Fused *v*-Triazolo-heterocycles. Part 2 [1]. Synthesis of 4*H*-*v*-Triazolo[1,5-*d*] [1,3,4]oxadiazin-4-ones from the 1-Aroylamino-*v*-triazole-5-carboxylic Acids

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The synthesis of some 4*H*-*v*-triazolo[1,5-*d*] [1,3,4]oxadiazin-4-ones is described. They are prepared by the reaction of the corresponding 1-aroylamino-*v*-triazole-5-carboxylic acids with thionyl chloride in the presence of pyridine. The spectroscopic data of these new compounds are also reported.

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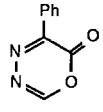
The 1,3,4-oxadiazin-6-one ring system has been prepared in the form of its *N*-oxide derivative by Freeman *et al.* [2] and by Steglich *et al.* [3], who first synthesized the 2,5-diphenyl-1,3,4-oxadiazin-6-one (**1**), from the phenylglyoxylic acid benzoylhydrazone on treatment with dicyclohexylcarbodiimide (DCC). Since then several 1,3,4-oxadiazin-6-ones [4,5] as well as 4,5-dihydro-1,3,4-oxadiazin-6-ones [6] have been synthesized. It has been observed that they undergo [4 + 2] cycloaddition reactions with



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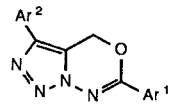

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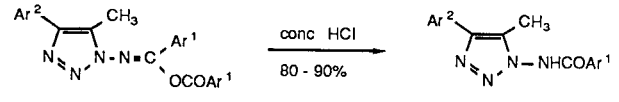
dienophiles, the products of which after nitrogen loss give in one step α-pyrone derivatives and other cyclic compounds [4,5,7].

On the other hand, working on the chemistry of 1-amino-*v*-triazole derivatives we have prepared a series of fused 4*H*-*v*-triazolooxadiazines **2** and studied their chemical and spectroscopic behavior [1,8]. Continuing on this study we now report the synthesis of some *v*-triazolooxadiazinones **7** which constitute a new fused heterocyclic ring system, and that of the corresponding 1-aroylamino-*v*-triazole-5-carboxylic acids **5**, from which they are prepared.

Results and Discussion.

Mild hydrolysis [9] of *v*-triazolylisoimides **3** gave in good yields the 1-aroylamino-4-aryl-5-methyl-1,2,3-triazoles **4**. In their ir spectra there are absorption peaks at 3180-3210 cm^{-1} (ν NH) and at 1680-1710 cm^{-1} (ν CO), whereas in the ^1H nmr the CH_3-5 appeared at δ 2.4 and the NH proton at δ 12.0. In the mass spectrum they showed the molecular ion peak ($M^{+\cdot}$), and peaks corresponding to the ions M^+-28, M^+-69, Ar^1CO^+, $Ar^2CN^{+\cdot}$, $Ar^2C\equiv CCH_3^{+\cdot}$, and $Ar^2C\equiv\overset{+}{C}CH_2$.



3a - h

a, Ar^2 = Ar^1 = Ph
b, Ar^2 = Ph, Ar^1 = *p*-MeO-C_6H_4
c, Ar^2 = Ph, Ar^1 = *p*-Cl-C_6H_4
d, Ar^2 = Ph, Ar^1 = *o*-Cl-C_6H_4

4a - h

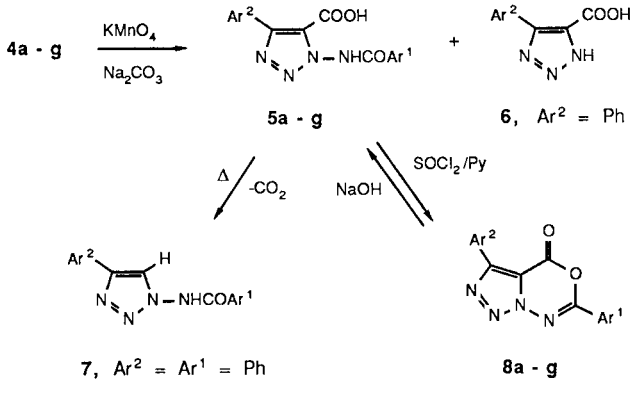
e, Ar^2 = Ph, Ar^1 = *p*-O_2N-C_6H_4
f, Ar^2 = Ph, Ar^1 = *o*-O_2N-C_6H_4
g, Ar^2 = *p*-MeO-C_6H_4, Ar^1 = Ph
h, Ar^2 = *p*-Br-C_6H_4, Ar^1 = Ph

Oxidation of compounds **4** with potassium permanganate under alkaline conditions gave in moderate yields (30-70%) the 1-aroylamino-4-aryl-1,2,3-triazole-5-carboxylic acids **5**. The yield on compounds **5** depends on the amount of the potassium permanganate used for the oxidation, as well as on the reaction time. Equivalent amounts of the reactants lead to a low yield of the acid **5** since a considerable amount of the starting triazolylamide **4** remained unoxidized, although all the permanganate was consumed. An over excess of the oxidizing reagent and a prolonged reaction time gave also a low yield on the acid **5**. In that case it is likely that oxidative degradation of the reaction products occurred, since the 4-phenyl-1,2,3-triazole-5-carboxylic acid **6** was isolated. The best results were obtained when the permanganate was in an excess of 4-6 equivalents and the reaction time was between 12-15 hours.

The triazole-5-carboxylic acids **5** showed in their ir spectra a broad absorption band at 3120-3300 cm^{-1} for the ν NH and at 1730-1740 cm^{-1} and at 1670-1700 cm^{-1} for the ν CO of the carboxy and amide carbonyls respectively. In their ^1H nmr spectra, besides the peaks of the aromatic protons at δ 7.0-8.2, they showed a broad peak at δ 12.1-12.6 for the NH proton, whereas the most mobile OH proton of the carboxylic group appeared at δ 4.2-5.0, in a broad peak together with the water protons of the solvent (DMSO-d_6). In the mass spectrum there was not the molecular ion peak but that of ions corresponding to a H_2O and/or a CO_2 loss from the molecular ion (M^+-18) and (M^+-44) respectively. Other prominent peaks were those corresponding to the ions M^+-72, $M^+-72-27$,

$Ar^2CN^{+\cdot}$, Ar^1CO^+, and $Ar^2C\equiv CH^{+\cdot}$ as the base peak.

Compounds **5** when heated above their melting points eliminated carbon dioxide giving the corresponding 1-aroylamino-4-aryl-1,2,3-triazoles **7**. This is a known behavior of the 1,2,3-triazole-4- or 5-carboxylic acids upon heating [10].



Conversion of compounds **5** to the 4*H*-[1,2,3]triazolo-[1,5-*d*][1,3,4]oxadiazin-4-ones **8** can be achieved either by their reaction with dicyclohexylcarbodiimide (DCC), which was mainly the method used by other authors for the preparation of the 1,3,4-oxadiazine-6-ones [3,7] or on treatment of compounds **5** with thionylchloride in the presence of pyridine. We found the thionyl chloride method most convenient for the preparation of compounds **8**, which gave very good yields, 70-90%, and pure products. The DCC-method gave also good yields, 60-80%, but the oxadiazinones thus prepared needed further purification, since they were contaminated with *N*,*N*'-dicyclohexylurea, which was coprecipitated from the reaction mixture.

The structure of compounds **8** was established on the basis of their analytical and spectral data. Thus, in the ir spectrum the CO group exhibits a strong band at 1780-1810 cm^{-1}, whereas the C=N bond of the oxadiazinone ring show a weak absorption band at 1620-1640 cm^{-1}. In the ^1H nmr spectra there were peaks only in the aromatic region at δ 7.1-8.4, in accord with structure **8**, and in the mass spectra, except of the molecular ion peak $M^{+\cdot}$, there were peaks corresponding to the ions M^+-28, M^+-56, and M^+-84, in agreement with the fragmentation pattern found in the analogous [8] compounds **2**. There were also peaks corresponding to the ions Ar^1CO^+, $Ar^1CN^{+\cdot}$, $Ar^2C\equiv CAr^1]^{+\cdot}$, and $Ar^2C\equiv C\text{-}CO^+$.

Hydrolysis of compound **8a** with a 10% solution of sodium hydroxide proceeded very easily, giving the corresponding 1,2,3-triazolo-5-carboxylic acid **5a**. On the contrary, **8a** remained unchanged when refluxed for 3 hours with 10% hydrochloric acid.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and were uncorrected. The ir spectra were recorded as Nujol mulls on a Perkin-Elmer 297 spectrometer. The ^1H nmr spectra were obtained on a Varian CFT-20 spectrometer in deuteriochloroform for compounds **3** and **8** and in deuteriochloroform + DMSO-d_6 for compounds **4** and **5**, with tetramethylsilane (TMS) as internal standard. The mass spectra were obtained on a Hitachi-Perkin-Elmer RMU 6L spectrometer and elemental microanalysis were performed with a Perkin-Elmer 240 CHN analyser. Light petroleum refers to that fraction bp 60-80 °C. Ether refers to diethyl ether.

Compounds **3**.

These were prepared by lead tetraacetate (LTA) oxidation of the corresponding bis-aroylhydrazones of the 1-arylpropane-1,2-dione as previously described [11] and their analytical and spectral data are in agreement with their structure. Analytical data of the new compounds are as follows:

Compound **3d**.

This compound had mp 147-149° (from methylene chloride-ether); ir (nujol): 1760 (C=O), 1655 (C=N) cm^{-1}.

Anal. Calcd. for $C_{23}H_{16}Cl_2N_4O_2$: C, 61.21; H, 3.57; N, 12.41. Found: C, 61.3; H, 3.6; N, 12.7.

Compound **3e**.

This compound had mp 185-187° (from methylene chloride-methanol); ir (nujol): 1765 (C=O), 1604 (C=N) cm^{-1}.

Anal. Calcd. for $C_{23}H_{16}N_6O_6$: C, 58.48; H, 3.41; N, 17.79. Found: C, 58.6; H, 3.5; N, 18.0.

Compound **3f**.

This compound had mp 172-173° (from methylene chloride-ether); ir (nujol): 1765 (C=O), 1650 (C=N) cm^{-1}.

Anal. Calcd. for $C_{23}H_{16}N_6O_6$: C, 58.48; H, 3.41; N, 17.79. Found: C, 58.7; H, 3.4; N, 17.9.

Hydrolysis of Compounds **3** to 1-Aroylamino-1,2,3-triazoles **4**.

According to a general procedure [9] 1 mmole of isoimide **3** was treated with 3-6 ml of concentrated hydrochloric acid at 50-60°. After 30 minutes the precipitate was filtered off and was treated on the filter with 10% sodium bicarbonate solution. With this treatment the corresponding benzoic acid was removed and on the filter remained compound **4**, washed with water several times, and recrystallized from the appropriate solvents. The yields were between 60-95%.

4-Phenyl-5-methyl-1-benzoylamino-1,2,3-triazole (**4a**).

Compound **3a** (3.0 g, 7.85 mmoles) and concentrated hydrochloric acid (5.0 ml), treated as above, gave **4a** (1.96 g, 90%), mp 197-199° (lit [12] 195-198°); ir (nujol): 3210 (NH), 1720 (C=O), 1610 cm^{-1}; nmr: δ 2.26 (3H, s, CH_3), 7.34-7.66 (6H, m), 7.70-7.82 (2H, m), 8.0-8.14 (2H, m), 12.2 (1H, br s, NH).

4-Phenyl-5-methyl-1-(*p*-methoxybenzoyl)amino-1,2,3-triazole (**4b**).

Compound **3b** (0.975 g, 2.2 mmoles) and concentrated hydrochloric acid (3 ml), treated as above, gave **4b** (0.61 g, 90%), mp 201-202° (from chloroform-diethyl ether); ir (nujol): 3210 (NH), 1680 (C=O), 1610 cm^{-1}; nmr: δ 2.40 (3H, s, CH_3), 3.85 (3H, s, CH_3O), 6.96 (2H, d, J = 8.9 Hz), 7.31-7.50 (3H, m), 7.67-7.79 (2H, m), 8.03 (2H, d, J = 8.9 Hz), 11.94 (1H, s, NH); ms: m/z 308 (M^+, 2), 280 (M^+-28, 2), 239 (3), 210 (3), 135 (48), 116 (78), 115 (100), 103 (56), 77 (32).

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.4; H, 5.2; N, 18.35.

4-Phenyl-5-methyl-1-(*p*-chlorobenzoyl)amino-1,2,3-triazole (**4c**).

Compound **3c** (2.182 g, 4.85 mmoles) and concentrated hydrochloric

acid (6 ml), treated as above, gave **4c** (1.33 g, 68%), mp 222-223° (from chloroform-ether); ir (nujol): 3180 (NH), 1710 (C=O), 1595 cm^{-1}; nmr: δ 2.43 (3H, s, CH_3), 7.38-7.50 (5H, m), 7.70-7.82 (2H, m), 7.99 (2H, d, J = 8.6 Hz), 12.37 (1H, s, NH); ms: m/z 314/312 (M^+, 0.2), 286/284 (M^+-28, 1), 245/243 (3), 141/139 (54), 116 (93), 115 (100), 103 (68), 77 (42).

Anal. Calcd. for $C_{16}H_{13}ClN_4O$: C, 61.44; H, 4.19; N, 17.91. Found: C, 61.2; H, 4.3; N, 17.9.

4-Phenyl-5-methyl-1-(*o*-chlorobenzoyl)amino-1,2,3-triazole (**4d**).

Compound **3d** (1.55 g, 3.4 mmoles) and concentrated hydrochloric acid (6 ml), treated as above, gave **4d** (0.997 g, 82%), mp 166-167.5° (from light petroleum-ether-chloroform 1:1:1); ir (nujol): 3200 (NH), 1710 (C=O), 1595 cm^{-1}; nmr: δ 2.49 (3H, s, CH_3), 7.28-7.50 (6H, m), 7.52-7.78 (3H, m), 11.70 (1H, s, NH); ms: m/z 314/312 (M^+, 0.2), 286/284 (M^+-28, 3), 245/243 (2), 141/139 (40), 116 (58), 115 (69), 103 (100), 76 (57).

Anal. Calcd. for $C_{16}H_{13}ClN_4O$: C, 61.44; H, 4.19; H, 17.91. Found: C, 61.4; H, 4.0; N, 18.1.

4-Phenyl-5-methyl-1-(*p*-nitrobenzoyl)amino-1,2,3-triazole (**4e**).

Compound **3e** (1.0 g, 2.12 mmoles) and concentrated hydrochloric acid (5 ml) heated at 90° for 2 hours and then treated as above, gave **4e** (0.637 g, 93%), mp 252-253° (from chloroform-methanol-ether); ir (nujol): 3200 (NH), 1720 (C=O), 1610 cm^{-1}; nmr: δ 2.45 (3H, s, CH_3), 7.36-7.55 (3H, m), 7.71-7.83 (2H, m), 8.33 (4H, s), 12.4 (v br s, NH); ms: m/z 323 (M^+, 0.1), 295 (M^+-28, 0.6), 254 (1), 150 (14), 116 (90), 115 (100), 103 (30), 77 (26).

Anal. Calcd. for $C_{16}H_{13}N_5O_3$: C, 59.44; H, 4.05; N, 21.66. Found: C, 59.3; H, 3.9; N, 21.55.

4-Phenyl-5-methyl-1-(*o*-nitrobenzoyl)amino-1,2,3-triazole (**4f**).

Compound **3f** (0.518 g, 1.1 mmoles) and concentrated hydrochloric acid (3 ml), heated at 70° for 30 minutes and then treated as above gave **4f** (0.29 g, 81%), mp 228-229° (from chloroform-methanol-light petroleum); ir (nujol): 3180 (NH), 1710 (C=O) cm^{-1}; nmr: δ 2.57 (3H, s, CH_3), 7.32-7.47 (3H, m), 7.54-7.80 (5H, m), 8.11-8.21 (1H, m), 12.38 (1H, s, NH); ms: m/z 323 (M^+, 0.7), 295 (M^+-28, 4), 254 (1.5), 207 (12), 150 (33), 116 (73), 115 (100), 103 (82), 77 (43), 76 (62).

Anal. Calcd. for $C_{16}H_{13}N_5O_3$: C, 59.44; H, 4.05; N, 21.66. Found: C, 59.5; H, 3.9; N, 21.5.

4-(*p*-Methoxyphenyl)-5-methyl-1-benzoylamino-1,2,3-triazole (**4g**).

Compound **3g** (0.825 g, 2.0 mmoles) and concentrated hydrochloric acid (3 ml), treated as above, gave **4g** (0.59 g, 95%), mp 206-208° (from chloroform-ether): ir (nujol): 3220 (NH), 1710 (C=O), 1610 cm^{-1}; nmr: δ 2.39 (3H, s, CH_3), 3.85 (3H, s, CH_3O), 6.99 (2H, d, J = 8.7 Hz), 7.48-7.60 (3H, m), 7.66 (2H, d, J = 8.7 Hz), 8.02-8.11 (2H, m), 12.14 (1H, s, NH); ms: m/z 308 (M^+, 2), 280 (M^+-28, 11), 239 (21), 146 (58), 134 (69), 133 (27), 105 (100), 77 (73).

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.2; H, 5.3; N, 18.3.

4-(*p*-Bromophenyl)-5-methyl-1-benzoylamino-1,2,3-triazole (**4h**).

Compound **3h** (1.0 g, 2.17 mmole) and concentrated hydrochloric acid (4 ml), treated as above, gave **4h** (0.70 g, 90%), mp 231-233° (from chloroform-methanol-ether); ir (nujol): 3260 (NH), 1675 (C=O), 1600 cm^{-1}; nmr: δ 2.42 (3H, s, CH_3), 7.49-7.62 (3H, m), 7.62 (4H, s), 8.02-8.12 (2H, m), 12.26 (1H, s, NH); ms: m/z 358/356 (M^+, 0.2), 330/328 (M^+-28, 0.2), 289/287 (3), 196/194 (21), 115 (53), 105 (100), 77 (58).

Anal. Calcd. for $C_{16}H_{13}BrN_4O$: C, 53.80; H, 3.67; N, 15.68. Found: C, 53.7; H, 3.65; N, 15.55.

Oxidation of Compounds **4** to 1-Aroylamino-1,2,3-triazole-5-carboxylic Acids **5**. General Procedure.

To a solution of compound **4** (2.0 to 4.0 mmoles) and sodium carbonate (0.15 g per mmoles) in water (25 ml per mmole) potassium permanganate (3-6 equivalents) are added and the mixture is refluxed until the solution is decolorized. A second and a third portion of small amounts of potassium permanganate are added and refluxing is continued for 12-15 hours in the whole. The manganese dioxide is filtered off and the remaining potassium permanganate is reduced by a 10% solution of sodium bisulfite. The clear solution is acidified with concentrated hydrochloric acid and the precipitated white solid is filtered and treated on the filter with a 10% solution of sodium bicarbonate, where the unreacted amide **4** remains in the filter. The sodium bicarbonate solution is acidified with concentrated hydrochloric acid to a $pH \sim 5$ and the precipitated acid **5** is filtered and washed with water. This acid was pure enough for further reaction. For elemental analysis it was recrystallized from the appropriate solvents.

1-Benzoylamino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5a**).

In a solution of **4a** (1.0 g, 3.6 mmoles) and sodium carbonate (0.6 g) in water (70 ml) potassium permanganate (2.5 g, 15.8 mmoles) were added in two portions. After refluxing for 12 hours the reaction mixture was treated as above to give **5a** (0.68 g, 58%), mp 162-164° dec (from chloroform-methanol-ether); ir (nujol): 3180 (NH), 1740, 1670 (C=O) cm^{-1}; nmr: δ 7.37-7.56 (6H, m), 7.87-8.11 (4H, m), 12.1 (1H, s, NH), 5.45 (br s, OH); ms: m/z 264 (M^+-44, 1), 236 (M^+-72, 9), 209 (13), 105 (99), 104 (43), 102 (78), 77 (100), 44 (86).

Anal. Calcd. for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 62.4; H, 3.75; N, 18.1.

1-(*p*-Methoxybenzoyl)amino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5b**).

In a solution of **4b** (0.616 g, 2 mmoles) and sodium carbonate (0.3 g) in water (50 ml) potassium permanganate (3.0 g, 19 mmoles) were added in three portions. After refluxing for 20 hours the reaction mixture was treated as above to give **5b** (0.225 g, 33%), mp 177-179° dec (from chloroform-methanol); ir (nujol): 3160 (NH), 1720 (C=O), 1665 (C=O), 1610 cm^{-1}; nmr: δ 3.87 (3H, s, CH_3O), 6.98 (2H, d, J = 8.9 Hz), 7.37-7.46 (3H, m), 7.85-7.95 (2H, m), 8.02 (2H, d, J = 8.9 Hz), 12.0 (s, NH), 4.20 (s, OH); ms: m/z 320 (M^+-18, 1), 294 (M^+-44, 1), 266 (M^+-72, 12), 239 (5), 135 (100), 104 (29), 102 (79), 77 (43), 44 (100).

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.2; H, 4.1; N, 16.4.

The acidified filtrates from the above reaction were extracted with ether which after drying and evaporation gave 4(5)-phenyl-1*H*-1,2,3-triazole-5(4)-carboxylic acid (**6**) (0.118 g, 18%), mp 200-202° dec (lit [13] 207.5° dec); ir (nujol): 3250, 2500-2800, 1730, 1690, 1610 cm^{-1}; ms: m/z 189 (M^+, 53), 172 (5), 145 (M^+-44, 34), 117 (100), 104 (12), 103 (8), 102 (6), 77 (26). Identification of **6** was made on the basis of its spectral data, as well from its mp, where it melted at 200-202° under carbon dioxide loss and the cooled melt crystallized and remelted at 139-142° (reported [14] mp for 5-phenyl-1,2,3-triazole, 143-145°).

1-(*p*-Chlorobenzoyl)amino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5c**).

In a solution of **4c** (0.624 g, 2 mmoles) and sodium carbonate (0.3 g) in water (50 ml) potassium permanganate (1.58 g, 10 mmoles) were added in one portion and refluxed for 12 hours. From the reaction mixture, treated as above, **5c** was isolated (0.438 g, 64%), mp 194-196° dec (from chloroform-methanol-ether); ir (nujol): 3120 (NH), 1750 (C=O), 1690 (C=O) cm^{-1}; nmr: δ 7.35-7.52 (5H, m), 7.87-7.95 (2H, m), 8.02 (2H, d, J = 8.6 Hz), 12.3 (s, NH), 4.23 (s, OH); ms: m/z 326/324 (M^+-18, 0.1), 300/298 (M^+-44, 0.2), 272/270 (2), 245/243 (1.5), 141/139 (33), 104 (22), 103 (28), 102 (100), 77 (28), 76 (44), 44 (98).

Anal. Calcd. for $C_{16}H_{11}ClN_4O_3$: C, 56.07; H, 3.24; N, 16.35. Found: C, 55.9; H, 3.05; N, 16.4.

1-(*o*-Chlorobenzoyl)amino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5d**).

In a solution of **4d** (0.624 g, 2 mmoles) and sodium carbonate (0.3 g) in water (50 ml) potassium permanganate (2.25 g, 17 mmoles) were added in three portions. After refluxing for 24 hours the reaction mixture was treated as above to give **5d** (0.255 g, 37%), mp 176-178° dec (from chloroform-methanol-light petroleum); ir (nujol): 3150 (NH), 1725 (C=O), 1680 (C=O) cm^{-1}; nmr: δ 7.37-7.50 (6H, m), 7.75-7.96 (3H, m), 12.2 (s,

NH), 4.60 (s, OH); ms: m/z 326/324 (M^+-18, 0.2), 300/298 (M^+-44, 0.3), 272/270 (17), 245/243 (5), 141/139 (73), 104 (76), 103 (72), 102 (100), 77 (88), 76 (59), 44 (99).

Anal. Calcd. for $C_{16}H_{11}ClN_4O_3$: C, 56.07; H, 3.24; N, 16.35. Found: C, 56.1; H, 3.1; N, 16.5.

From the acidified filtrates, after extracting with ether, and treating as above, **6** was obtained (0.085 g, 13%) mp 198-200°, identical to that obtained from the reaction of **4b** with potassium permanganate.

1-(*p*-Nitrobenzoyl)amino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5e**).

In a solution of **4e** (0.875 g, 2.7 mmoles) and sodium carbonate (0.3 g) in water (50 ml), potassium permanganate (1.9 g, 12 mmoles) were added in three portions. The mixture was refluxed for 20 hours and then treated as above to give **5e** (0.426 g, 45%), mp 173-175° dec (from chloroform-methanol); ir (nujol): 3250 (NH), 1740, 1720, 1690 (C=O) cm^{-1}; nmr: δ 7.35-7.47 (3H, m), 7.87-7.99 (2H, m), 8.22 (2H, d, J = 9.0 Hz), 8.36 (2H, d, J = 9.0 Hz), 4.40 (s, OH); ms: m/z 309 (M^+-44, 0.1), 281 (2), 254 (2), 150 (11), 104 (23), 103 (35), 102 (100), 77 (28), 76 (56), 44 (98).

Anal. Calcd. for $C_{16}H_{11}N_5O_5$: C, 54.40; H, 3.14; N, 19.82. Found: C, 54.6; H, 3.2; N, 19.9.

1-(*o*-Nitrobenzoyl)amino-4-phenyl-1,2,3-triazole-5-carboxylic Acid (**5f**).

In a solution of **4f** (0.824 g, 2.55 mmoles) and sodium carbonate (0.3 g) in water (50 ml), potassium permanganate (1.4 g, 8.5 mmoles) were added in two portions and refluxed for 12 hours. The reaction mixture was treated as above to give **5f** (0.53 g, 59%), mp 183-185° dec (from chloroform-methanol-ether); ir (nujol): 3300, 3190, 2400-2600, 1745, 1730, 1700 (C=O) cm^{-1}; nmr: δ 7.37-7.49 (3H, m), 7.63-7.97 (5H, m), 8.06-8.11 (1H, m), 12.63 (s, NH), 5.03 (s, OH); ms: m/z 335 (M^+-18, 0.1), 309 (M^+-44, 0.1), 281 (3), 254 (0.3), 150 (9), 104 (19), 103 (26), 102 (100), 77 (16), 76 (24), 44 (99).

Anal. Calcd. for $C_{16}H_{11}N_5O_5$: C, 54.40; H, 3.14; N, 19.82. Found: C, 54.5; H, 3.1; N, 19.8.

1-Benzoylamino-4-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxylic Acid (**5g**).

In a solution of **4g** (0.617 g, 2 mmoles) and sodium carbonate (0.3 g) in water (50 ml), potassium permanganate (0.8 g, 5 mmoles) were added. After refluxing for 15 hours the reaction mixture was treated as bove to give **5g** (0.24 g, 35%), mp 179-180° dec (from chloroform-methanol-ether); ir (nujol): 3180 (NH), 1740 (C=O), 1680 (C=O) cm^{-1}; nmr: δ 3.85 (3H, s, CH_3O), 6.95 (2H, d, J = 9.0 Hz), 7.45-7.58 (3H, m), 7.90 (2H, d, J = 9.0 Hz), 7.96-8.11 (2H, m), 12.11 (s, NH), 4.80 (s, OH); ms: m/z 320 (M^+-18, 0.1), 294 (M^+-44, 1), 266 (13), 239 (15), 134 (52), 133 (32), 132 (83), 105 (100), 77 (78), 44 (95).

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.57. Found: C, 60.4; H, 4.4; N, 16.6.

Preparation of 3,6-Diaryl-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-ones (**8**). General Procedure.

In a mixture of thionyl chloride (2 ml) and pyridine (0.2 ml) compound **5** (0.5-1.0 mmole) was added. The mixture was kept at room temperature for 20 minutes and then refluxed for about 30 minutes. Thionyl chloride was then removed by distillation with benzene and in the residue crushed iced was added. The precipitated triazolooxadiazinone **8** was filtered, washed with water and ether, and recrystallized from the appropriate solvents. In another way, the reaction mixture, after refluxing for 20 minutes, was poured into crushed ice, and after decomposition of thionyl chloride compound **8** separated, was filtered off, and washed with water and ether. The yields on compounds **8** were 70-90%.

3,6-Diphenyl-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8a**).

From compound **5a** (0.308 g, 1 mmole) in thionyl chloride (2 ml) and pyridine (0.2 ml), treated as above, **8a** was obtained (0.26 g, 90%), mp 255-256° (from chloroform-methanol); ir (nujol): 1795 (C=O), 1625 (C=N), 1620 cm^{-1}; nmr: δ 7.49-7.65 (6H, m), 8.22-8.46 (4H, m); ms: m/z 290 (M^+, 9), 262 (M^+-28, 1), 234 (1), 206 (23), 178 (29), 129 (100), 105 (77), 103 (22), 77 (45).

Anal. Calcd. for $C_{16}H_{10}N_4O_2$: C, 66.20; H, 3.47; N, 19.30. Found: C, 66.1; H, 3.3; N, 19.4.

Preparation of **8a** by Reaction of **5a** with Dicyclohexylcarbodiimide (DCC).

In a solution of **5a** (0.332 g, 1.07 mmoles) in dry tetrahydrofuran (THF) (15 ml), DCC (0.65 g, 3.1 mmoles) were added under stirring. After 10 minutes the precipitated urea was filtered off and THF was evaporated. The residue were treated with chloroform and ether to give **8a** (0.176 g, 57%), mp 256-257°, identical with that obtained in the preceding reaction. From the $CHCL_3$ filtrates another fragment was obtained (0.73 g), mp 220-250°, which was a mixture of **8a** and *N,N'*-dicyclohexylurea (ir, ms) and its purification was very difficult.

3-Phenyl-6-(*p*-methoxyphenyl)-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8b**).

A mixture of **5b** (0.169 g, 0.5 mmole) in thionyl chloride (1.5 ml) and pyridine (0.2 ml), treated as above, gave **8b** (0.13 g, 81%), mp 208-209° (from chloroform-ether); ir (nujol): 1790 (C=O), 1615 (C=N) cm^{-1}; nmr: δ 3.92 (3H, s, CH_3O), 7.06 (2H, d, J = 9.0 Hz), 7.49-7.58 (3H, m), 8.23 (2H, d, J = 9.0 Hz), 8.34-8.43 (2H, m); ms: m/z 320 (M^+, 4), 292 (M^+-28, 1), 264 (1), 236 (6), 208 (8), 135 (100), 133 (12), 129 (22), 103 (43), 102 (24), 77 (24).

Anal. Calcd. for $C_{17}H_{12}N_4O_3$: C, 63.75; H, 3.78; N, 17.49. Found: C, 63.7; H, 3.6; N, 17.45.

3-Phenyl-6-(*p*-chlorophenyl)-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8c**).

A mixture of **5c** (0.342 g, 1 mmole) in thionyl chloride (2 ml) and pyridine (0.2 ml), treated as above, gave **8c** (0.27 g, 83%), mp 237-238° (from chloroform-methanol); ir (nujol): 1800 (C=O), 1625 (C=N) cm^{-1}; nmr: δ 7.49-7.62 (5H, m), 8.22 (2H, d, J = 8.8 Hz), 8.34-8.46 (2H, m); ms: m/z 326/324 (M^+, 2), 298/296 (M^+-28, 1), 270/268 (1), 242/240 (13), 214/212 (19), 141/139 (53), 137 (55), 129 (96), 103 (100), 102 (32), 77 (39).

Anal. Calcd. for $C_{16}H_9ClN_4O_2$: C, 59.18; H, 2.79; N, 17.25. Found: C, 59.1; H, 2.7; N, 17.4.

3-Phenyl-6-(*o*-chlorophenyl)-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8d**).

Compound **5d** (0.15 g, 0.44 mmole) in thionyl chloride (1.5 ml) and pyridine (0.2 ml) treated as above, gave **8d** (0.12 g, 84%), mp 195-198° (from chloroform-ether); ir (nujol): 1805 (C=O), 1625 (C=N) cm^{-1}; nmr: δ 7.41-7.62 (6H, m), 7.91-8.03 (1H, m), 8.35-8.47 (2H, m); ms: m/z 326/324 (M^+, 2), 298/296 (M^+-28, 0.1), 270/268 (1), 242/240 (10), 214/212 (16), 141/139 (41), 137 (9), 129 (100), 103 (7), 102 (8), 77 (12), 75 (25).

Anal. Calcd. for $C_{16}H_9ClN_4O_2$: C, 59.18; H, 2.79; N, 17.25. Found: C, 59.2; H, 2.7; N, 17.3.

3-Phenyl-6-(*p*-nitrophenyl)-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8e**).

A mixture of **5e** (0.177 g, 0.5 mmole) in thionyl chloride (1.5 ml) and pyridine (0.2 ml), treated as above, gave **8e** (0.122 g, 73%), mp 275-277° (insoluble in all common solvents and therefore not recrystallized. Because of this, elemental analysis is given only for H and N); ir (nujol): 1780 (C=O), 1625 (C=N) cm^{-1}; nmr: δ insoluble in all solvents; ms: m/z 335 (m^+, 1), 307 (M^+-28, 0.5), 279 (0.4), 251 (8), 223 (4), 150 (7), 129 (100) 103 (8) 75 (17).

Anal. Calcd. for $C_{16}H_9N_5O_4$: H, 2.71; N, 20.89. Found: H, 2.65; N, 20.6.

3-Phenyl-6-(*o*-nitrophenyl)-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8f**).

A mixture of **5f** (0.30 g, 0.85 mmole) in thionyl chloride (2 ml) and pyridine (0.2 ml), treated as above, gave **8f** (0.25 g, 88%), mp 190-192° (from chloroform-ether); ir (nujol): 1810 (C=O), 1645 (C=O) cm^{-1}; nmr: δ 7.50-7.68 (3H, m), 7.80-7.99 (3H, m), 8.11-8.45 (3H, m); ms: m/z 335 (M^+, 6), 307 (M^+-28, 0.4), 279 (0.1), 251 (0.1), 223 (0.3), 150 (10), 129 (100), 105

(55), 104 (32), 103 (14), 77 (28), 76 (36), 75 (26).

Anal. Calcd. for $C_{16}H_9N_5O_4$: C, 57.32; H, 2.71; N, 20.89. Found: C, 57.25; H, 2.85; N, 20.8.

3-(*p*-Methoxyphenyl)-6-phenyl-4*H*-[1,2,3]triazolo[1,5-*d*][1,3,4]oxadiazin-4-one (**8g**).

A mixture of **5g** (0.342 g, 1.01 mmoles) in thionyl chloride (2 ml) and pyridine (0.2 ml), treated as above, gave **8g** (0.23 g, 71%), mp 221-223° (from chloroform-methanol); ir (nujol): 1805 (C=O), 1610 (C=N) cm^{-1}; nmr: δ 3.89 (3H, s, CH_3O), 7.05 (2H, d, J = 9.0 Hz), 7.50-7.68 (3H, m), 8.21-8.32 (2H, m), 8.38 (2H, d, J = 9.0 Hz); ms: m/z 320 (M^+, 6), 292 (M^+-28, 3), 264 (1), 236 (19), 208 (9), 159 (100), 133 (7), 132 (12), 105 (15), 103 (22), 77 (18).

Anal. Calcd. for $C_{17}H_{12}N_4O_3$: C, 63.75; H, 3.78; N, 17.49. Found: C, 63.7; H, 3.7; N, 17.2.

Hydrolysis of **8a** with 10% Sodium Hydroxide.

Compound **8a** (0.06 g) in 5 ml of 10% sodium hydroxide were heated in a steam bath for 10 minutes. All the solid went into solution, from which after acidifying with hydrochloric acid **5a** were isolated (0.026 g, 41%), mp 170-173°.

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