Ester, Amide and Ether Derivatives of 1-(*p*-Phenyl-substituted)-1,2,3-triazoles

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This paper describes the preparation of three series of 1-phenyl-1,2,3-triazol derivatives with an ester, amide or ether group on the phenyl ring. These derivatives were obtained from 4-hydroxyphenyl- and 4-aminophenyltriazoles, previously synthesized by us, by means of a nucleophilic substitution reaction with acetic anhydride, acyl and alkyl halides. The largest part of compounds were tested in an agricultural chemicals, nutrition and animal health screening programme.

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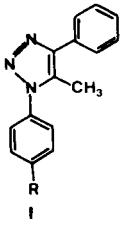
Previously, we described the synthesis and biological activity of many 1,2,3-triazole derivatives [1-6]. More recently we prepared several 1,2,3-triazole derivatives of aryloxyalcanoic acids I, II and III (R = oxyalcanoic groups) [7], some of which showed interesting antimicrobial, insecticide and herbicide activities.



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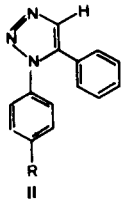

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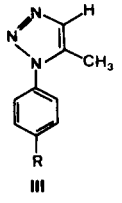

III

We have now continued our studies in this field by preparing and testing three series of new analogous 1,2,3-triazole derivatives corresponding to the general formulas I, II and III, with a neutral substituent (R = ester, amide, ether, aliphatic or aromatic group).

This structural change sometimes caused an increase in the antimicrobial and antifoliar pathogens activities [7].

Thus, from 4-hydroxyphenyltriazoles Ia, IIa, IIIa (R = OH) and 4-aminophenyltriazoles Ib, IIb, IIIb (R = NH_2), previously prepared [7], the corresponding phenylester, phenylether and phenylamide derivatives were obtained by reaction with acetic anydride, acyl chlorides and alkyl halides (Table I).

Acetates Ic, IIc and IIIc were prepared in good yields by heating 4-hydroxyphenyltriazoles Ia, IIa, IIIa with an excess of acetic anhydride; propionates Id and IIId, benzoates Ie, IId and IIIe and 4-chlorobenzoates If and IIe were prepared by reaction with the corresponding acyl chlorides in anhydrous pyridine.

Under the same conditions, from 4-aminophenyltriazoles Ib, IIb, IIIb amido and imidoderivatives were prepared (Table I). The reaction with an excess of acetic anhydride gave disubstitution on the aminogroup and imidoderivatives Ig, IIf and IIIf were obtained. Compound IIIf was isolated in 32% yield together with monoacetyl derivative IIIg (34% yield). The products of the reaction with propionyl chloride in pyridine were Ih and IIg together with disubstituted compound IIh, isolated in 60%, 30% and 17% yield respectively; IIg and IIh were separated by fractional crystallization. Benzamides Ii, IIi, IIIh and 4-chlorobenzamides Il, IIl, IIIi were obtained in good yields.

The ether derivatives were prepared by reaction of 4-hydroxyphenyltriazoles Ia, IIa, IIIa with an excess of a suitable alkyl halide under the reaction conditions reported in Table I. The yields of compounds Im-q and IIm-q were generally good, considering that variable amounts of the corresponding unreacted triazoles Ia or IIa were recovered.

The reaction with allyl, *n*-butyl and *n*-hexyl bromides was carried out in refluxing acetone in presence of anhydrous potassium carbonate.

Compounds IIIl, IIIm and IIIn were isolated from the crude and tarry reaction products by several extractions with boiling petroleum ether (60-80°); compound IIIn is liquid at room temperature.

The reaction with isopropyl bromide was carried out in refluxing ethanol in presence of sodium ethoxide to give In and IIn. Compound IIn, isolated from the reaction mixture, melted at 102-105°, whereas, after crystallization from ethanol-water 4:1, at 90-93°. Elemental analysis showed that it retained 0.5 moles of crystallization water.

Moreover heating at 120° Ia or IIa with 2-dimethylaminoethyl chloride in DMF solution in presence of anhydrous potassium carbonate, aminoether derivatives Iq and IIq were respectively obtained in low yield.

The structure of new triazole derivatives Ic-q, IIc-q and IIIc-n, prepared by usual nucleophilic substitution reactions, was confirmed by analytical and spectroscopic data (ir and ^{1}H-nmr, Table II).

Most of the compounds listed in Table I are being tested for biological activity in agricultural chemicals, nutri-

Table I

Preparation of 1,2,3-Triazolderivatives

Compound	R	Temperature °C	Time hours	Yield %	Mp °C	Formula	Elemental Analyses Calcd. %/Found % C	H	N
Ic	$OCOCH_3$	reflux	1	74-93	144-147 [d]	$C_{17}H_{15}N_3O_2$	69.61	5.15	14.33
							69.38	5.38	14.56
Id	$OCOCH_2CH_3$	70	2.5	36-49	134-137 [e]	$C_{18}H_{17}N_3O_2$	70.34	5.58	13.67
							70.02	5.39	13.61
Ie	$OCOC_6H_5$	70	3.5	92	189-192 [f]	$C_{22}H_{17}N_3O_2$	74.35	4.82	11.84
							74.50	4.67	11.83
If	$OCOC_6H_4Cl(p)$	70	3.5	57	242-243 [f]	$C_{22}H_{16}N_3O_2Cl$	67.78	4.13	10.78
							67.82	4.15	10.76
Ig	$N(COCH_3)_2$	reflux	1.5	85-92	182-185 [f]	$C_{19}H_{18}N_4O_2$	68.24	5.42	16.76
							67.98	5.25	16.91
Ih	$NHCOCH_2CH_3$	70	8	50-66	214-215 [e]	$C_{18}H_{18}N_4O$	70.56	5.92	18.29
							70.39	5.89	17.92
Ii	$NHCOC_6H_5$	70	3.5	62-79	239-241 [f]	$C_{22}H_{18}N_4O$	74.55	5.12	15.81
							74.28	4.94	15.65
Il	$NHCOC_6H_4Cl(p)$	70	4	70	290-291 [f]	$C_{22}H_{17}N_4OCl$	67.95	4.40	14.41
							67.66	4.24	14.61
Im	$OCH_2CH=CH_2$	reflux	48	53-84	120-123 [g]	$C_{18}H_{17}N_3O$	74.20	5.88	14.42
							74.09	5.76	14.50
In	$OCH(CH_3)_2$	reflux	24	62-68	142-144 [f]	$C_{18}H_{19}N_3O$	73.69	6.53	14.33
							74.03	6.74	14.50
Io	$O(CH_2)_3CH_3$	reflux	48	72-82	103-106 [g]	$C_{19}H_{21}N_3O$	74.24	6.89	13.67
							73.93	6.91	14.02
Ip	$O(CH_2)_5CH_3$	reflux	48	48-55	98-100 [g]	$C_{21}H_{25}N_3O$	75.19	7.51	12.53
							74.98	7.47	12.75
Iq	$O(CH_2)_2N(CH_3)_2$	120	8	33	85-87 [h]	$C_{19}H_{22}N_4O$	70.78	6.88	17.38
							70.51	6.67	17.48
IIc	$OCOCH_3$	reflux	2	80-95	107-110 [i]	$C_{16}H_{13}N_3O_2$	68.80	4.69	15.05
							68.53	4.76	15.27
IId	$OCOC_6H_5$	70	3.5	67-73	150-152 [f]	$C_{21}H_{15}N_3O_2$	73.89	4.43	12.31
							74.08	4.39	11.99
IIe	$OCOC_6H_4Cl(p)$	70	3.5	61	179-180 [f]	$C_{21}H_{14}N_3O_2Cl$	67.11	3.75	11.18
							66.98	3.73	10.95
IIf	$N(COCH_3)_2$	reflux	1.5	70-76	158-160 [g]	$C_{18}H_{16}N_4O_2$	67.48	5.03	17.49
							67.43	4.89	17.72
IIg	$NHCOCH_2CH_3$	70	1.5	30	180-182 [j]	$C_{17}H_{16}N_4O$	69.84	5.52	19.17
							70.10	5.60	18.91
IIh	$N(COCH_2CH_3)_2$			17	140-142 [a,g]	$C_{20}H_{20}N_4O_2$	68.95	5.79	16.08
							69.27	5.95	15.86
IIi	$NHCOC_6H_5$	70	5	82-95	236-238 [k]	$C_{21}H_{16}N_4O_2$	74.10	4.74	16.46
							74.36	4.61	16.32
IIl	$NHCOC_6H_4Cl(p)$	70	3	80	234-237 [f]	$C_{21}H_{15}N_4OCl$	67.29	4.03	14.95
							66.94	3.95	14.68
IIm	$OCH_2CH=CH_2$	reflux	24	69-89	113-115 [g]	$C_{17}H_{15}N_3O$	73.63	5.45	15.15
							73.71	5.66	14.90
IIn	$OCH(CH_3)_2$	reflux	24	62-71	104-106 [g]	$C_{17}H_{17}N_3O$	73.09	6.13	15.04
							72.83	6.10	14.91
IIo	$O(CH_2)_3CH_3$	reflux	32	78-88	105-108 [l]	$C_{18}H_{19}N_3O$	73.69	6.53	14.33
							73.73	6.76	14.47
IIp	$O(CH_2)_5CH_3$	reflux	48	62-86	73-75 [l]	$C_{20}H_{23}N_3O$	74.74	7.21	13.07
							74.54	7.24	13.07
IIq	$O(CH_2)_2N(CH_3)_2$	120	8	27	103-104 [h]	$C_{18}H_{20}N_4O$	70.10	6.54	18.17
							69.80	6.36	18.14
IIIc	$OCOCH_3$	120	2.5	88	68-70 [b,g]	$C_{11}H_{11}N_3O_2$	60.82	5.10	19.35
							60.96	5.18	19.42
IIId	$OCOCH_2CH_3$	70	20	27	80-81 [l]	$C_{12}H_{13}N_3O_2$	62.32	5.67	18.17
							62.40	5.59	18.27
IIIe	$OCOC_6H_5$	70	5	65	121-123 [g] / 123-125 [d]	$C_{16}H_{13}N_3O_2$	68.80	4.69	15.05
							68.93	4.62	15.06

Table I continued

Compound	R	Temperature °C	Time hours	Yield %	Mp °C	Formula	Elemental Analyses Calcd. %/Found % C	H	N
IIIf	$N(COCH_3)_2$	reflux	1.5	32	176-178 [d]	$C_{13}H_{14}N_4O_2$	60.45	5.46	21.70
							60.31	5.47	21.71
IIIg	$NHCOCH_3$			34	147-150 [m]	$C_{11}H_{12}N_4O$	61.09	5.59	25.91
							61.11	5.55	25.97
IIIh	$NHCOC_6H_5$	70	3	63-70	171-173 [f]	$C_{16}H_{14}N_4O$	69.05	5.07	20.13
							69.34	5.00	19.98
IIIi	$NHCOC_6H_4Cl(p)$	70	3	55	184-186 [k]	$C_{16}H_{13}N_4OCl$	61.44	4.19	17.91
							61.66	4.12	17.77
IIIl	$OCCH_2CH=CH_2$	reflux	26	25	74-76 [l]	$C_{12}H_{13}N_3O$	66.95	6.09	19.52
							66.78	5.96	19.74
IIIm	$O(CH_2)_3CH_3$	reflux	48	44	55-58 [l]	$C_{13}H_{17}N_3O$	67.50	7.41	18.17
							67.74	7.52	18.33
IIIn	$O(CH_2)_5CH_3$	reflux	48	46	[c]	$C_{15}H_{21}N_3O$	69.46	8.16	16.21
							69.28	8.05	16.08

[a] It changes crystalline form at 110-112°. [b] The uncrystallized compound melts at 80-85°. [c] See experimental part. Recrystallization solvent: [d] Methanol-water. [e] Ethyl acetate. [f] Ethanol. [g] Benzene-petroleum ether 60-80°. [h] Petroleum ether 60-80°-benzene (9:1). [i] Ethanol-water. [j] Benzene. [k] Methanol. [l] Petroleum ether 60-80°. [m] Water.

tion and animal health screening programmes.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. The ir spectra in nujol mulls were recorded on a Perkin-Elmer Model 197 spectrophotometer. The ^{1}H-nmr spectra were obtained with a Jeol Model C-60 HL spectrometer for solutions in DMSO-d_6 or deuteriochloroform and an internal TMS standard. The results of the elemental analyses (C, H, N) were within ± 0.4% of the theoretical values.

4-Phenyl-5-methyl-, 5-Phenyl-, 5-Methyl-1-(4-acetyloxyphenyl)-1*H*-1,2,3-triazole and 4-Phenyl-5-methyl-, 5-Phenyl-1-(4-*N*,*N*-diacetylaminophenyl)-1*H*-1,2,3-triazole (Ic, IIc, IIIc and Ig, IIf).

A solution of 0.50 g of hydroxyphenyltriazole (Ia, IIa, IIIa) or aminophenyltriazole (Ib, IIb) and 4 ml of acetic anhydride was allowed to react in the experimental conditions reported in Table I. After cooling the reaction mixture was poured into crushed ice and the title compounds separated as solids which were collected by filtration, washed with water and purified by crystallization (Table I).

1-(4-*N*,*N*-Diacetylaminophenyl)-5-methyl-1*H*-1,2,3-triazole and 1-(4-Acetylaminophenyl)-5-methyl-1*H*-1,2,3-triazole (IIIf and IIIg).

A solution of 0.78 g of IIIb and 7 ml of acetic anhydride was gently refluxed for 1.5 hours; after cooling the reaction mixture was poured into curshed ice and 0.37 g of IIIf precipitated. The acid mother liquors were neutralized with solid sodium carbonate, then extracted with chloroform. The extracts, after evaporation of the solvent, gave a residue (0.56 g) of IIIg and little of IIIf, from which IIIg was isolated by crystallization (Table I).

4-Phenyl-5-methyl-, 5-Methyl-1-(4-propionyloxyphenyl)-1*H*-1,2,3-triazole and 4-Phenyl-5-methyl-1-(4-*N*-propionylaminophenyl)-1*H*-1,2,3-triazole (Id, IIId and Ih).

To an ice-cooled solution of 2.0 mmoles of Ia, IIIa, Ib in 5 ml of anhydrous pyridine, 4.0 mmoles of propionyl chloride was added. The mixture was allowed to react under the experimental conditions reported in Table I, poured into crushed ice and then the separated crude product, extracted with chloroform. The combined extracts were washed with 2*N* hydrochloric acid, 2*N* sodium hydroxide, water and the solvent was evaporated to give a semisolid residue. Compounds Id and Ih were obtained from ethyl acetate (temperature about −10°) by fractional crystallization of respective residues; compound IIId, extracted with a boiling mixture of petroleum ether-benzene 4:1, crystallized by cooling.

1-(4-Propionylaminophenyl)-5-phenyl-1*H*-1,2,3-triazole and 1-(4-*N*,*N*-Dipropionylaminophenyl)-5-phenyl-1*H*-1,2,3-triazole (IIg and IIh).

To an ice-cooled solution of 2.36 g (10 mmoles) of IIb in 30 ml of anhydrous pyridine, 2.55 ml (30 mmoles) of propionyl chloride were added and the mixture was allowed to react in the experimental conditions reported in Table I. After evapcration of the solvent *in vacuo*, the residue was poured into crushed ice ad extracted with chloroform. The combined extracts were washed with saturated sodium bicarbonate solution, 2*N* hydrochloric acid, water and evaporated to dryness *in vacuo*. The resulting oily residue was fractionated with benzene, then with benzene-petroleum ether to give some fractions of crude IIg (1.12 g). The benzene mother liquors were evaporated to obtain crude IIh in low yield. Compounds IIg and IIh were purified by crystallization from benzene (Table I).

4-Phenyl-5-methyl-, 5-Phenyl-, 5-Methyl-1-(4-benzoyloxyphenyl)-1*H*-1,2,3-triazole and 4-Phenyl-5-methyl-, 5-Phenyl-, 5-Methyl-1-(4-benzoylaminophenyl)-1*H*-1,2,3-triazole (Ie, IId, IIIe and Ii, IIi, IIIh).

To an ice-cooled solution of 3.0 mmoles of hydroxyphenyltriazole (Ia, IIa, IIIa) or aminophenyltriazole (Ib, IIb, IIIb) in 5 ml of anhydrous pyridine, 3.6 mmoles of benzoyl chloride was added. The mixture was allowed to react in the conditions reported in Table I, poured into crushed ice and then the precipitate extracted with chloroform. The extracts were washed with 2*N* hydrochloric acid, saturated sodium bicarbonate solution (or 2*N* sodium hydroxide only for recovering unreacted hydroxyphenyltriazole) and water, dried (magnesium sulfate) and evaporated to dryness. The residue was purified by crystallization to give the title compounds (Table I).

4-Phenyl-5-methyl-, 5-Phenyl-1-[4-(4-chlorobenzoyloxy)phenyl]-1*H*-1,2,3-triazole and 4-Phenyl-5-methyl-, 5-Phenyl-, 5-Methyl-1-[4-(4-chlorobenzoylamino)phenyl]-1*H*-1,2,3-triazole (If, IIe and Il, III, IIIi).

To a ice-cooled solution of 4.0 mmoles of hydroxyphenyltriazole (Ia, IIa) or aminophenyltriazole (Ib, IIb, IIIb) in 6 ml of anhydrous pyridine, 4.8 mmoles of 4-chlorobenzoyl chloride was added. The mixture was allowed to react in the conditions reported in Table I and then worked up as described for the preparation of Ie and Ii. The residues, which consisted of the title compounds and little of 4-chlorobenzoic anhydride (mp

Table II

^{1}H NMR Chemical Shifts (δ) and IR Data (μ) of Compounds Ia-q, IIa-q and IIIa-n

Compound	Solvent [a]	1-C_6H_4 (d)	(d)	4-C_6H_5 (m)	5-CH_3 (s)	R	
Ia	A	6.90	7.35	7.35-8.35	2.43	NH_2, 5.70 (s)	NH_2 2.95, 3.02 [7]
Ib	A	7.20	7.48	7.48-8.12	2.48	OH 10.25 (broad)	OH 3.25 (broad) [7]
Ic	B	7.37-8.12 (m)			2.54	$OCCH_3$ 2.40 (s)	COO 5.76, 8.50
Id	B	7.37-8.10 (m)			2.62	$OCCH_2CH_3$ 2.75 (q), 1.36 (t)	COO 5.78, 8.85
Ie	B	7.35-8.05 (m)			2.61	OCC_6H_5 7.35-8.05, 8.25-8.47 (m)	COO 5.88, 8.02
If	B	7.10-8.22 (m)			2.52	OCC_6H_4 7.10-8.22 (m)	COO 5.87, 8.05
Ig	A	7.53-8.18 (m)			2.57	$(OCCH_3)_2$ 2.31 (s)	$N(CO)_2$ 5.90, 6.00
Ih	C	7.38-8.06 (m)			2.50	$OCCH_2CH_3$ 2.58 (q), 1.24 (t), NH 9.80 (s)	NHCO 3.08, 6.04
Ii	A	7.40-8.32 (m)			2.56	OCC_6H_5 7.40-8.32 (m), NH 10.05 (s)	NHCO 3.07, 6.15
Il	A	7.55-8.42 (m)			2.62	OCC_6H_4 7.55-8.42 (m), NH 10.80 (s)	NHCO 3.08, 6.15
Im	B	7.12	7.45	7.25-7.95	2.55	$OCH_2CH{=}CH_2$ 4.66 (d), 6.05 (m), 5.23-5.71 (m)	COC 8.07, 9.80
In	B	7.20	7.55	7.40-8.10	2.55	$OCH(CH_3)_2$ 4.76 (m), 1.45 (d)	COC 8.08, 9.10
Io	B	7.17	7.50	7.37-8.05	2.54	$OCH_2(CH_2)_2CH_3$ 4.13 (t), 1.25-2.12 (m), 1.05 (t)	COC 8.09, 9.64
Ip	B	7.15	7.50	7.37-8.02	2.49	$OCH_2(CH_2)_4CH_3$ 4.12 (t), 1.10-2.10 (m), 0.97 (t)	COC 8.00, 9.60
Iq	B	7.20	7.52	7.39-8.05	2.55	$OCH_2CH_2N(CH_3)_2$ 4.25 (t), 2.88 (t), 2.48 (s)	COC 8.04, 9.60

		1-C_6H_4 (d)	(d)	5-C_6H_5 (s)	4-H (s)		
IIa	A	6.72	7.10	7.45	8.16	NH_2 5.65 (s)	NH_2 2.93, 3.03
IIb	A	7.04	7.36	7.51	8.25	OH 10.20 (broad)	OH 3.23 (broad) [7]
IIc	B	7.35	7.46	7.50	8.02	$OCCH_3$ 2.35 (s)	COO 5.73, 8.40
IId	B	7.32-7.87 (m)			8.05	$OCCH_6H_5$ 7.32-7.87 (m), 8.28-8.51 (m)	COO 5.84, 8.00
IIe	B	7.62	8.25	7.48	8.02	OCC_6H_4 7.30-7.77 (m)	COO 5.84, 8.05
IIf	B	7.37	7.55	7.25-7.61	7.95	$(OCCH_3)_2$ 2.32 (s)	$N(CO)_2$ 5.92, 5.99
IIg	B	7.50	7.85	7.52	8.07	$OCCH_2CH_3$ 2.56 (q), 1.28 (t), NH 8.73 (s)	NHCO 3.01, 5.98
IIh	B	7.32	7.58	7.25-7.62	7.98	$(OCCH_2CH_3)_2$ 2.65 (q), 1.15 (t)	$N(CO)_2$ 5.99
IIi	C	7.21-7.71 (m)			8.10	OCC_6H_5 7.21-7.71 (m), 7.90-8.22 (m), NH 10.22 (s)	NHCO 3.02, 6.11
IIl	A	7.45-8.32 (m)		7.52	8.27	OCC_6H_5 7.45-8.32 (m), NH 10.70 (s)	NHCO 3.00, 6.08
IIm	B	7.03	7.31	7.15-7.50	7.92	$OCH_2CH{=}CH_2$ 4.59 (d), 5.95 (m), 5.18-5.62 (m)	COC 8.16, 9.84
IIn	B	7.05	7.34	7.22-7.55	7.95	$OCH(CH_3)_2$ 4.65 (m), 1.38 (d)	COC 8.15, 9.12
IIo	B	7.06	7.37	7.25-7.60	7.97	$OCH_2(C\ H_2)_2CH_3$ 4.10 (t), 1.22-2.20 (m), 1.02 (t)	COC 8.03, 9.52
IIp	B	7.05	74.0	7.25-7.66	7.97	$OCH_2(CH_2)_4CH_3$ 4.08 (t), 1.15-2.15 (m), 0.95 (t)	COC 8.06, 9.50
IIq	B	7.07	7.43	7.25-7.62	8.05	$OCH_2CH_2N(CH_3)_2$ 4.20 (t), 2.82 (t), 2.41 (s)	COC 8.10, 9.65

		1-C_6H_4 (d)	(d)	5-CH_3 (s)	4-H (s)		
IIIa	A	6.75	7.17	2.24	7.63	NH_2 5.52 (s)	NH_2 3.00, 3.07 [7]
IIIb	A	6.98	7.36	2.27	7.67	OH 10.10 (broad)	OH 3.20 (broad) [7]
IIIc	B	7.50	7.72	2.42	7.84	$OCCH_3$ 2.42 (s)	COO 5.82, 8.35
IIId	B	7.38	7.62	2.43	7.68	$OCCH_2CH_3$ 2.72 (q), 1.30 (t)	COO 5.82, 8.83
IIIe	B	7.35-7.83 (m)		2.43	7.69	OCC_6H_5 7.35-7.83 (m), 8.19-8.44 (m)	COO 5.87, 8.45
IIIf	B	7.52	7.78	2.49	7.75	$(OCCH_3)_2$ 2.37 (s)	$N(CO)_2$ 5.89, 5.98
IIIg	B	7.42	7.85	2.38	7.66	$OCCH_3$ 2.25 (s), NH 9.10 (s)	NHCO 3.12, 6.05
IIIh	B	7.55	8.02	2.42	7.67	OCC_6H_5 7.57-7.77 (m), 7.93-8.20 (m), NH 9.00 (s)	NHCO 3.08, 6.16
IIIi	B	7.52	8.06	2.40	7.65	OCC_6H_4 7.54 (d), 8.14 (d), NH 10.25 (s)	NHCO 3.07, 6.14
IIIl	B	7.12	7.49	2.38	7.63	$OCH_2CH{=}CH_2$ 4.69 (d), 6.09 (m), 5.23-5.70 (m)	COC 8.06, 9.90
IIIm	B	7.11	7.48	2.35	7.60	$OCH_2(CH_2)_2CH_3$ 4.10 (t), 1.22-2.18 (m), 1.00 (t)	COC 8.14, 9.60
IIIn	B	7.12	7.48	2.35	7.65	$OCH_2(CH_2)_4CH_3$ 4.10 (t), 1.20-2.10 (m), 0.96 (t)	COC 8.08, 9.40

[a] A = DMSO-d_6; B = deuteriochloroform; C = deuteriochloroform + DMSO-d_6.

189-191°), were extracted with boiling ethanol to remove the anhydride then were purified by crystallization (Table I). Moreover, on washing the chloroform solution of 4-chlorobenzamides II and III with 2*N* hydrochloric acid, some persistent emulsions which retained variable amounts of the prepared derivatives, could develop; in this case the product had to be recovered from the mixture by filtration with suction.

4-Phenyl-5-methyl-, 5-Penyl-, 5-Methyl-1-(4-alkyloxyphenyl)-1*H*-1,2,3-triazole (Im, IIm, IIIl, Io, IIo, IIIm, Ip, IIp, IIIn).

To a solution of 3.0 mmoles of hydroxyphenyltriazole (Ia, IIa, IIIa) in 40 ml of anhydrous acetone, 1.4 g of anhydrous potassium carbonate and 9.9 mmoles of allyl bromide, 9.0 mmoles of 1-bromobutane or 7.5 mmoles of 1-bromohexane were added. The mixture was refluxed for the time re-

ported in Table I, evaporated *in vacuo*, diluted with water and then extracted with chloroform. The combined extracts were washed with 2*N* sodium hydroxide (variable amounts of unreacted Ia or IIa were recovered from which), dried (magnesium sulfate) and evaporated to give a crude residue; compounds Im, Io, Ip and IIm, IIo, IIp were isolated from the solid or semisolid residue by fractional crystallization with benzene-petroleum ether; compounds IIIl and IIIm were isolated by extraction with boiling petroleum ether portion wise, concentration of the combined extracts and on cooling the solution at −10°. The liquid compound IIIn was purified by elimination of the volatile impurities at 75°/1.5 mm Hg in a tabular oven.

4-Phenyl-5-methyl-, 5-Phenyl-1-(4-isopropyloxyphenyl)-1*H*-1,2,3-triazole (In, IIn).

To a suspension of 5.0 mmoles of hydroxyphenyltriazole (Ia, IIa) and 15 mmoles of 2-bromopropane in 30 ml of anhydrous ethanol a solution of 6.5 mmoles of sodium ethoxide in 15 ml of anhydrous ethanol was added under stirring. After 30 minutes at room temperature the reaction mixture was refluxed for 24 hours. The solution obtained was concentrated *in vacuo*, diluted with water and extracted with chloroform. The extracts were washed with 2*N* sodium hydroxide, water, dried (magnesium sulfate) and evaporated to dryness. The residue was purified by crystallization to give the title compounds (Table I). By acidification of alkaline solution 0.8-1.2 mmoles of unreacted Ia or IIa were recovered.

4-Phenyl-5-methyl-, 5-Phenyl-1-[4-(2-dimethylaminoethyloxy)phenyl]-1*H*-1,2,3-triazole (Iq, IIq).

A mixture of 2.0 mmoles of hydroxyphenyltriazole (Ia, IIa), 6.0 mmoles of 2-dimethylaminoethyl chloride hydrochloride and 2.2 g of anhydrous potassium carbonate in 5 ml of anhydrous DMF was heated at 120° for 8 hours. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was washed with 2*N* sodium hydroxide and extracted with 2*N* hydrochloric acid. The acidic solution was made basic to give an oily product which was extracted with chloroform. After removal of the solvent the reaction product was obtained as a solid residue which was purified by crystallization (Table I).

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