Ring Transformations of Heterocycles. Part 1. Transformation of 4-Amino-Δ^2-1,2,4-oxadiazolines into 1,3,4-Oxadiazoles

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3-Aryl-4-amino-Δ^2-1,2,4-oxadiazolines **3** and their *N*-chloroacetyl derivatives **4**, upon treatment with chloroacetic anhydride in refluxing toluene, afford 2-chloromethyl-5-aryl-1,3,4-oxadiazoles **5**, suggesting the conversion sequence **3** → **4** → **5**. The generality of the new ring transformation **4** → **5** is supported similar conversion of other 4-(acylamino)-1,2,4-oxadiazolines **8** to 1,3,4-oxadiazoles **9**.

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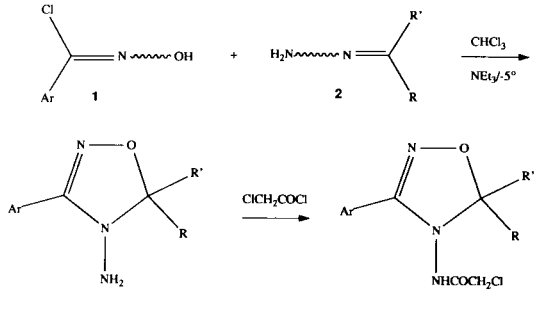
Recently we reported [1] on the synthesis of 4-amino-Δ^2-1,2,4-oxadiazolines **3** *via* 1,3-dipolar cycloaddition of aliphatic ketohydrazones **2** to aryl nitrile oxides, generated *in situ* from the appropriate hydroxamoyl chloride **1** (Scheme 1). Agro-screening tests indicate that 3-(*m*-nitrophenyl)oxadiazolines **3a-c,g,h** [1] exhibit a level of herbicidal activity [2] that warrants further study. This led us to prepare additional derivatives **3d-f,i-l** with a variety of substituents at position 5, while retaining the nitrophenyl grouping at C-3 (Scheme 1 and Table 1). Introduction of the chloroacetyl grouping at the N-4-amino functionality appears desirable, as this group is well-known to enhance considerably the herbicidal action in related systems [3]. Consequently, we have prepared a series of 4-(chloroacetylamino)-Δ^2-1,2,4-oxadiazolines **4a-l** by reacting **3a-l** with chloroacetyl chloride or chloroacetic anhydride at ambient temperature (Scheme 1). Analytical and spectral data, presented in Tables 1-3, are in agreement with the assigned structures.

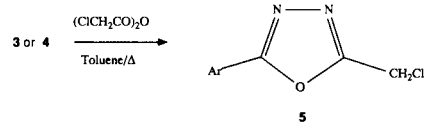
Scheme 1



R	R'	Ar	No.		Ar	No.	
-$(CH_2)_4$-		*p*-$(NO_2)C_6H_4$	**3a**	**4a**	*m*-$(NO_2)C_6H_4$	**3g**	**4g**
-$(CH_2)_5$-			**3b**	**4b**		**3h**	**4h**
-$(CH_2)_2CHCH_3(CH_2)_2$-			**3c**	**4c**		**3i**	**4i**
-$(CH_2)_6$-			**3d**	**4d**		**3j**	**4j**
-$(CH_2)_7$-			**3e**	**4e**		**3k**	**4k**
CH_3	CH_3		**3f**	**4f**		**3l**	**4l**

However, when compounds **3** were refluxed in dry toluene with excess chloroacetic anhydride or chloroacetyl chloride (5 equivalents) for 1 hour, a product identified as 2-chloromethyl-5-(nitrophenyl)-1,3,4-oxadiazoles **5a,b**, from the respective **3** was obtained instead of the expected *N*-chloroacetyl derivatives **4a-l** (Scheme 2). Under similar conditions, chloroacetic acid has proven to be an inadequate reagent for the conversion process **3g** → **5b**. Assignment of the structures of **5a,b** was based on spectral data. The ir spectra of **5** exhibit two absorption peaks at *ca.* 1620 and 1590 cm^{-1} ascribed to the azomethine stretching modes, but lack the N–H and the amide carbonyl absorptions around 3320 and 1700 cm^{-1}, respectively, that characterize the *N*-chloroacetyl derivatives **4**. The ^{1}H-nmr spectra of **5** show, in additon to the aromatic protons' signals (4H), a singlet at 4.8 ppm (2H) assigned to the chloromethyl protons at C-2, but again lack the signals of the exchangeable NH, and the aliphatic protons at C-5, present in **4**. The ^{13}C-nmr spectra account for the seven different carbon atoms of the 1,3,4-oxadiazole structure representing **5**. The mass spectra also display the correct molecular ions as suggested by the molecular formulae for **5**. The melting points of the ring-transformed products **5a,b** are in good agreement with those reported [4] for the known 2-chloromethyl-5-(*p*-nitrophenyl)-1,3,4-oxadiazole **5a**, and the corresponding *m*-nitrophenyl isomer **5b**, obtained *via* a different route.

Scheme 2



No.	Ar
5a	*p*-$(NO_2)C_6H_4$
5b	*m*-$(NO_2)C_6H_4$

Table 1

Physical and Analytical Dataa for Compounds **3,4,5,8** and **9**

No.	Mp (°C)	Yield [a] %	Molecular Formula (M+)	Analyses % Calcd./Found C	H	N
3d	135-136	75	$C_{14}H_{18}N_4O_3$	57.92	6.25	19.30
			(290)	58.02	6.26	19.29
3e	137-138	80	$C_{15}H_{20}N_4O_3$	59.19	6.62	18.41
			(304)	59.31	6.59	18.38
3f	134-135	45	$C_{10}H_{12}N_4O_3$	50.85	5.12	23.72
			(236)	50.78	5.27	23.50
3i	154-155	64	$C_{14}H_{18}N_4O_3$	57.92	6.25	19.30
			(290)	58.11	6.34	19.20
3j	121-122	70	$C_{14}H_{18}N_4O_3$	57.92	6.25	19.30
			(290)	57.84	6.19	19.25
3k	149-150	80	$C_{15}H_{20}N_4O_3$	59.19	6.62	18.41
			(304)	59.27	6.70	18.25
3l	112-113	38	$C_{10}H_{12}N_4O_3$	50.85	5.12	23.72
			(236)	50.66	5.03	23.58
4a	170-171	70	$C_{14}H_{15}ClN_4O_4$	49.64	4.46	16.54
			(338/340)	49.72	4.45	16.36
4b	197-198	80	$C_{15}H_{17}ClN_4O_4$	51.07	4.86	15.88
			(352/354)	51.25	4.96	15.82
4c	190-191	74	$C_{16}H_{19}ClN_4O_4$	52.39	5.22	15.27
			(366/368)	52.43	5.44	15.18
4d	168-169	88	$C_{16}H_{19}ClN_4O_4$	52.39	5.22	15.27
			(366/368)	52.51	5.29	15.08
4e	200-201	90	$C_{17}H_{21}ClN_4O_4$	53.62	5.56	14.71
			(380/382)	53.53	5.79	14.60
4f	172-173	60	$C_{12}H_{13}ClN_4O_4$	46.09	4.19	17.92
			(312/314)	46.27	4.31	17.99
4g	173-174	72	$C_{14}H_{15}ClN_4O_4$	49.64	4.46	16.54
			(338/340)	49.75	4.60	16.28
4h	178-179	82	$C_{15}H_{17}ClN_4O_4$	51.07	4.86	15.88
			(352/354)	51.08	4.87	15.65
4i	185-186	75	$C_{16}H_{19}ClN_4O_4$	52.39	5.22	15.27
			(366/368)	52.08	5.36	15.00
4j	175-176	90	$C_{16}H_{19}ClN_4O_4$	52.39	5.22	15.27
			(366/368)	52.20	5.29	15.10
4k	170-171	92	$C_{17}H_{21}ClN_4O_4$	53.62	5.56	14.71
			(380/382)	53.70	5.70	14.56
4l	188-189	62	$C_{12}H_{13}ClN_4O_4$	46.09	4.19	17.92
			(312/314)	46.22	4.26	17.72
5a	134-135 [b]	75	$C_9H_6ClN_3O_3$	45.11	2.52	17.54
			(239/241)	44.83	2.40	17.52
5b	118-119 [c]	84	$C_9H_6ClN_3O_3$	45.11	2.52	17.54
			(239/241)	44.95	2.44	17.51
8a	174-175	60	$C_{19}H_{19}N_3O_2$	71.01	5.96	13.07
			(321)	71.10	6.21	12.89
8b	150-151	75	$C_{14}H_{16}N_4O_4$	55.26	5.30	18.41
			(304)	55.47	5.49	18.25
8c	176-177	80	$C_{13}H_{14}N_4O_4$	53.79	4.86	19.30
			(290)	54.00	5.10	19.06
9a	139-140 [d]	75	$C_{14}H_{10}N_2O$	75.66	4.54	12.60
			(222)	75.48	4.50	12.49
9b	156-157	90	$C_9H_7N_3O_3$	52.69	3.44	20.48
			(205)	52.56	3.56	20.22
9c	124-125 [e]	85	$C_8H_5N_3O_3$	50.27	2.64	21.98
			(191)	50.03	2.54	21.72

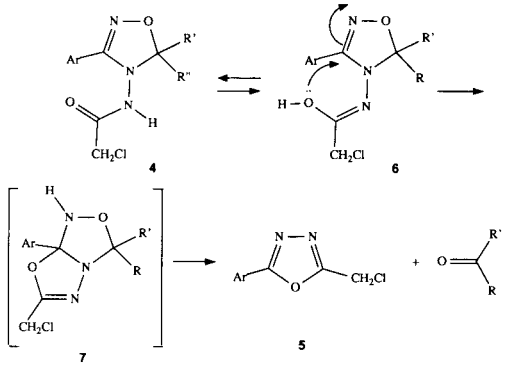
[a] Based on recrystallized products, using chloroacetic anhydride and the respective *N*-chloroacetyl- or *N*-acyloxadiazolines. [b] Lit [4], mp = 133-135°. [c] Lit [4], mp = 118°. [d] Lit [8], mp = 138°. [e] Lit [9], mp = 125-126°.

The same products **5a,b** were obtained from the respective 4-(chloroacetylamino) derivatives **4** and chloroacetic anhydride in refluxing toluene for 30 minutes. This latter result indicates that compounds **4** are actual intermediates in this ring transformation reaction of 4-amino-Δ^2-1,2,4-oxadiazolines **3** into the corresponding 1,3,4-oxadiazoles **5**.

This hetero ring-transformation reaction, performed on **4g** as a model of the series, also took place when chloroacetyl chloride, chloroacetic acid, or trichloroacetic acid were employed in place of chloroacetic anhydride. However, **4g** was recovered unchanged when refluxed in glacial acetic acid or acetic anhydride for 3 hours.

Apparently, the conversion of **4** to **5** described above, proceeds with concurrent extrusion of the ketone component (RR' C=O) in **4**. This was ascertained by the formation of cyclopentanone (isolated as its 2,4-dinitrophenylhydrazone) in the conversion reaction of **4g** with chloroacetic anhydride. From the data so far available, this transformation can be pictured to start with initial attack of the nucleophilic amide oxygen (in tautomer **6** shown below) at the azomethine-ring carbon, followed by breakdown of the resulting transient intermediate bicyclic adduct **7** into **5** (Scheme 3). The driving force for such conversion is linked with the aromaticity of the hetero ring system **5** formed thereof. This process (**4** → **5**) is reminescent of the ring-closure reactions of α-(acylamino)carbonyl compounds to form oxazoles [5,6], and of 1,2-diacylhydrazines to produce 1,3,4-oxadiazoles [7].

Scheme 3



According, the choice of ambient temperature for the reaction of **3** with haloacid halide or haloacid anhydride ensures the formation of the respective 4-(haloacylamino) derivative **4** as the end product. On the other hand, employment of elevated reaction temperature causes the conversion of the target **4** into 1,3,4-oxadiazoles **5**.

Table 2

NMR Spectral Data [a] (δ -values, ppm) for Compounds

No.	NH_2	C-5	C-3
3d	3.55	104.1	156.9
3e	3.55	103.7	157.6
3f	3.52	100.4	156.9
3i	3.33	99.7	156.4
3j	3.62	103.7	156.4
3k	3.58	103.3	156.9
3l	3.60	100.2	156.6

[a] Solvent: deuteriochloroform, **3i**, DMSO-d_6.

Table 3

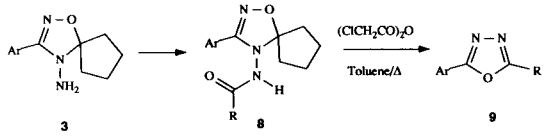
NMR Spectral Data [a] (δ-values, ppm) for Compounds **4a-l** and **8a-c**

No.	N-H (s)	CH_2Cl (s)	C-3	C-5	H O | || N–C———CH_2Cl	
4a	10.63	3.99	155.6	110.9	165.1	40.9
4b	10.54	4.00	155.3	101.7	165.1	41.0
4c	10.52	3.99	154.3	101.4	165.1	41.0
4d	10.60	4.00	154.3	104.6	166.3	40.7
4e	10.57	4.00	154.4	104.2	166.2	40.8
4f	10.54	4.00	154.8	100.9	165.6	40.9
4g	10.62	4.00	154.7	109.9	166.6	40.5
4h	10.59	3.98	154.3	100.4	166.4	40.6
4i	10.58	3.96	154.5	100.3	166.5	40.8
4j	10.62	3.99	154.2	104.4	166.5	40.6
4k	10.56	3.98	154.4	104.2	166.2	40.8
4l	10.63	3.99	154.1	100.2	166.5	40.8
					H O | || N–C———R	
8a	10.67		156.1	108.9	166.6	Ph
8b	10.2		154.8	109.5	169.5	20.1 (CH_3)
8c	10.32		154.8	109.7	161.0	H

[a] ^{13}C-nmr spectra for compounds **4b,c,f** were run in deuteriochloroform; all other measurements were run in DMSO-d_6.

Our desire to explore the generality of this transformation reaction led us to prepare a few relevant *N*-acyl derivatives **8** from the respective 4-amino-Δ^2-1,2,4-oxadiazolines **3** (Scheme 4, Table 1). These *N*-acyl derivatives **8** were also found to undergo similar hetero ring-transformation reaction, under the influence of chloroacetic anhydride, yielding the corresponding 1,3,4-oxadiazoles **9** (Scheme 4, Table 1). Analytical and spectral data for **8** and **9** conform with the assigned structures. The melting points of **9a,c** correspond well with the literature data [8,9].

Scheme 4

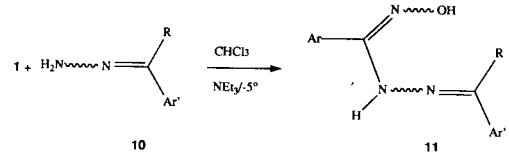


3 8 9

No.		Ar	R
8a	**9a**	C_6H_5	C_6H_5
8b	**9b**	*m*-$(NO_2)C_6H_4$	CH_3
8c	**9c**	*m*-$(NO_2)C_6H_4$	H

In an attempt to prepare 5-aryl substituted 1,2,4-oxadiazolines to test their conversion into 1,3,4-oxadiazoles, we reacted hydrazones of aryl aldehydes and ketones **10** with nitrile oxide precursors **1**. Only the corresponding acyclic adducts **11** were, however, obtained by way of nucleophilic addition (Scheme 5). 1,3-Dipolar cycloaddition across the azomethine π-bond in **10** is not observed here. The structures assigned to compounds **11** follow from their elemental microanalyses (Table 4) and spectral data. The mass

Scheme 5



10 11

No.	R	Ar	Ar'
11a	H	*p*-ClC_6H_4	*p*-$(NO_2)C_6H_4$
11b	H	*p*-ClC_6H_4	2-Thienyl
11c	H	*p*-ClC_6H_4	2-Furyl
11d	CH_3	*p*-ClC_6H_4	C_6H_5
11e	CH_3	*p*-ClC_6H_4	*p*-ClC_6H_4
11f	CH_3	*m*-$(NO_2)C_6H_4$	*p*-ClC_6H_4
11g	H	*p*-MeC_6H_4	*p*-MeC_6H_4

spectra displayed the correct molecular ions as calculated from their molecular formulae. The ir spectra revealed the presence of an N-H absorption at about 3380 cm^{-1}. The broad absorption in the range 2900-3300 cm^{-1} is assigned to the O-H stretching mode, while the C=N-stretching appeared at 1600-1640 cm^{-1}. The ^{1}H-nmr spectra of compounds **11** exhibit two exchangeable broad singlets in the range 8-9 (1H) and 10-11 ppm (1H) assigned respectively, to the N-H and O-H protons. The vinylic proton in **11a-c,g** appears as a singlet in the region 7.6-7.8 ppm. The ^{13}C-nmr spectra exhibit two signals in the lowest field region, at 144-147 and 147-151 ppm, belonging to the two azomethine carbons of these acyclic adducts.

EXPERIMENTAL

Melting points were determined on an electrothermal Mel-

Table 4

Physical and Analytical Data for Compounds **11a-g**

Compound	Mp (°C)	Yield (%)	Molecular Formula (M+)	Analysis % Calcd./Found C	H	N
11a	134-135	32	$C_{14}H_{11}ClN_4O_3$ (318)	52.76 52.74	3.84 3.66	17.58 17.39
11b	119-120	34	$C_{12}H_{10}ClN_3OS$ (279/281)	51.52 51.60	3.60 3.78	15.02 15.14
11c	101-102	35	$C_{12}H_{10}ClN_3O_2$ (263/265)	54.66 54.58	3.82 3.87	15.94 15.63
11d	135-136	42	$C_{15}H_{14}ClN_3O$ (287/289)	62.61 62.86	4.90 5.09	14.60 14.67
11e	146-147	36	$C_{15}H_{13}Cl_2N_3O$ (321/323/325)	55.92 55.68	4.07 4.14	13.04 12.76
11f	160-161	25	$C_{15}H_{13}ClN_4O_3$ (332/334)	54.15 54.32	3.94 4.02	16.84 16.73
11g	118-119	38	$C_{16}H_{17}N_3O$ (267)	71.89 71.86	6.41 6.42	15.72 15.58

Temp apparatus and are uncorrected. Ir spectra were recorded as potassium bromide pellets on a Perkin Elmer 577 spectrophotometer. The ^1H and ^{13}C-nmr spectra were recorded on a Varian XL 200 instrument, for solutions in deuteriochloroform (unless otherwise stated) at 21°. The EI mass spectra were run on a Finnigan MAT 731 spectrometer at 70 eV. Elemental microanalyses were performed at MHW Laboratories, Phoenix, Arizona, USA.

Unsubstituted Hydrazones **2** and **10**.

Simple hydrazones derived from cycloalkanones and acetone, employed in the present work, were prepared as previously described [1]. Those hydrazones of *p*-tolualdehyde [10], *p*-nitrobenzaldehyde [10-12], acetophenone [12,13], *p*-chloroacetophenone [14], thiophene-2-carboxaldehyde [15], and furan-2-carboxaldehyde [15] were prepared following literature methods.

Hydroxamoyl Chlorides **1** (Precursors of Nitrile Oxides).

Benzhydroxamoyl chloride [16], *p*-chlorobenzhydroxamoyl chloride [16], *m*-nitrobenzhydroxamoyl chloride [16], *p*-nitrobenzhydroxamoyl chloride [16] and *p*-methylbenzhydroxamoyl chloride [17], used in this study, were prepared by direct chlorination of the respective aldoximes following published procedures.

Preparation of 4-Amino-Δ^2-1,2,4-Oxadiazolines **3d-f,i-l**.

These heterocycles were prepared following a similar procedure reported for closely related analogues [1]. Thus, to a stirred and cooled (−5 to −10°) solultion of the appropriate hydrazone (0.05 mole) and triethyl amine (0.05 mole) in chloroform (40 ml) was added, dropwise, a solution of the partner hydroxamoyl chloride (0.02 mole) in chloroform (40 ml). The resulting reaction mixture was then allowed to warm up slowly to room temperature (2 hours) and washed with water (2 x 50 ml). The organic layer was separated, dried (magnesium sulfate), the solvent was then removed *in vacuo*, and the residue was recrystallized from chloroform/petroleum ether (bp 40-60°). Physical and analytical data for these, and all related derivatives **3-9**, prepared in this study, are presented in Table 1.

Preparation of the *N*-Chloroacetyl Derivatives **4a-l**.

(i) To a stirred solution of the appropriate oxadiazoline **3** (0.01 mole) in dry benzene (20 ml) was added, at room temperature, chloroacetyl chloride (0.04 mole). The resulting reaction mixture was then warmed (35-40°) for 30 minutes. Upon cooling of the warm solution, the desired product **4** began to crystallize out. Petroleum ether (40 ml, bp 40-60°) was added to effect complete precipitation of **4** which was then collected and recrystallized from chloroform/petroleum ether.

(ii) To a stirred solution of a model oxadiazoline (**3g**, 0.01 mole) in dry benzene (20 ml) was added, at room temperature, chloroacetyl chloride (0.04 mole). The resulting reaction mixture was further stirred for 1 hour at ambient temperature. Comparable yield of the respective *N*-chloroacetyl product **4g** was obtained as in (i) above.

(iii) To a stirred solution of **3g** (0.01 mole) in dry benzene (20 ml) was added, at room temperature, chloroacetic anhydride (0.05 mole). The resulting reaction mixture was further stirred for 2 hours at ambient temperature. Comparable yield of **4g** was obtained as in (ii) above.

(iv) A stirred solution of **3g** (0.01 mole) and chloroacetic anhydride (0.05 mole) in benzene (20 ml) was warmed at 45-50° for 1 hour. Upon cooling of the resulting reaction mixture, the desired product **4g** was precipitated, filtered off, and recrystallized, yield = 55%.

The filtrate was washed with water (2 x 20 ml), the organic layer was dried (magnesium sulfate), and the solvent was removed *in vacuo*. The residual solid was crystallized from chloroform/-petroleum ether, and identified as the conversion product **5b**, yield = 15%.

Preparation of the *N*-Benzoyl Derivative **8a**.

To a stirred solution of **3** (Ar = phenyl, 0.01 mole) [1] in ethanol (50 ml) was added at 15-20° excess benzoyl chloride (15 ml), followed by addition of aqueous sodium hydroxide solution (8%, 25 ml). The resulting solution was stirred for 2 hours at ambient temperature, then diluted with water (100 ml) and extracted with dichloromethane (2 x 60 ml). The combined dichloromethane extracts were dried (magnesium sulfate) and the solvent was evaporated. The residual product, that solidified upon soaking with petroleum ether, was collected and recrystallized from chloroform/petroleum ether.

Preparation of the *N*-Acetyl Derivative **8b**.

A solution of **3g** (0.01 mole) in acetic anhydride (20 ml) was refluxed for 1 hour. Water (80 ml) was then added to the cooled solution, the precipitated product was collected and recrystallized from chloroform/petroleum ether.

Preparation of the *N*-Formyl Derivative **8c**.

A solution of **3g** (0.01 mole) in formic acid (20 ml) was refluxed for 15-20 minutes. The resulting solution was then cooled, diluted with cold water (100 ml), the solid product that precipitated out was collected and recrystallized from chloroform/petroleum ether.

Conversion of 4-Amino-Δ^2-1,2,4-Oxadiazolines **3** into 1,3,4-Oxadiazoles **5**.

General Procedures.

(i) A solution of **3g** (0.01 mole) and chloroacetic anhydride (0.05 mole) in dry toluene (30 ml) was refluxed for 1 hour. The resulting solution was cooled to 10-15° and then treated portionwise, with stirring, with 10% aqueous sodium bicarbonate solution until effervescence ceased. The organic layer was separated, washed with water (20 ml), dried (magnesium sulfate), and the solvent was evaporated *in vacuo*. The residual product **5b**, that solidified upon trituration with petroleum ether, was collected and recrystallized from chloroform/petroleum ether.

In a separate run, the organic layer was diluted with ethanol (10 ml) and treated with freshly prepared 2,4-dinitrophenylhydrazine solution (0.02 mole). An orange solid precipitated out, which was collected and recrystallized from aqueous ethanol, yield = 30%, mp = 141-142° (undepressed upon admixture with an authentic sample of cyclopentanone 2,4-dinitrophenylhydrazone).

(ii) A solution of **3g** (0.01 mole) and chloroacetyl chloride (0.05 mole) in dry toluene (30 ml) was refluxed for 1 hour. Work up of the dark reaction mixture, as described in (i) above, gave **5b**, yield = 72%.

Compounds **3h-l** were refluxed in toluene with chloroacetic anhydride, following the above general procedure as applied to **3g**. In each case, the isolated product was identified as 2-chloromethyl-5-(*m*-nitrophenyl)-1,3,4-oxadiazole **5b**.

Compound **3a**, under similar conditions, gave 2-chloromethyl-5-(*p*-nitrophenyl)-1,3,4-oxadiazole **5a**.

However, **3g** and chloroacetic acid, under similar conditions, gave a mixture of over ten compounds (as monitored by tlc) whose identification was not attempted.

Conversion of 4-(Chloroacetylamino)-1,2,4-Oxadiazolines **4** into 1,3,4-Oxadiazoles **5**.

General Procedures.

(i) A solution of **4g** (0.01 mole) and chloroacetic anhydride (0.05 mole) in dry toluene (20 ml) was refluxed for 30 minutes. Work up of the reaction mixture as described in (i) above for **3g**, gave **5b**.

Compounds **4h-l** were similarly refluxed, in toluene, with chloroacetic anhydride for 30 minutes. In each case, the isolated product was identified as **5b**. Yields were in the range of 70-80%.

Compound **4a**, under identical conditions, gave **5a**, yield = 70%.

(ii) A solution of **4g** (0.01 mole) and chloroacetyl chloride (0.05 mole) in dry toluene (20 ml) was refluxed for 1 hour. Work up of the dark reaction mixture, as noted in (i) above, afforded **5b**, yield = 60%.

(iii) A solution of **4g** (0.01 mole) and chloroacetic acid (0.1 mole) in dry toluene (20 ml) was refluxed for 2 hours. Work up of the reaction mixture, as described above for **3g**, gave **5b**, yield = 50%.

(iv) A solution of **4g** (0.01 mole) and trichloroacetic acid (0.1 mole) in dry toluene (20 ml) was refluxed for 1 hour. Work up of the dark reaction mixture, as described above for **3b**, gave **5b**, yield = 60%.

4g and Acetic Acid.

A solution of **4g** (0.01 mole) in glacial acetic acid (10 ml) was refluxed for 3 hours. Work up of the resulting solution, as described above for **3g**, gave unchanged **4g** (90% recovery).

4g and Acetic Anhydride.

A solution of **4g** (0.01 mole) in acetic anhydride (10 ml) was refluxed for 3 hours. Work up of the resulting mixture, as described above for **3g**, resulted in the recovery (85%) of **4g**, unchanged.

Conversion of *N*-Acyl-1,2,4-Oxadiazolines **8** into 1,3,4-Oxadiazoles **9**.

A solution of **8a** (0.01 mole) and chloroacetic anhydride (0.05 mole) in dry toluene (20 ml) was refluxed for 30 minutes. Work up of the reaction mixture, as described above for **3g**, gave 2,5-diphenyl-1,3,4-oxadiazole **9a**.

Compound **8b**, under similar conditions, gave 2-methyl-5-(*m*-nitrophenyl)-1,3,4-oxadiazole **9b**.

Compound **8c**, under similar conditions, gave 2-(*m*-nitrophenyl)-1,3,4-oxadiazole **9c**.

Preparation of Compounds **11**.

These acyclic derivatives were prepared from the appropriate hydrazone **10** (0.05 mole) and the respective hydroxamoyl chloride **1** (0.02 mole) following the procedure described above for the oxadiazolines **3d-f,i-l**. The isolated products were purified by recrystallization, first from ethanol, then from chloroform/-petroleum ether (bp 40-60°).

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