5-Oxazolones, II [1]

2,4-Diaryl-4-(2,4-dinitroaryl)-5(4*H*)-oxazolones: Synthesis and Acid-Catalyzed Transformation into 1-Hydroxy-1*H*-indazole Derivatives

Matteo D'Anello, Emanuela Erba, Maria Luisa Gelmi*, and Donato Pocar

Istituto di Chimica Organica – Facoltà di Farmacia dell'Università,
Via Venezian 21, 20133 Milano, Italy

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2,4-Diaryl-4-(2,4-dinitroaryl)-5(4*H*)-oxazolones **2** were prepared by arylation of the corresponding 5(4*H*)-oxazolones **1** under phase-transfer conditions with the corresponding 1-halo-2,4-dinitrobenzenes. 2,4-Diaryl-4-(3,5-dinitro-2-pyridyl)-5(4*H*)-oxazolones **5** were obtained similarly from the corresponding **1** and 2-chloro-3,5-dinitropyridine. On reaction with methanol and *p*-toluenesulfonic acid, oxazolones **2** rearranged to the corresponding 1-hydroxy-1*H*-indazole derivatives **8**. Under the same conditions oxazolones **5** afforded a mixture of the correspondingly substituted 1*H*-pyrazolo[4,3-*b*]pyridines **7** and substituted imidazo[1,5-*a*]pyridines **12**. In all cases the solvolysis reaction, yielding substituted glycine esters **9** and **11**, was competitive with the rearrangement. Reaction paths are discussed.

5-Oxazolone, II [1]. – 2,4-Diaryl-4-(2,4-dinitroaryl)-5(4*H*)-oxazolone: Synthese und säurekatalysierte Umwandlung in 1-Hydroxy-1*H*-indazol-Derivate

2,4-Diaryl-4-(2,4-dinitroaryl)-5(4*H*)-oxazolone **2** wurden durch Arylierung der entsprechenden 5(4*H*)-oxazolone **1** mit 1-Halo-2,4-dinitrobenzol-Derivaten unter Phasentransfer-Bedingungen dargestellt. 2,4-Diaryl-4-(3,5-dinitro-2-pyridyl)-5(4*H*)-oxazolone **5** wurden ähnlich aus den entsprechenden Derivaten **1** und 2-Chlor-3,5-dinitropyridin erhalten. Durch Reaktion mit Methanol und *p*-Toluolsulfonsäure lagerten die Oxazolone **2** in die entsprechenden 1-Hydroxy-1*H*-indazol-Derivate **8** um. Unter denselben Bedingungen lieferten die Oxazolone **5** eine Mischung der entsprechend substituierten 1*H*-Pyrazolo[4,3-*b*]pyridine **7** und der substituierten Imidazo[1,5-*a*]pyridine **12**. In allen Fällen trat als Konkurrenzreaktion Solvolyse zu substituierten Glycinestern **9** und **11** auf. Reaktionswege werden diskutiert.

Recently we described an alkylation method of 2,4-disubstituted 5(4*H*)-oxazolones under phase-transfer conditions [1]. An example of arylation was also reported. In the course of our research program on the use of 5-oxazolones in the synthesis of heterocyclic compounds, we extended the above procedure to a series of 4-(2-nitroaryl)-substituted 5(4*H*)-oxazolones aiming to explore their reactivity. We now report that these thermally stable oxazolones can be rearranged to indazoles under acidic catalysis.

1. Synthesis of Oxazolones

The reaction of compounds **1a**, **b**, **d**–**f** with 1-fluoro-2,4-dinitrobenzene in dichloromethane solution with an aqueous solution of sodium carbonate containing tetrabutylammonium bromide as phase-transfer catalyst at room temperature resulted in the formation of substituted 5(4*H*)-oxazolones **2a**, **b**, **f**, **g**, **h**. Products **2a**, **b**, **f**, **h** were easily purified by column chromatography, but **2g** partially rearranged when contacted with silica gel yielding **8f** as discussed later. Under analogous phase-transfer conditions **1a** and 2,4,6-trinitrochlorobenzene yielded oxazolone **2c**. From **1b** and 2-nitrobenzyl chloride product **3** was similarly obtained. When oxazolone **1c** was treated with 1-fluoro-2,4-dinitrobenzene under phase-transfer catalysis a mixture of **2e** and the isomeric 5(2*H*)-oxazolone derivative **4** was formed. This outcome exactly parallels the results obtained in homogeneous phase in the presence of triethylamine [2]. As further example of arylating reagent, 2-chloro-3,5-dinitropyridine afforded **5a** and **5b** from **1a** and **1f** under PTC conditions. They behaved similarly to **2g**, showing a very high rearrangement rate in the presence of silica gel which prevented the purification by chromatography. **5a** could be purified by crystallization and fully characterized. **5b** was identified by its IR data and studied without further purification. **1a** and methyl 2-chloro-3,5-dinitrobenzoate afforded **2d** and a by-product which was recognized as deriving from **1a** and two mol of the aromatic chloride with CO_2 elimination (M = 643). This compound was not studied further.

The oxazolones were identified on the basis of their analytical and/or spectroscopical data, mainly from the characteristic IR absorption in the ranges of 1800–1820 cm^{-1} (C=O). The IR CO absorption at a frequency above 1800 cm^{-1} was considered evidence of the 5(4*H*)-oxazolone structure, ruling out the alternative structure of 5(2*H*)-oxazolone (from arylation at C-2). To our knowledge a systematic study of the IR spectra of substituted 5-oxazolones has not been reported yet. However, from the available literature data [2,3] it is seen that substituted 5(2*H*)-oxazolones show a band at about 1800 cm^{-1} when the substituent on C-4 is an alkyl group, the frequency being lowered to 1775 cm^{-1} when the substituent is aryl. 5(4*H*)-Oxazolones show a CO absorption above 1800 cm^{-1} irrespective of the kind of the substituent. According to this, **6a,b**, which were prepared by an unequivocal synthesis [4], showed an absorption band at 1815 cm^{-1}.

2. Rearrangement of Oxazolones

Oxazolones **2g**, **5a** and **5b** underwent a partial transformation reaction during attempted chromatography on silica gel yielding **8f**, **7b**, and **7c**, respectively. **7b** was also obtai-

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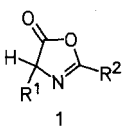
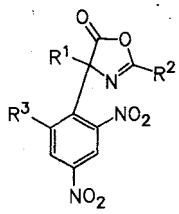


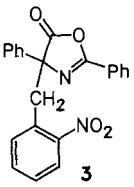
1

	R^1	R^2
a	Ph	4-$MeOC_6H_4$
b	Ph	Ph
c	*i*Pr	Ph
d	Ph	*i*Pr
e	4-ClC_6H_4	4-MeC_6H_4
f	4-$MeOC_6H_4$	4-MeC_6H_4



2

	R^1	R^2	R^3
a	Ph	Ph	H
b	Ph	4-$MeOC_6H_4$	H
c	Ph	4-$MeOC_6H_4$	NO_2
d	Ph	4-$MeOC_6H_4$	CO_2Me
e	*i*Pr	Ph	H
f	Ph	*i*Pr	H
g	4-ClC_6H_4	4-MeC_6H_4	H
h	4-$MeOC_6H_4$	4-MeC_6H_4	H



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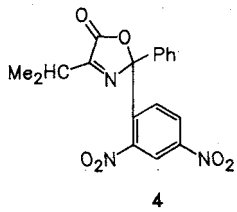

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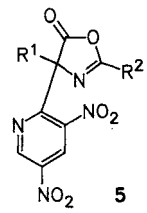

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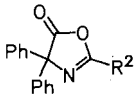
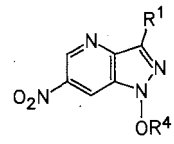


6a: R^2 = $C_6H_4NO_2$-(2)
b: R^2 = Ph

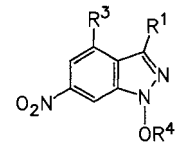
	R^1	R^2
a	Ph	4-$MeOC_6H_4$
b	4-$MeOC_6H_4$	4-MeC_6H_4

ned by stirring an ethyl acetate/cyclohexane solution of pure **5a** with silica gel. Products **7b**, **7c** and **8f** were identified by analytical and spectral data (typical IR absorption at 1765–1770 cm^{-1}). **8f** and **7b** were easily hydrolyzed to give the corresponding 1-hydroxy-1*H*-indazole **8d** and 1-hydroxy-1*H*-pyrazolopyridine **7a**, respectively. Since silica gel was found unable to promote the reaction of the other 4-(2-nitrophenyl)-substituted 5(4*H*)-oxazolones, other acidic catalysts were tested. Compound **2b** did not react in tetrahydrofuran in the presence of catalytic amount of *p*-toluenesulfonic acid (*p*TSA), even at the boiling point. In acetonitrile and xylene only extensive degradation was observed. On the contrary, **2b** reacted smoothly when refluxed in methanol solution with a catalytic amount of *p*TSA. Three products, namely **9a**, **10b**, and **8a**, were formed and could be separated. **9a** was readily characterized by its typical IR absorptions and **10b** by comparison with an authentic sample. The structure of the main reaction product, 6-nitro-3-phenyl-1*H*-indazol-1-ol (**8a**), was inferred from analytical and spectral data and confirmed both by agreement with literature data[2] and conversion into its 1-methoxy derivative **8g** with diazomethane. Other alkanols in place of methanol (ethanol or 1,2-ethanediol) afforded similar results. With 2-propanol or *tert*-butyl alcohol the reaction was slower and several unidentified by-products were formed besides **8**. The corresponding ester derivatives were not isolated.



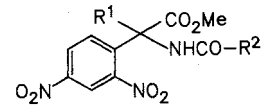
7

	R^1	R^4
a	Ph	H
b	Ph	4-$MeOC_6H_4CO$
c	4-$MeOC_6H_4$	4-MeC_6H_4CO
d	4-$MeOC_6H_4$	H



8

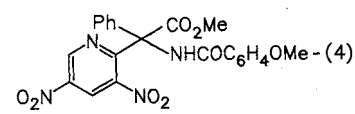
	R^1	R^3	R^4
a	Ph	H	H
b	Ph	NO_2	H
c	Ph	CO_2Me	H
d	4-ClC_6H_4	H	H
e	4-$MeOC_6H_4$	H	H
f	4-ClC_6H_4	H	4-MeC_6H_4CO
g	Ph	H	Me



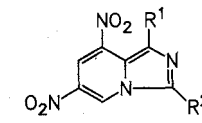
R^2–CO_2Me

	R^1	R^2
9a	Ph	4-$MeOC_6H_4$
b	*i*Pr	Ph
c	4-ClC_6H_4	4-MeC_6H_4

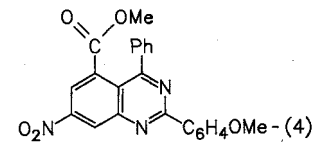
	R^2
10a	Ph
b	4-$MeOC_6H_4$
c	4-MeC_6H_4



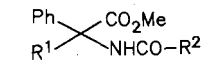
11



	R^1	R^2
12a	Ph	4-$MeOC_6H_4$
b	4-$MeOC_6H_4$	4-MeC_6H_4



13



	R^1	R^2
14a	2-$O_2NC_6H_4CH_2$	Ph
b	Ph	2-$O_2NC_6H_4$

The reaction was satisfactorily extended to oxazolones **2a,c,f,g,h**, and **4** which all give the corresponding 1-hydroxy-1*H*-indazoles **8a,b,d,e**. The correspondingly methyl benzoates **10a–c** were isolated and/or identified in the crude mixture. A minor or trace amount of the corresponding substituted glycine esters **9a,c** was present and could be separated by chromatography in most cases. Starting from **5a** and **5b** two main reaction products were formed,

namely **7a, 12a** with a minor amount of **11** and **7d, 12b**, respectively.

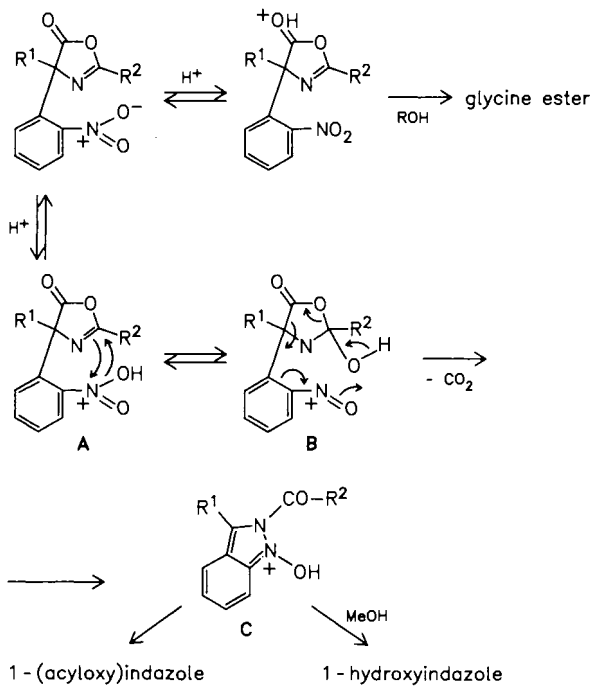
The structural assignment for compounds **12a,b** as imidazo[1,5-*a*]pyridines rests on ^{1}H-NMR and MS data. Besides the expected indazole derivative **8c**, oxazolone **2d** also produced compound **13**, to which the quinazoline structure was assigned on the basis of its ^{1}H-NMR spectrum which shows an AB system associated with the nuclear hydrogens and two singlets associated with the OCH_3 and CO_2CH_3 groups, respectively[5].

In the absence of *p*TSA, **2b** and **5a** reacted in boiling methanol affording **9a** and **11**, respectively, as the sole reaction products. Interestingly, oxazolone **2e** afforded exclusively the corresponding glycine methyl ester **9b** on reaction with methanol both in the presence and absence of *p*TSA. Oxazolones **3** and **6a** reacted with MeOH/*p*TSA affording exclusively **14a,b.**

3. Discussion and Proposed Reaction Path

In the arylation of **1** in all cases considered here only products of arylation at C-4 were obtained. This confirms the rule, first stated by Steglich[2], that the more reactive position of the oxazolone anion is C-4. As confirmed by **1c**, the arylation product at C-2 can by expected only when the more anion-stabilizing substituents is linked to it. As shown, compounds **2** and **5** are converted into indazoles or pyrazolopyridines, respectively, by action of acids in alkanol solution. 1-Hydroxy-1*H*-indazoles were first prepared by Steglich et al.[2] starting from **4** and analogues, namely from oxazolones bearing a 2-nitroaryl substituent at C-2, by a thermally induced rearrangement. However, the same authors found that the thermal rearrangement is not possible starting from oxazolones bearing the 2-nitroaryl group at C-4. This was confirmed by the fact that **2e** (i.e. the isomer of **4**) did not react and yielded only decomposition products at very high temperature. On our side we confirmed the thermal stability of compounds **2a, 5b,** and **6a,b** which were recovered unchanged after refluxing in toluene or anisol for several hours excluding that a thermally initiated rearrangement is responsible for the transformation of oxazolones **2** and **5**. In fact, the reaction occurs at a moderate temperature and both a protic solvent and an acidic catalyst must be present. This is confirmed by the failure of **2b** to give an indazole product when heated with *p*TSA in toluene or tetrahydrofuran and by the exclusive formation of solvolysis products from **2b** and **5a** in neat methanol. Though methanol/*p*TSA appeared to meet the best conditions, **8e** was also obtained by a less smooth reaction from **2h** in other alkanols or in dioxane/water/*p*TSA. The mechanism depicted in Scheme 1 is proposed.

Scheme 1



The nucleophilic attack of the oxazolone nitrogen to the protonated nitro group (intermediate **A**) accompanied by migration of a OH group to C-2 produces intermediate **B**. Subsequent rearrangement with carbon dioxide elimination forms **C** from which both 1-hydroxy- and 1-(acyloxy) derivatives can derive depending on the presence (deacylation of the *N*-acylated intermediate) or absence (transposition of the acyl group from nitrogen to oxygen) of the alkanol solvent. The greater reactivity of **2g** and **5a,b** is to be ascribed to the higher electron deficiency of C-4 making easier the carbon dioxide elimination step. Noticeably, 1-(acyloxy)-1*H*-indazoles are not intermediates in the formation of the 1-hydroxy compounds in methanol as shown by **7b** which resisted refluxing in methanol/*p*TSA for a longer time as required for the rearrangement of **2b**. In compounds **5a,b**, as a further possibility, the pyridine N-atom can attack C-2, eventually forming compounds **12** with loss of carbon dioxide. Both in the case of **2** and **5** the alternative solvolytic attack at the (protonated) lactone produces glycine esters (**9, 11, 14**). This process must prevail when electronic and/or steric and/or structural factors (as in the case of **2e, 3, 6a**) slow down or make impossible the intramolecular process, and should be unfavoured with less nucleophilic solvents. However 2-propanol and *tert*-butyl alcohol did not result in the expected increase of the yield of **8** owing to the formation of by-products.

Experimental

Melting points: Uncorrected, Büchi 150 (capillary) apparatus. – ^{1}H-NMR spectra: $(CH_3)_4Si$ as internal standard in the solvent indicated; Varian EM-390, 90 MHz. – Mass spectra: Varian Mat-311-A instrument. – IR spectra: Perkin-Elmer 197 spectrophotometer. – Thin layer chromatography (TLC): ready-to-use silica gel 60 F_{254} plates (Merck). – Column chromatographies: silica gel with the eluant indicated. – Physical, analytical, and spectroscopic data for new compounds are listed in Tables 1 and 2.

5(4*H*)-Oxazolones **1a**[6], **1b**[7], **1c**[8], **1d**[9], **2a**[1], **6b**[4], methyl 2-chloro-3,5-dinitrobenzoate[10], and 2-chloro-3,5-dinitropyridine[11] were obtained by known procedures.

4-(4-Chlorophenyl)-2-(4-methylphenyl)-5(4H)-oxazolone (**1e**): 2-(4-Chlorophenyl)-*N*-(4-methylbenzoyl)glycine was prepared by

Table 1. IR and ^{1}H-NMR data

	IR cm^{-1} a) NH or OH band (broad)	IR cm^{-1} a) C=O band	IR cm^{-1} a) C=N band	^{1}H NMR b)
1e			1660	c)
1f		1825,1795	1550	2.45 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 5.40 (s, 1H, CH), 6.80-8.05 (m, 8H, aromatic H)
2b		1815	1640	3.90 (s, 3H, OCH_3), 6.70-8.70 (m, 12H, aromatic H)
2c		1805	1645	3.90 (s, 3H, OCH_3), 6.90-8.15 (m, 9H, aromatic H), 8.70 (s, 2H, aromatic H)
2d		1810,1730	1640	3.65 (s, 3H, $COOCH_3$), 3.90 (s, 3H, OCH_3), 6.90-8.15, 8.50-8.65 (m, 11H, aromatic H)
2f		1805	1660	1.30 (d, J = 6 Hz, 6H, CH_3), 2.85 (sept, J = 6 Hz, 1H, CH), 7.30-8.55 (m, 8H, aromatic H)
2g		1820	1650	2.45 (s, 3H, CH_3), 7.15-8.50 (m, 11H, aromatic H)
2h		1820	1650	2.45 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.80-8.50 (m, 11H, aromatic H)
3		1820	1640	3.90, 4.25 (AB system, J = 13 Hz, 2H, CH_2), 7.00-8.10 (m, 14H, aromatic H)
5a		1815	1640	3.90 (s, 3H, OCH_3), 6.90-8.15 (m, 9H, aromatic H), 8.70, 9.55 (AX system, J = 3 Hz, 2H, aromatic H)
5b		1820	1640	2.50 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.85 7.95 (m, 8H, aromatic H), 8.68, 9.48 (AX system, J = 3 Hz, 2H, aromatic H)
6a		1810	1660	7.20-8.10 (m, 14H, aromatic H)
7a	3600-2400			7.35-8.55 (m, 5H, aromatic H), 8.85, 9.35 (AX system, J = 2 Hz, 2H, aromatic H)
7b		1760		3.95 (s, 3H, OCH_3), 7.00-8.55 (m, 9H, aromatic H), 8.60, 9.50 (AX system, J = 2 Hz, 2H, aromatic H)
7c		1775		2.50 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 7.00-8.50 (m, 8H, aromatic H), 8.55, 9.50 (AX system, J = 2 Hz, 2H, aromatic H)
7d	3100-2200			4.00 (s, 3H, OCH_3), 7.10-8.40 (m, 4H, aromatic H), 8.80, 9.35 (AX system, J = 2 Hz, 2H, aromatic H)
8b	3200-2300			7.25-7.50 (m, 5H, aromatic H), 8.55, 8.75 (AB system, J = 1.5 Hz, 2H, aromatic H)
8c	3200-2300	1720		3.40 (s, 3H, $COOCH_3$), 7.25-7.60 (m, 5H, aromatic H), 8.25, 8.60 (AB system, J = 1.5 Hz, 2H, aromatic H)
8d	3200-2300			7.45-8.50 (m, 7H, aromatic H)
8e	3200-2300			3.90 (s, 3H, OCH_3), 6.90-8.60 (m, 7H, aromatic H)
8f		1765		2.50 (s, 3H, CH_3), 7.25-8.35 (m, 11H, aromatic H)
8g	d)			4.30 (s, 3H, OCH_3), 7.35-8.65 (m, 8H, aromatic H)
9a	3240	1745	1635	3.85 (s, 3H, $COOCH_3$), 3.90 (s, 3H, OCH_3), 6.75 8.70 (m, 13H, aromatic H and NH exchangeable)
9b	3400	1740	1665	1.15 (d, J = 6 Hz, 6H, CH_3), 3.75 (sept, J = 6 Hz, 1H, CH), 3.85 (s, 3H, $COOCH_3$), 7.25-8.60 (m, 9H, aromatic H and NH exchangeable)
9c	3420	1750	1670	2.40 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.15-8.75 (m, 12H, aromatic H and NH exchangeable)
11	3400	1740	1660	3.90, 3.95 (2s, 3+3 H, OCH_3), 6.85-7.85 (m, 10H, aromatic H and NH exchangeable), 8.85, 9.50 (AX system, J = 2 Hz, 2H, aromatic H)
12a	d)			3.94 (s, 3H, OCH_3), 7.25-7.96 (m, 9H, aromatic H), 8.30, 9.55 (AX system, J = 2 Hz, 2H, aromatic H).
12b	d)			2.55 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.85 7.80 (m, 8H, aromatic H), 8.05,9.35 (AX system, J = 2 Hz, 2H, aromatic H).
13		1720		3.25 (s, 3H, $COOCH_3$), 3.90 (s, 3H, OCH_3), 6.90-7.80, 8.45-9.05 (m, 11H, aromatic H).
14a	3420	1725	1650	3.70 (s,3H,$COOCH_3$), 4.55 (m, 2H, CH_2), 7.20-7.90 (m, 14H, aromatic H and NH exchangeable)
14b	3360	1730	1660	3.80 (s, 3H, $COOCH_3$), 7.20-8.10 (m, 15H, aromatic H and NH exchangeable)

a) IR in nujol. – b) ^{1}H NMR in $CDCl_3$ solution except compounds 7a, 8b, 8c (CD_3OD) and 7d, 8d, 8e, 8g and 12a (C_3D_6O). – c) Owing to insolubility only a very poor spectrum was obtained. – d) No significant signals.

Schotten-Baumann method from 2-(4-chlorophenyl)glycine[12] and 4-methylbenzoyl chloride: yield 80%; m.p. 204–207°C (dec.). – IR (nujol): 3340 cm^{-1} (NH), 1725, 1620 (C=O). – ^{1}H NMR (DMSO): δ = 2.40 (s, 3H, CH_3), 5.75 (d, *J* = 8 Hz, 1H, CH), 7.15–8.00 (m, 9H, aromatic H and CO_2H), 9.00 (d, *J* = 8 Hz, 1H, NH). – The acylated glycine (12.0 g, 39.5 mmol) was suspended in Ac_2O (22 ml) under nitrogen and the suspension stirred at room temperature for 1 h. The yellow solid was filtered and washed with CH_2Cl_2 yielding 8.5 g (85%) of **1e**.

4-(4-Methoxyphenyl)-2-(4-methylphenyl)-5(4H)-oxazolone (**1f**): 2-(4-Methoxyphenyl)-*N*-(4-methylbenzoyl)glycine was obtained by the Schotten-Baumann procedure from 2-(4-methoxyphenyl)glycine[13] and 4-methylbenzoyl chloride: yield 94%; m.p. 178–180°C. – IR (nujol): 3345 cm^{-1} (NH), 1720, 1610 (C=O). – ^{1}H NMR (DMSO): δ = 2.40 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 5.55 (d, *J* = 8 Hz, 1H, CH), 6.85–7.90 (m, 9H, aromatic H and CO_2H), 8.85 (d, *J* = 8 Hz, 1H, NH).

$C_{17}H_{17}NO_4$ (299.3) Calcd. C 68.21 H 5.73 N 4.68
Found C 68.43 H 5.84 N 4.54

The glycine derivative (12.0 g, 40 mmol) was suspended in Ac_2O (30 ml) and the suspension stirred under N_2 for 4 h. The solid product was filtered and washed with *n*-pentane, then recrystallized affording pure **1f** (8.5 g, 76%).

4-(2,4-Dinitrophenyl)-2-(4-methoxyphenyl)-4-phenyl-5(4H)-oxazolone (**2b**): A solution of $Na_2CO_3 \cdot 10\ H_2O$ (2.0 g, 7.3 mmol) in H_2O (10 ml) was emulsified, under vigorous stirring and at room temperature, with a solution of 1-fluoro-2,4-dinitrobenzene (800 mg, 4.25 mmol) and tetrabutylammonium bromide (20.0 mg, 0.06 mmol) as phase-transfer catalyst in CH_2Cl_2 (12 ml). Compound **1a** (1.5 g, 5.6 mmol) was added in several portions during 1 h. The layers were separated and the aqueous phase was washed with CH_2Cl_2 (10 ml). The combined organic solutions were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on silica gel starting with petroleum ether to which CH_2Cl_2 was gradually added. The main fraction was recrystallized yielding 0.70 g (35%[14]) of **2b**.

2-(4-Methoxyphenyl)-4-phenyl-4-(2,4,6-trinitrophenyl)-5(4H)-oxazolone (**2c**) was prepared and elaborated analogously to **2b** using H_2O (10 ml)/CH_2Cl_2 (12 ml), $Na_2CO_3 \cdot 10\ H_2O$ (2.0 g, 7.3 mmol), **1a** (1.8 g, 6.7 mmol), 1-chloro-2,4,6-trinitrobenzene (1.05 g, 4.25 mmol), and the ammonium catalyst (19 mg, 0.059 mmol); reaction time 1 h. After chromatography with petroleum ether/CH_2Cl_2

Table 2. Physical and analytical data

Compd.	M. p. °C	Crystallization solvent	M. w.	Molecular formula	Analysis Calcd. C	H	N	Found C	H	N
1e	168-170[a]	b)	285.72	$C_{16}H_{12}NO_2Cl$	67.25	4.23	4.90	66.88	4.26	4.82
1f	111-113	C_6H_6-n-pentane	281.30	$C_{17}H_{15}NO_3$	72.58	5.37	4.98	72.36	5.35	4.79
2b	147-148	CH_2Cl_2/iPr_2O	433.36	$C_{22}H_{15}N_3O_7$	60.97	3.49	9.70	60.58	3.37	9.67
2c	172-173	CH_3O/n-pentane	478.36	$C_{22}H_{14}N_4O_9$	55.23	2.95	11.71	55.18	2.97	11.49
2d	85-87[a]	$CHCl_3$/n-pentane	491.40	$C_{24}H_{17}N_3O_9$	58.66	3.49	8.55	58.59	3.71	8.37
2f	95-96	CH_2Cl_2/iPr_2O	369.32	$C_{18}H_{15}N_3O_6$	58.53	4.09	11.38	58.39	3.97	11.40
3	116	CH_2Cl_2/Et_2O	372.36	$C_{22}H_{16}N_2O_4$	70.96	4.33	7.52	70.86	4.44	7.47
5a	168-170	$CHCl_3$/n-pentane	434.35	$C_{21}H_{14}N_4O_7$	58.06	3.25	12.90	58.22	3.33	12.78
5b	150-151	CH_2Cl_2/iPr_2O	448.38	$C_{22}H_{16}N_4O_7$	58.93	3.60	12.50	58.80	3.58	12.10
6a	98-100	C_2H_5OH	358.34	$C_{21}H_{14}N_2O_4$	70.38	3.94	7.82	70.19	3.89	7.71
7a	238-240	CH_3OH	256.22	$C_{12}H_8N_4O_3$	56.25	3.15	21.87	56.41	3.24	21.76
7b	217-220[a]	$CHCl_3$	390.34	$C_{20}H_{14}N_4O_5$	61.53	3.61	14.35	61.15	3.46	14.32
7c	190-192[a]	CH_2Cl_2	404.37	$C_{21}H_{16}N_4O_5$	62.37	3.99	13.86	61.94	3.92	13.58
7d	215-218[a]	$(CH_3)_2CO$	286.24	$C_{13}H_{10}N_4O_4$	54.54	3.52	19.57	54.10	3.74	19.08
8b	208[a]	CH_3OH	300.23	$C_{13}H_8N_4O_5$	52.00	2.68	18.66	52.04	2.71	18.33
8c	140	iPr_2O	313.26	$C_{15}H_{11}N_3O_5$	57.50	3.54	13.41	57.71	3.86	13.01
8d	234-235	CH_3OH	289.67	$C_{13}H_8N_3O_3Cl$	53.90	2.78	14.51	53.49	2.74	14.26
8e	218-220[a]	CH_3OH	285.25	$C_{14}H_{11}N_3O_4$	58.94	3.89	14.73	58.63	4.13	14.30
8f	186-189[a]	$CHCl_3$	407.80	$C_{21}H_{14}N_3O_4Cl$	61.85	3.46	10.30	61.83	3.54	10.31
8g	107-108	MTBE/n-pentane	269.25	$C_{14}H_{11}N_3O_3$	62.45	4.12	15.61	62.05	4.05	15.26
9a	155-157	CH_3OH/n-pentane	465.41	$C_{23}H_{19}N_3O_8$	59.35	4.11	9.03	59.31	4.07	9.12
9b	79-81[a]	CH_3OH/n-pentane	401.37	$C_{19}H_{19}N_3O_7$	56.85	4.77	10.47	56.68	4.65	10.90
9c	135-138[a]	CH_2Cl_2/iPr_2O	483.85	$C_{23}H_{18}N_3O_7Cl$	57.09	3.75	8.68	56.80	3.98	8.43
11	112-115[a]	CH_2Cl_2/iPr_2O	466.40	$C_{22}H_{18}N_4O_8$	56.65	3.89	12.01	57.03	4.04	11.89
12a	249-250	CH_3OH	390.34	$C_{20}H_{14}N_4O_5$	61.53	3.61	14.35	61.73	3.54	14.38
12b	195-196	CH_3OH	404.37	$C_{21}H_{16}N_4O_5$	62.37	3.99	13.86	62.06	3.85	13.54
13	247-250	$CHCl_3$	415.39	$C_{23}H_{17}N_3O_5$	66.50	4.12	10.12	66.12	3.90	10.18
14a	130	CH_2Cl_2/iPr_2O	404.41	$C_{23}H_{20}N_2O_5$	68.30	4.98	6.93	68.65	5.20	6.93
14b	123-124	$CHCl_3/iPr_2O$	390.34	$C_{22}H_{18}N_2O_5$	67.69	4.61	7.18	67.30	4.58	7.08

[a] Decomposition. — [b] See Experimental.

(1:0 to 0:1 v/v) the main fraction was recrystallized to give **2c** (700 mg, 34%[14]).

4-[2-(Methoxycarbonyl)-4,6-dinitrophenyl]-2-(4-methoxyphenyl)-4-phenyl-5(4H)-oxazolone (**2d**) was obtained from methyl 2-chloro-3,5-dinitrobenzoate (1.8 g, 7.0 mmol) and **1a** (2.50 g, 0.35 mmol) under PTC conditions [H_2O (15 ml)/CH_2Cl_2 (15 ml), Na_2CO_3 (1.5 g, 14.0 mmol), catalyst (66 mg, 0.20 mmol)] as described for **2b**; reaction time 2 h. The chromatography with *n*-pentane/Et_2O (1:0 to 0:1 v/v) afforded **2d** which was recrystallized yielding 550 mg (16%[14]). A more polar product was obtained: m.p. 175–178°C (dec.). — IR (nujol): 1780 cm^{-1} (C=O). — MS: m/z = 643 (M^+). Not further identified.

4-(2,4-Dinitrophenyl)-4-isopropyl-2-phenyl-5(4H)-oxazolone (**2e**) *and 2-(2,4-Dinitrophenyl)-4-isopropyl-2-phenyl-5(2H)-oxazolone* (**4**) were synthesized as described for **2b** under PTC conditions [H_2O (10 ml)/CH_2Cl_2 (20 ml), $Na_2CO_3 \cdot 10\ H_2O$ (1.8 g, 6.4 mmol); catalyst (32 mg, 0.10 mmol)] from **1c** (1.0 g, 4.9 mmol) and 1-fluoro-2,4-dinitrobenzene (0.80 g, 4.3 mmol); reaction time 2 h. The crude mixture was crystallized from *tert*-butyl methyl ether/*n*-pentane yielding **4** which was purified further from CCl_4 (450 mg, 25%[14]); m.p. 115°C (ref.[2] 114°C). The mother liquor was chromatographed (cyclohexane/ethyl acetate, 100:7) yielding two main fractions containing **2e**, which was purified by washing with *tert*-butyl methyl ether/*n*-pentane yielding 450 mg (28%[14]); m.p. 111–113°C (ref.[2] 116°C) and **4** which after crystallization from CCl_4 yielded 100 mg (6%[14]).

4-(2,4-Dinitrophenyl)-2-isopropyl-4-phenyl-5(4H)-oxazolone (**2f**) was obtained under PTC conditions [H_2O (15 ml)/CH_2Cl_2 (20 ml), $Na_2CO_3 \cdot 10\ H_2O$ (2.0 g, 7.0 mmol) and the catalyst (30 mg, 0.09 mmol)] from **1d** (1.0 g, 4.9 mmol) and 1-fluoro-2,4-dinitrobenzene (0.60 g, 3.3 mmol) as described above; reaction time 2 h. The crude reaction mixture was chromatographed (cyclohexane/Et_2O, 4:1) and the main fraction was recrystallized yielding 140 mg (49%[14]) of **2f**.

4-(4-Chlorophenyl)-4-(2,4-dinitrophenyl)-2-(4-methylphenyl)-5(4H)-oxazolone (**2g**) *and 3-(4-Chlorophenyl)-1-(4-methylbenzoyloxy)-6-nitro-1H-indazole* (**8f**): By reaction of **1e** (2.5 g, 8.7 mmol) with 1-fluoro-2,4-dinitrobenzene (1.6 g, 8.7 mmol) under PTC conditions [H_2O (15 ml)/CH_2Cl_2 (25 ml), Na_2CO_3 (1.3 g, 12.5 mmol), and the catalyst (40 mg, 0.12 mmol)] after 2 h and after work-up (as above), crude **2g** was obtained [IR (nujol): 1820 cm^{-1} (C=O)]. Every attempt to crystallize failed and the compound was used in this form for subsequent reactions. In another experiment the crude **2g** was chromatographed (cyclohexane/ethyl acetate 17:3), obtaining a main fraction which after evaporation afforded **8f** (0.70 g, 20%[14]).

4-(2,4-Dinitrophenyl)-4-(4-methoxyphenyl)-2-(4-methylphenyl)-5(4H)-oxazolone (**2h**): Under PTC conditions [H_2O (10 ml)/CH_2Cl_2

(20 ml), Na_2CO_3 (1.7 g, 16 mmol), and catalyst (32 mg, 0.10 mmol)] **1f** (2.5 g, 8.89 mmol) and 1-fluoro-2,4-dinitrobenzene (1.52 g, 8.2 mmol) reacted to afford after 2 h a crude mixture which was chromatographed twice with cyclohexane/AcOEt (7:1) and petroleum ether/CH_2Cl_2 (1:0 to 0:1 v/v). **2h** (1.9 g, 52%[14]) was obtained as a sticky product which could not be brought to crystallization and was used directly for the acid-catalyzed rearrangement.

4-(3,5-Dinitro-2-pyridyl)-2-(4-methoxyphenyl)-4-phenyl-5(4H)-oxazolone (**5a**) was prepared as described for **2b** starting from **1a** (3.0 g, 11.2 mmol) and 2-chloro-3,5-dinitropyridine (2.3 g, 11.3 mmol) under PTC conditions [H_2O (15 ml)/CH_2Cl_2 (30 ml), Na_2CO_3 (2.4 g, 22.6 mmol), catalyst (40 mg, 0.13 mmol)]; reaction time 1 h. The crude mixture was taken up in CH_2Cl_2 (20 ml) and the solution was kept at room temperature for 24 h. A precipitate was formed. After filtration the solid was recrystallized affording pure **5a** (3.3 g, 68%[14]).

5a *and 1-(4-Methoxybenzoyloxy)-6-nitro-3-phenyl-1H-pyrazolo[4,3-b]pyridine* (**7b**): By purification of the crude reaction mixture obtained from the reaction described in the above section on a silica gel column (petroleum ether/CH_2Cl_2 1:2) a partial conversion of **5a** into **7b** took place. **7b** was eluted first (higher R_f) (350 mg, 20%[14]). **5a** (lower R_f) was obtained in the second fraction (410 mg, 21%[14]).

4-(3,5-Dinitro-2-pyridyl)-4-(4-methoxyphenyl)-2-(4-methylphenyl)-5(4H)-oxazolone (**5b**) *and 3-(4-Methoxyphenyl)-1-(4-methylbenzoyloxy)-6-nitro-1H-pyrazolo[4,3-b]pyridine* (**7c**): The oxazolone **1f** (2.5 g, 8.9 mmol) was treated with 2-chloro-3,5-dinitropyridine (1.65 g, 8.09 mmol) under PTC conditions [H_2O (10 ml)/CH_2Cl_2 (20 ml), Na_2CO_3 (1.4 g, 13.2 mmol), and the catalyst (32 mg, 0.10 mmol)]; reaction time 1 h. After work-up, as described for **2b**, the mixture was chromatographed with *n*-pentane/CH_2Cl_2 (1:0 to 0:1 v/v). A main fraction was obtained containing both **5b** and **7c**. After evaporation of the solvent, the residue was taken up with CH_2Cl_2 (20 ml) and pure **7c** was precipitated (910 mg, 25%[14]). By adding iPr_2O to the mother liquor, a mixture of **5b** and **7c** was again precipitated (500 mg). The mother liquor was evaporated and the residue crystallized affording pure **5b** (800 mg, 22%[14]).

4-(2-Nitrobenzyl)-2,4-diphenyl-5(4H)-oxazolone (**3**): By treating **1b** (1.3 g, 5.6 mmol) with 2-nitrobenzyl chloride (720 mg, 42 mmol) under PTC conditions [H_2O (10 ml)/CH_2Cl_2 (15 ml), $Na_2CO_3 \cdot 10\ H_2O$ (3.6 g, 12 mmol), catalyst (140 mg, 0.40 mmol)], reaction time 1 h, pure **3** (600 mg, 38%[14]) was obtained after chromatography (petroleum ether/CH_2Cl_2 1:0 to 0:1 v/v) and recrystallization.

2-(2-Nitrophenyl)-4,4-diphenyl-5(4H)-oxazolone (**6a**): 2-Nitrobenzoyl chloride (3.3 g, 18 mmol) and 2,2-diphenylglycine (1.2 g, 5.5 mmol) were suspended in pyridine (15 ml) under vigorous stirring at 60–70°C for 7 h. After cooling, the mixture was filtered and the mother liquor diluted with H_2O (15 ml). The separated oil, after scratching, yielded a solid product which was filtered and washed with hot ethanol giving **6a** (1.1 g, 58%).

Acid-Catalyzed Reactions of Oxazolones **2** *and* **5**. *General Procedure:* Compounds **2** and **5** were rearranged to the corresponding heterocyclic compounds **8** and **7**, respectively, and/or solvolyzed to the corresponding glycine esters **9**, **11**, and **14**, respectively, by refluxing in MeOH to which a catalytic amount of *p*-toluenesulfonic acid (*p*TSA) had been added. In most cases products **7** or **8** were obtained as a precipitate on cooling of the reaction solution. The mother liquor was evaporated and the residue chromatographed to isolate the other by-products when present, namely **9**, **10**, and **11**, besides a further crop of the indazole product. The esters **10**, which were formed with a yield of the same magnitude order as the corresponding indazole compounds, were identified by comparison (TLC) with an authentical sample.

6-Nitro-3-phenyl-1H-indazol-1-ol (**8a**)

a) According to the general procedure **2a** (1.5 g, 3.7 mmol) in MeOH/*p*TSA (20 ml) afforded, after 2 h and cooling at −10°C, indazole **8a** (500 mg). The mother liquor after solvent evaporation was taken up with CCl_4 obtaining another crop of pure **8a** (400 mg). Total yield of **8a** 95%, m.p. 224–225°C (ref.[2] 215°C).

b) According to the general method, **2b** (550 mg, 1.15 mmol) in MeOH/*p*TSA (10 ml) afforded, after 2 h, pure **8a** (110 mg) as a precipitate. By chromatography of the mother liquor residue (*n*-pentane/CH_2Cl_2 1:0 to 0:1 v/v) the following fractions were obtained: **10b** (150 mg, 78%), **9a** (50 mg, 9%), and **8a** (120 mg). Total yield of **8a**: 78%.

c) According to the general procedure, **2f** (250 mg, 0.68 mmol) in MeOH/*p*TSA (12 ml) afforded, after 30 min and after solvent evaporation, a crude product which was purified by washing with CCl_4 and then by crystallization from MeOH yielding pure **8a** (160 mg, 92%).

d) According to the general method compound **4** (250 mg, 0.67 mmol) was refluxed in MeOH/*p*TSA (12 ml) for 3 h. After solvent evaporation the crude mixture was washed with CCl_4 and the yellow solid was filtered and recrystallized from MeOH yielding pure **8a** (150 mg, 88%).

4,6-Dinitro-3-phenyl-1H-indazol-1-ol (**8b**): According to the general method, **2c** (500 mg, 1.0 mmol) in MeOH/*p*TSA (20 ml) yielded, after 3 h and after chromatography (*n*-pentane/CH_2Cl_2 1:0 to 0:1 v/v), **10b** (160 mg, 93%) and **8b** (160 mg, 52%).

Methyl 1-Hydroxy-6-nitro-3-phenyl-1H-indazole-4-carboxylate (**8c**) *and Methyl 2-(4-Methoxyphenyl)-7-nitro-4-phenyl-5-quinazolinecarboxylate* (**13**): According to the general procedure, **2d** (650 mg, 1.3 mmol) in MeOH/*p*TSA (15 ml) afforded in 10 h compound **13** as an orange precipitate (180 mg, 33%). – MS: *m/z* (%) = 415 (68, M^+), 400 (9, $M^+ - CH_3$), 384 (8, $M - OCH_3$), 356 (30, $M - CO_2CH_3$), 310 (26, $M - CO_2CH_3 - NO_2$), 236 (5), 208 (30), 169 (34), 133 (33), 75 (100). – Chromatography of the residue from the mother liquor (petroleum ether/CH_2Cl_2 1:0 to 0:1 v/v), afforded **10b** (90 mg, 48%), unreacted **2d** (100 mg), and **8c** (210 mg, 60%).

Methyl N-Benzoyl-2-(2,4-dinitrophenyl)valinate (**9b**): According to the general procedure, **2e** (300 mg, 0.80 mmol) in MeOH/*p*TSA (15 ml) afforded after 16 h a crude mixture which was chromatographed (petroleum ether/acetone 3:1) yielding pure **9b** (200 mg, 62%).

3-(4-Chlorophenyl)-6-nitro-1H-indazol-1-ol (**8d**): Crude **2g**, prepared as above from **1e** and 1-fluoro-2,4-dinitrobenzene (3.6 mmol), was refluxed in MeOH/*p*TSA (20 ml) for 3 h. Pure **8d** (440 mg, 43%) separated out from the solution. The mother liquor was chromatographed (petroleum ether/Et_2O 1:0 to 0:1 v/v) and three main fractions were obtained: **10c** (210 mg, 39%); **9c** (150 mg, 9%); **8d** (100 mg, 10%[14]).

3-(4-Methoxyphenyl)-6-nitro-1H-indazol-1-ol (**8e**): The oxazolone **2h** (1.6 g, 3.57 mmol) in MeOH/*p*TSA (20 ml) was refluxed, according to the general procedure, for 3 h and kept at room temperature. A solid was formed, filtered and washed with Et_2O (2 × 10 ml) yielding pure **8e** (600 mg, 59%). The residue of the mother liquor was chromatographed (petroleum ether/CH_2Cl_2 1:0 to 0:1 v/v). Two main fractions were obtained: **10c** (250 mg, 47%) and pure **8e** (200 mg, 20%).

6-Nitro-3-phenyl-1H-pyrazolo[4,3-b]pyridin-1-ol (**7a**) *and 3-(4-Methoxyphenyl)-6,8-dinitro-1-phenylimidazo[1,5-a]pyridine* (**12a**): According to the general procedure, **5a** (600 mg, 1.38 mmol) was

refluxed in MeOH/*p*TSA (20 ml). A dark solid was formed which was filtered from the warm solution and then washed with Et_2O (2 × 10 ml) yielding **12a** (190 mg, 34%). – MS: *m/z* (%) = 390 (3, M^+), 135 (100), 77 (14). Compound **7a** (100 mg) was separated from the concentrated methanolic solution. The mother liquor was chromatographed (cyclohexane/acetone 4:1). Three main fractions were obtained: **10b** (90 mg, 39%); **11** (70 mg, 11%), and **7a** (170 mg, total yield 79%).

3-(4-Methoxyphenyl)-6-nitro-1H-pyrazolo[4,3-b]pyridin-1-ol (**7d**) *and 1-(4-Methoxyphenyl)-3-(4-methylphenyl)-6,8-dinitroimidazo[1,5-a]pyridine* (**12b**): **5b** (1.6 g, 3.57 mmol) was treated according to the general method with MeOH/*p*TSA (10 ml). A mixture was obtained which was chromatographed (petroleum ether/CH_2Cl_2/acetone). Three main fractions were obtained: **10c** (80 mg, 48%); **12b** as a dark solid (100 mg, 22%), and **7d** (150 mg, 47%).

Methyl N-Benzoyl-2-(2-nitrophenyl)-2-phenylalaninate (**14a**): According to the general procedure compound **3** (200 mg, 0.54 mmol) in MeOH/*p*TSA (10 ml) afforded, after 4 h, **14a** (135 mg, 62%).

Methyl N-(2-Nitrobenzoyl)-2,2-diphenylglycinate (**14b**): According to the general procedure compound **6a** (500 mg, 1.4 mmol) in MeOH/*p*TSA (12 ml) afforded, after 2 h, **14b** (380 mg, 69%).

1-Methoxy-6-nitro-3-phenyl-1H-indazole (**8g**): A solution of **8a** (350 mg, 1.4 mmol) in absol. MeOH (20 ml) was cooled to 0°C. An ethereal solution of diazomethane was added dropwise until no more N_2 was evolved. The reaction course was checked by TLC (cyclohexane/ethyl acetate 7:3). After evaporation of the solvent and recrystallization, compound **8g** (290 mg, 79%) was obtained.

Hydrolysis of **7b**: The suspension of **7b** (100 mg, 0.25 mmol) in a mixture of H_2O (1 ml), MeOH (5 ml), and NaOH (150 mg, 3.75 mmol) was stirred at room temperature for 10 h. Water (15 ml) was added to the red solution. The aqueous layer was extracted with CH_2Cl_2 (20 ml). From the aqueous solution, made acidic with HCl conc., a solid, corresponding to **7a** (40 mg, 61%), separated out and was filtered. The acidic solution was extracted with *tert*-butyl methyl ether giving 4-methoxybenzoic acid (30 mg, 84%) which was identified by comparison with an authentic sample.

Hydrolysis of **8f**: Compound **8f** (102 mg, 0.25 mmol) was stirred at room temperature with H_2O (1 ml), MeOH (5 ml), and NaOH (150 mg, 3.75 mmol) for 10–12 h. After dilution with H_2O (15 ml) the reaction mixture was extracted with CH_2Cl_2 (20 ml). The aqueous layer was made acidic with HCl and the precipitate was filtered yielding **8d** (50 mg, 69%). The solution was extracted with CH_2Cl_2 giving *p*-toluic acid (28 mg, 1%) which was identified by comparison with an authentic sample.

Solvolysis of **2b**: A solution of **2b** (165 mg, 0.40 mmol) in MeOH (15 ml) was refluxed for 48 h. After solvent evaporation and recrystallization, pure **9a** (140 mg, 79%) was obtained.

CAS Registry Numbers

1a: 28172-58-9 / **1b**: 28687-81-2 / **1c**: 5839-93-0 / **1d**: 60050-54-6 / **1e**: 110314-98-2 / **1f**: 110314-99-3 / **2a**: 95885-60-2 / **2b**: 110315-02-1 / **2c**: 110315-03-2 / **2d**: 110315-04-3 / **2e**: 50709-70-1 / **2f**: 110315-05-4 / **2g**: 110315-06-5 / **2h**: 110315-07-6 / **3**: 110315-08-7 / **4**: 50709-69-8 / **5a**: 110315-09-8 / **5b**: 110315-10-1 / **6a**: 110315-11-2 / **7a**: 110315-12-3 / **7b**: 110315-13-4 / **7c**: 110315-14-5 / **7d**: 110315-15-6/ **8a**: 50709-78-9 / **8b**: 110315-16-7 / **8c**: 110315-17-8 / **8d**: 110315-18-9 / **8e**: 110315-19-0 / **8f**: 110315-20-3 / **8g**: 110315-21-4 / **9a**: 110315-22-5 / **9b**: 110315-23-6 / **9c**: 110315-24-7 / **10a**: 93-58-3 / **10b**: 121-98-2 / **10c**: 99-75-2 / **11**: 110315-25-8 / **12a**: 110315-26-9 / **12b**: 110315-27-0 / **13**: 110330-17-1 / **14a**: 110315-28-1 / **14b**: 110315-29-2 / 2-(4-chlorophenyl)glycine: 6212-33-5 / 2-(4-methoxyphenyl)glycine: 2540-53-6 / 2-(4-chlorophenyl)-*N*-(4-methylbenzoyl)glycine: 110315-00-9 / 2-(4-methoxyphenyl)-*N*-(4-methylbenzoyl)glycine: 110315-01-0 / 2,2-diphenylglycine: 3060-50-2 / 4-methylbenzoyl chloride: 874-60-2 / 2-nitrobenzoyl chloride: 610-14-0 / 2-nitrobenzyl chloride: 612-23-7 / 1-fluoro-2,4-dinitrobenzene: 70-34-8 / 1-chloro-2,4,6-trinitrobenzene: 88-88-0 / methyl 2-chloro-3,5-dinitrobenzoate: 2213-79-8 / 2-chloro-3,5-dinitropyridine: 2578-45-2

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