon heating with hydrogen halides to 5-halo-1,2,3-triazoles.[2] It is known that *cis*-addition of hydrogen halides to the cyano group is forbidden by the Woodward–Hoffmann rules, and the activation energy for this reaction is about 57 Kcal.[7]

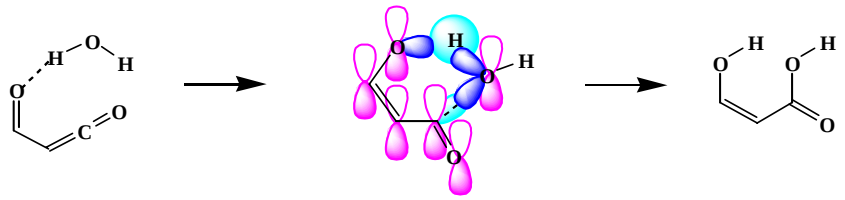
Why does the addition of hydrogen halides to the cyano group of DAN occur so easily?

It is assisted by hydrogen bonding of HHal with the carbonyl or phosphonyl group and presumably occurs via a pseudopericyclic mechanism.[8–12] The term *pseudopericyclic reactions* was introduced in Lemal[13] and Snyder[14] reports. According to these, *a pseudopericyclic reaction is a concerted transformation in which primary changes in bonding compass a cyclic array of atoms, at one (or more) of which non-bonding and bonding atomic orbitals interchange roles*. More lately, L. Burke,[15,16] D. Birney,[8–10,17–23] V. Bakulev and W. Fabian[25–30] have used the idea

of pseudopericyclic reactions in their work. Following these works, one can make generalizations for this type of reactions:

other type of symmetry;
- lower (or zero) activation energy;
- planarity;
- higher polarity of the transition state;
- and, there are reactions with one or more orbital disconnections in a closed loop of interacting orbitals.

Birney and his co-workers [9,17–20] in a series of papers have extensively studied pseudopericyclic reactions with two disconnections. It was shown that the similar process of the addition of water to formylketene (Scheme 6) has low activation energy (6.3 Kcal mol^{-1}).



Scheme 6

This process and the addition of hydrogen halides to the cyano group of α-carbonyl diazonitriles is similar and is consistent with the group-transfer type of pseudopericyclic reactions. In contrast to classic pericyclic group-transfer reactions, both these π-conjugated heteroatomic systems have the orbitals lying in the plane of molecule and new σ-bonding takes place from these orbitals rather than from π-orbitals.

The intermediate diazoimine **15** can cyclize to 1,2,3-triazoles **1** via two different mechanisms: *electrocyclic*, where the new N–N σ-bond occurs from the terminal orbitals of π-systems, and *heteroelectrocyclic*, where a new N–N σ-bond occurs from orbitals that are orthogonal to the π-system. In our previous work [24,28,30] we showed that the cyclization of diazoimines into 1,2,3-triazoles goes via the *heteroelectrocyclic* mechanism without rotation of the terminal bonds of the π-conjugated systems, and has a low energy of activation (in the range 8.8–12.2 The classic *electrocyclic* route for these systems has a higher activation energy (about 21.9–26.0 Kcal mol-1).

The experimental energies of cyclization of the diazo compounds, **1**, and adduct **4** (Table 1) are 17–22, and 15–18 Kcal mol^{-1}. We can propose that this cyclization occurs via two steps. The first step is the addition of HHal to α-carbonyl-diazonitriles *via a pseudopericyclic group-transfer reaction to form intermediate α-diazo haloimines* **15**, and the second step is the

cyclization of **15** to 5-halo-1,2,3-triazoles *via the hetero-electrocyclic mechanism*. Therefore, the cyclization of α-carbonyl-diazonitriles is a tandem of *pseudopericyclic* processes.

Conclusions

General Procedures. The scope and limitations have been determined for the reaction of DAN derivatives with hydrogen halides leading to a variety of 5-chloro-, 5-bromo-, and 5-iodo-1,2,3-triazoles. This reaction is limited to diazo compounds bearing groups at the α-position that can form hydrogen-bonds with hydrogen halides and thus assist their addition to the cyano groups of the DAN derivatives. The mechanism of this new reaction includes the addition of two molecules to one molecule of α-carbonyl- (or α-phosphonyl) DAN, the carbonyl- (or phosphonyl-) function- assisted addition of HHal to the cyano group as a *pseudopericyclic* process, and *hetero-electrocyclization* of the intermediate diazo-imidoyl halides to give the final 5-halo-1,2,3-triazoles.

Experimental Section

General Procedures. NMR chemical shifts are given in δ units, and were recorded in d_6-DMSO solution with a Bruker WH-250 spectrometer at 250 MHz; IR spectra in KBr were recorded using a UR-20 spectrometer. Mass-spectroscopy was performed on a Finnigan MAT-212 instrument using the direct inlet system, with electron energy 70eV, source temperature 180°C. All reaction mixtures and the products were examined by TLC on DC-Plastikfolen Kieselgel-60 F 254 plates. UV spectra were measured in EtOH. Melting points are uncorrected. 1H NMR
The syntheses of the diazo compounds **1-a,-b,-h**, 5-halo-1,2,3-triazoles **3-a,-b,-h** were reported previously. DAN,[31] 2-phosphonyl-2-diazoacetonitrile[6] and 5-halo-4-phosphonyl-1,2,3-triazole[6] were prepared as described.

2-Hydroxyiminoacetonitriles 13a–h. General procedure
Sodium ethoxide (0.68 g, 0.1 mol) was added to a suspension of 0.1 mol 2-cyanoacetamides **12a–h** in 150 mL ethanol. The solution was cooled to 0°C and 10 mL (0.12 mol) ethyl nitrite was added. After stirring for 1 h, 10 mL HCl was added. The precipitate was filtered and washed (hot ethanol). The filtrate was concentrated and cooled. The product was filtered, crystallized from ethanol and dried.
***N-cyclo*-Hexyl-2-amino-2-cyano-2-hydroxyimino-acetamide (13c).** Yield, 78%, white crystals, m.p. 210°C. IR spectrum/cm^{-1}, 3350, 2960, 2870, 2225 (CN), 1665 (CO). ^{1}H NMR (ppm), 8.21 (1H, br. s, NH), 2.5– 3.1 (1H, m, CH), 0.7–2.0 (10H, m, C_5H_{10}). Found, C, 55.4; H, 6.7; N, 21.5. $C_9H_{13}N_3O_2$ requires C, 55.4; H, 6.7; N, 21.5%.

***N*-Phenyl-2-cyano-2-hydroxyimino-acetamide (13d).** Yield, 81%, white crystals, m.p. 230°C. IR /cm^{-1}: 3340, 3232, 3027, 2865, 2250 (CN), 1680 (CO). ^{1}H NMR (ppm), 9.98 (1H, s, NH), 8.1–6.8 (5H, m, Ph). Found, C, 57.2; H, 3.8; N, 22.4. $C_9H_7N_3O_2$ requires C, 57.1; H, 3.7; N, 22.2%.

***N*-(*p*-Methoxyphenyl)-2-cyano-2-hydroxyimino-acetamide (13e).** Yield, 73%, white crystals, m.p. 218°C. IR /cm^{-1}: 3350, 3140, 2980, 2860, 2240 (CN), 1680 (CO). ^{1}H NMR (ppm), 9.40 (1H, s, NH), 7.61 (2H, d, J=9 Hz, ArH), 6.88 (2H, d, J=9 Hz, ArH), 3.77 (3H, s, OMe). Found, C, 54.5; H, 4.2; N, 19.0. $C_{10}H_9N_3O_3$ requires C, 54.8; H, 4.1; N, 19.1%.

***N*-(*p*-Methylphenyl)-2-cyano-2-hydroxyimino-acetamide (13f).** Yield, 77%, white crystals, m.p. 244°C. IR /cm^{-1}: 3335, 3140, 2980, 2860, 2240 (CN), 1680 (CO). ^{1}H NMR (ppm), 10.26 (1H, s, NH), 7.55 (2H, d, J=8 Hz, ArH), 7.12 (2H, d, J=8 Hz, ArH), 2.26 (3H, s, Me). Found, C, 59.4; H, 4.5; N, 21.0. $C_{10}H_9N_3O_2$ requires C, 59.1; H, 4.5; N, 20.7%.

***N*-(*p*-Bromophenyl)-2-cyano-2-hydroxyimino-acetamide (13g).** Yield, 71%, white crystals, m.p. 245°C. IR /cm^{-1}: 3300, 3210, 3155, 3005, 2840, 2235 (CN), 1650 (CO). ^{1}H NMR (ppm), 10.51 (1H, s, NH), 7.85–7.40 (4H, m, C_6H_4). Found, C, 40.4; H, 2.3; N, 16.6. $C_{10}H_6BrN_3O_2$ requires: C, 40.3; H, 2.3; N, 15.7%.

2-Aminoacetonitriles 14a–h. General procedure

A solution of 0.02 mol oxime 7 in 30 mL ethanol was dropped onto aluminum amalgam (3.51 g, 0.13 mol) at 0°C. After stirring for 4 h the reaction mixture was filtered and washed with hot ethanol. The filtrate was concentrated and cooled, the product filtered off, crystallized (EtOH) and dried.

2-Amino-2-cyanoacetamide (14a). Yield, 48%, white crystals, m.p. 93°C. Found, C, 59.4; H, 8.4; N, 23.2. $C_9H_{15}N_3O$ requires: C, 59.6; H, 8.3; N, 23.2%.

***N*-Methyl-2-amino-2-cyanoacetamide (14b).** Yield, 40 %, white crystals, m.p. 104°C. Found, C, 63.2; H, 5.7; N, 22.0. $C_{10}H_{11}N_3O$ requires: C, 63.5; H, 5.9; N, 22.2%.

***N-cyclo*-Hexyl-2-amino-2-cyanoacetamide (14c).** Yield, 48%, white crystals, m.p. 91–93°C. IR spectrum, 3365, 3320, 3190, 2951, 2882, 2255 (CN), 1665 (CO) cm^{-1}. ^{1}H NMR (ppm), 7.87 (1H, d, J=8 Hz, NH), 4.39 (1H, s, CH), 2.7–3.2 (1H, m, CH), 0.5–2.2 (10H, m, C_5H_{10}). Found, C, 59.4; H, 8.4; N, 23.2. $C_9H_{15}N_3O$ requires: C, 59.6; H, 8.3; N, 23.2%.

***N*-Phenyl-2-amino-2-cyanoacetamide (14d).** Yield, 46%, white crystals, m.p. 117°C. IR spectrum, 3410, 3323, 3073, 2942, 2260 (CN), 1707 (CO) cm^{-1}. ^{1}H NMR (ppm): 9.92 (1H, s, NH), 8.1–6.7 (5H, m, Ph), 4.67 (1H, s, CH). Found, C, 61.6; H, 5.4; N, 24.1. $C_9H_9N_3O$ requires: C, 61.7; H, 5.2; N, 24.0%.

***N*-(*p*-Methoxyphenyl)-2-amino-2-cyanoacetamide (14e).** Yield, 42%, white crystals, m.p. 129°C. IR spectrum, 3410, 3315, 3025, 2945, 2850, 2260 (CN), 1700 (CO) cm^{-1}. ^{1}H NMR 9.40 (1H, s, NH), 7.56 (2H, d, J=9.0 Hz, ArH), 6.85 (2H, d, J=9.0 Hz, ArH), 4.65 (1H, s, CH), 3.75 (3H, s, OMe). Found: C, 58.9; H, 5.6; N, 20.5. $C_{10}H_{11}N_3O_2$ requires: C, 58.5; H, 5.4; N, 20.5%.

***N*-(*p*-Methylphenyl)-2-amino-2-cyanoacetamide (14f).** Yield, 46%, white crystals, m.p. 131°C. IR spectrum, 3428, 3242, 2940, 2890, 2252 (CN), 1700 (CO) cm^{-1}. ^{1}H NMR 9.90 (1H, s, NH),

7.48 (2H, d, J=8.0 Hz, ArH), 7.10 (2H, d, J=8.0 Hz, ArH), 4.67 (1H, s, CH), 2.25 (3H, s, Me). Found: C, 63.6; H, 5.9; N, 22.1. $C_{10}H_{11}N_3O$ requires: C, 63.5; H, 5.9; N, 22.2%.

***N*-(*p*-Bromophenyl)-2-amino-2-cyanoacetamide (14g).** Yield, 40 %, white crystals, m.p. 143°C. IR spectrum, 3405, 3335, 3050, 2910, 2240 (CN), 1685 (CO) cm^{-1}. ^1H NMR: 10.40 (1H, s, NH), 7.78–7.36 (4H, m, C_6H_4), 4.72 (1H, s, CH). Found: C, 42.5; H, 3.2; N, 16.3. $C_9H_8BrN_3O$ requires: C, 42.5; H, 3.2; N, 16.5%.

Table 2. The diazo compounds, 1a–n

Comp.	m.p. °C	Yield (%)	IR (KBr), cm^{-1}			m/z, [$M^{+\cdot}$] (%)	Formula
			C=O	CN	CN_2		
1a	116	75	1684	2235	2151	110 (25)	$C_3H_2N_4O$
1b	118	86	1668	2228	2151	124 (12)	$C_4H_4N_4O$
1c	101	74	1640	2238	2160	192 (39)	$C_9H_{12}N_4O$
1d	66	86	1660	2232	2150	186 (43)	$C_9H_6N_4O$
1e	137	79	1685	2235	2132	216 (71)	$C_{10}H_8N_4O_2$
1f	124	85	1670	2235	2145	200 (100)	$C_{10}H_8N_4O$
1g	153	87	1680	2225	2130	266 (64), 264 (54)	$C_9H_5BrN_4O$
1h	oil	89	1720	2238	2145	139 (66)	$C_5H_5N_3O_2$
1i	oil	56	1654	2220	2115	109 (15)	$C_4H_3N_3O$
1j	oil	75	1770	2220	2135	171 (54)	$C_9H_5N_3O$
1k	oil	59	1750	225	2120	201 (65)	$C_{10}H_{17}N_3O_2$
1l	oil	68	1710	2230	2120	185 (78)	$C_{10}H_{17}N_3O$
1m	oil	38	1710	2250	2130	163 (17)	$C_4F_3N_3O$
1n	oil	45	1714	2210	2115	222 (8)	$C_{12}H_6N_4O$

2-Cyano-2-diazoacetamides 1a–h (General procedure)

A solution of 2.8 g (41 mmol) sodium nitrite in 15 mL H_2O was added to the solution of 40 mmol of the amino-nitrile **8** in 120 mL 1*M* HCl at 0°C. **For compounds 1a-g:** The precipitate was filtered, washed with water and dried to yield **1a-g** as yellow crystals. For compound **1h:** the reaction mixture was extracted with ether (3 x 60 ml). The combined organics were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residual oil was purified by flash chromatography (9:1 dichloromethane–petroleum) to yield **1h** as a red oil.

General procedure for acylation of DAN

10 mmol acyl chloride (or acid anhydride) was added to the solution of 0.67 g (10 mmol) DAN and 1.4 mL (10 mmol) Et_3N in 50 mL CH_2Cl_2 at –10 to 0°C. After stirring at this temperature for 2 hr the reaction mixture was washed by 3 x 50 mL water. The organic layer was dried by Na_2SO_4 and concentrated under reduced pressure at 20°C. The product was purified by chromatography on silica gel (60 mesh) with dichloromethane–petroleum (9:1) as eluent to yield **1i-n** as yellow oils.

General procedure for preparation of adducts 2, 4 of diazonitrile with HHal

A 4.54 *N* solution of HHal in dry diethyl ether (4 mL) was added to the solution of 1 mmol diazo compound **1** in 50 mL dry diethyl ether at 0°C. The precipitate was filtered, washed with 50 mL dry ether and dried at 0°C under reduced pressure.

5-Halo-1,2,3-triazoles 3, 5, 6a–l. General procedure

A solution of 1 mmol diazoacetonitrile **1** in 20 mL $CHCl_3$ was added to 20 mL $CHCl_3$ saturated with HHal. The reaction mixture was stirred for 10 h at 40°C. The solvent was removed under reduced pressure, the product crystallized from ethanol, and dried.

Table 3. The adducts 2, and 4 diazo compound and HHal

Comp.	Yield (%)	IR (KBr), cm^{-1}			Find, %		Calc., %	Formula
		C=O	CN	CN_2	Hal	Hal^-	Hal	
2a	98	1690	2235	2155	38.7	38.7	38.8	$C_3H_4Cl_2N_4O$
2b	95	1685	2220	2150	36.3	36.2	36.0	$C_4H_6Cl_2N_4O$
2c	98	1680	2220	2160	26.6	26.5	26.7	$C_9H_{10}Cl_2N_4O$
2d	99	1675	2225	2153	27.4	27.3	27.4	$C_9H_2Cl_2N_4O$
4a	96	1700	2255	2157	58.8	58.8	58.8	$C_3H_4Br_2N_4O$
4b	98	1664	2231	2146	56.0	56.0	55.9	$C_4H_6Br_2N_4O$
4c	99	1660	2225	2150	45.1	44.9	45.1	$C_9H_{10}Br_2N_4O$
4d	98	1665	2220	2140	45.8	45.3	45.9	$C_9H_2Br_2N_4O$
4e	97	1645	2220	2145	42.4	42.4	42.3	$C_{10}H_{10}Br_2N_4O_2$
4f	99	1668	2215	2135	44.1	44.1	44.1	$C_{10}H_{10}Br_2N_4O$
4g	99	1670	2230	2140	56.3	37.9	56.2	$C_9H_7Br_3N_4O$
4h	98	1670	2220	2150	53.1	53.0	53.1	$C_5H_7Br_2N_3O_2$
4i	87	1645	2220	2135	59.1	58.7	59.0	$C_4H_5Br_2N_3O$
4j	89	1648	2220	2115	48.1	47.8	48.0	$C_9H_7Br_2N_3O$
4k	92	1640	2220	2135	44.1	44.0	44.0	$C_{10}H_9Br_2N_3O_2$
4l	96	1650	2220	2130	46.2	46.2	46.1	$C_{10}H_9Br_2N_4O$
4m	98	1670	2230	2120	49.3	49.1	49.2	$C_4H_2Br_2F_3N_3O$
4n	90	1685	2210	2115	41.5	41.4	41.6	$C_{12}H_8Br_2N_4O$

5-Chloro-1,2,3-triazole-4-carboxamide (3a). Yield 87%, white crystals, m.p. 192–4°C. IR, 3485 (NH), 1685 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 231 (3.81). Found: C, 24.7; H, 1.9; Cl, 24.2; N, 38.6. $C_3H_3ClN_4O$ requires C, 24.6; H, 2.1; Cl, 24.2; N, 38.2%.

***N*-Methyl-5-chloro-1,2,3-triazole-4-carboxamide (3b).** Yield 91%, white crystals, m.p. 192–3°C. IR, 3390 (NH), 1640 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 207 (3.84), 237 (3.91). ^1H NMR 8.82 (1H, br s, NH), 2.86 (3H, d, Me). Found: C, 92.8; H, 3.0; Cl, 21.9; N, 34.9. $C_3H_5ClN_4O$ requires: C, 29.9; H, 3.1; Cl, 22.1; N, 34.9%.

***N*-cyclo-Hexyl-5-chloro-1,2,3-triazole-4-carboxamide (3c).** Yield 69%, white crystals, m.p. 186–7°C. IR, 3410 (NH), 3085,2930, 2850 (CH), 1650 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 237 (4.28). ^{1}H NMR 8.02 (1H, d, 8.0 Hz, NH), 2.9–3.0 (1H, m, NCH), 0.5–2.2 (10H, m, C_6H_{10}). Found: C, 47.5; H, 5.9; Cl, 15.3; N, 24.5. $C_9H_{13}ClN_4O$ requires: C, 47.3; H, 5.7; Cl, 15.5; N, 24.5%.

***N*-Phenyl-5-chloro-1,2,3-triazole-4-carboxamide (3d).** Yield 87%, white crystals, m.p. 193–5°C. IR 3395 (NH), 3120, 2975, 2885 (CH), 1680 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 241 (4.18). ^{1}H NMR 10.43 (1H, s, NH), 7.10-7.95 (5H, m, Ph). Found: C, 48.8; H, 3.7; Cl, 15.9; N, 25.1. $C_9H_7ClN_4O$ requires C, 48.6; H, 3.7; Cl, 15.9; N, 25.2%.

***N*-*p*-Methoxyphenyl-5-chloro-1,2,3-triazole-4-carboxamide (3e).** Yield 84%, white crystals, m.p. 205–7°C. IR: 3395 (NH), 3140, 2960, 2835 (CH), 1680 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 240 (4.05). ^{1}H NMR: 10.20 (1H, s, NH), 7.65 (2H, d, 9.0 Hz, ArH), 6.87 (2H, d, 9.0 Hz, ArH), 3.75 (3H, s, OMe). Found: C, 47.2; H, 3.7; Cl, 14.2; N, 22.0. $C_{10}H_9ClN_4O_2$ requires: C, 47.5; H, 3.6; Cl, 14.0; N, 22.3%.

***N*-*p*-Methylphenyl-5-chloro-1,2,3-triazole-4-carboxamide (3f).** Yield 87%, white crystals, m.p. 197–9°C. IR: 3395 (NH), 3140, 2965, 2855 (CH), 1680 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 243 (4.10). ^{1}H NMR: 10.20 (1H, s, NH), 7.65 (2H, d, 9.0 Hz, ArH), 7.10 (2H, d, 9.0 Hz, ArH), 2.24 (3H, s, OMe). Found: C, 51.0; H, 3.9; Cl, 15.2; N, 23.8. $C_{10}H_9ClN_4O$ requires: C, 50.8; H, 3.8; Cl, 15.0; N, 23.7 %.

Ethyl 5-chloro-1,2,3-triazole-4-carboxylate (3h). Yield 59%, white crystals, m.p. 74–7°C. IR: 3540 (NH), 1715 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 237 (4.08). ^{1}H NMR 4.47 (2H, q, 7.2 Hz, CH_2), 1.39 (3H, t, 7.2 Hz, Me). Found: C, 34.0; H, 3.3; Cl, 19.9; N, 23.8. $C_5H_6ClN_3O_2$ requires: C, 34.2; H, 3.4; Cl, 20.2; N, 23.9%.

5-Chloro-4-phenylcarbonyl-1,2,3-triazole (3j). Yield 88%, white crystals, m.p. 152–3°C. IR: 1645 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 203 (3.97), 258 (4.07). Found: C, 52.4; H, 3.2; Cl, 16.8; N, 20.5. $C_9H_6ClN_3O$ requires: C, 52.1; H, 2.9; Cl, 17.1; N, 20.2%.

5-Bromo-1,2,3-triazole-4-carboxamide (**5a**). Yield 70%, white crystals, m.p. 181–3°C. IR: 3385 (NH), 1695 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 234 (3.72). Found: C, 18.7; H, 1.8; Br, 41.4; N, 29.5. $C_3H_3BrN_4O$ requires: C, 18.9; H, 1.6; Br, 41.8; N, 29.3%.

***N*-Methyl-5-bromo-1,2,3-triazole-4-carboxamide (5b).** Yield 67%, white crystals, m.p. 184–6°C. IR: 3400 (NH), 1650 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 232 (3.96). ^{1}H NMR 8.82 (1H, br s, NH), 2.83 (3H, d, NMe). Found: C, 23.4; H, 2.7; Br, 39.1; N, 27.7. $C_4H_5BrN_4O$ requires: C, 23.4; H, 2.5; Br, 39.0; N, 27.3%.

***N*-cyclo-Hexyl-5-bromo-1,2,3-triazole-4-carboxamide (5c).** Yield 90%, white crystals, m.p. 188–190°C. IR: 3405 (NH), 3085, 2925, 2850 (CH), 1650 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 237 (4.28). ^{1}H NMR: 8.02 (1H, d, 8.0 Hz, NH), 2.80–2.98 (1H, m, NCH), 0.80–2.05 (10H, m, C_6H_{10}). Found, %: C, 39.6; H, 4.9; Br, 29.6; N, 20.9. $C_9H_{13}BrN_4O$. Calc., %: C, 39.6; H, 4.8; Br, 29.3; N, 20.5.

***N*-Phenyl-5-bromo-1,2,3-triazole-4-carboxamide (5d).** Yield 89%, white crystals, m.p. 186–8°C. IR: 3400 (NH), 3105, 2972, 2887 (CH), 1680 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 241

(4.18). ^{1}H NMR: 10.43 (1H, s, NH), 7.10–7.95 (5H, m, Ph). Found: C, 40.7; H, 2.7; Br, 30.0; N, 20.7. $C_9H_7BrN_4O$. Calc. C, 40.5; H, 2.6; Br, 30.0; N, 21.0%.

Ethyl 5-bromo-1,2,3-triazole-4-carboxylate (5h). Yield 94%, white crystals, m.p. 71–4°C. IR: 3445 (NH), 1705 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 237 (3.84). NMR: 4.49 (2H, q, 7.2 Hz, CH_2), 1.33 (3H, t, 7.2 Hz, Me). Found: C, 27.4; H, 3.1; Br, 36.2; N, 18.9. $C_5H_6BrN_3O_2$ requires C, 27.3; H, 2.8; Br, 36.3; N, 19.1%.

5-Bromo-4-methylcarbonyl-1,2,3-triazole (5i). Yield 86%, white crystals, m.p. 58–62°C. IR: 1750 (C=O) cm^{-1}. Found: C, 25.4; H, 2.2; Br, 42.1; N, 22.1. $C_4H_4BrN_3O$ requires: C, 25.2; H, 2.1; Br, 42.0; N, 22.1%.

5-Bromo-4-phenylcarbonyl-1,2,3-triazole (5j). Yield 92%, white crystals, m.p. 137–8°C. IR: 1650 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 257 (3.95), 241 (3.75). Found: C, 43.2; H, 2.5; Br, 31.6; N, 16.9. $C_9H_6BrN_3O$ requires: C, 42.9; H, 2.4; Br, 31.7; N, 16.7%.

5-Bromo-4-p-methoxyphenylcarbonyl-1,2,3-triazole (5k). Yield 97%, white crystals, m.p. 87–93°C. IR: 3170 (CH), 1720 (C=O) cm^{-1}. Found: C, 43.2; H, 3.0; Br, 29.0; N, 15.2. $C_{10}H_8BrN_3O_2$ requires: C, 43.0; H, 2.9; Br, 28.9; N, 15.0%.

5-Bromo-4-p-methylphenylcarbonyl-1,2,3-triazole (5l). Yield 89%, white crystals, m.p. 98–100°C. IR: 2970 (CH), 1700 (C=O) cm^{-1}. Found: C, 45.6; H, 3.0; Br, 30.6; N, 16.0. $C_{10}H_8BrN_3O$ requires: C, 45.1; H, 3.0; Br, 30.0; N, 15.8%.

5-Iodo-1,2,3-triazole-4-carboxamide (**3a**). Yield 70%, white crystals, m.p. 181–3°C. IR: 3385 (NH), 1670 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 218 (3.96), 242 (3.77). Found: C, 18.7; H, 1.8; N, 29.5. $C_3H_3IN_4O$ requires: C, 15.1; H, 1.3; N, 23.5%.

***N*-Methyl-5-iodo-1,2,3-triazole-4-carboxamide (3b).** Yield 93%, white crystals, m.p. 182–4°C. IR: 3330 (NH), 1660 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 219 (3.94). NMR: 8.9 (1H, br s, NH), 2.81 (3H, s, NMe). Found: C, 19.4; H, 1.8; N, 22.5. $C_4H_5IN_4O$ requires: C, 19.1; H, 2.0; N, 22.2%.

***N*-Phenyl-5-iodo-1,2,3-triazole-4-carboxamide (3d).** Yield 45%, white crystals, m.p. 184–7°C. IR: 1650 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 256 (4.08). Found: C, 30.5; H, 3.5; N, 11.9. $C_9H_6IN_3O$. Calc.: C, 30.6; H, 3.4; N, 11.9%.

Ethyl 5-iodo-1,2,3-triazole-4-carboxylate (3h). Yield 82%, white crystals, m.p. 67–8°C. IR: 3485 (NH), 1730 (C=O) cm^{-1}. UV, λ_{max}, nm, (log ε): 241 (3.75). NMR: 4.48 (2H, q, 7.3 Hz, CH_2), 1.37 (3H, t, 7.3 Hz, Me). Found, %: C, 22.9; H, 2.6; N, 15.6. $C_5H_6IN_3O_2$ requires: C, 22.5; H, 2.3; N, 15.7%.

Kinetic experiments. Kinetic data were obtained by UV spectroscopy at the absorption maxim (λ_{max}=254 nm) of the diazo compounds **1** by sampling, acidification to pH 4–5 with a solution of HCl in ethanol, followed by dilution with ethanol of the reaction mixtures kept at 30°, 40°, or 50°C. The concentrations of the diazo compounds were 0.3 mM, and 3M HCl. Kinetic data for the solid cyclization of adducts **2** were obtained by IR spectroscopy at the absorption of diazo group of the mixture of compounds **2** (0.11 mol) and KBr. The reaction rate constant was calculated using a linear regression program.

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References and Notes

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