

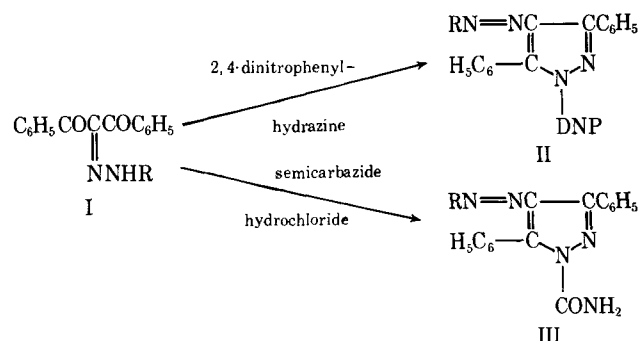
New Compounds: Potential Antidiabetics IV: 1-(2,4-Dinitrophenyl)-3,5-diphenyl- 4-arylazopyrazoles and 1-Carbamoyl- 3,5-diphenyl-4-arylazopyrazoles

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Abstract □ A series of 1-(2,4-dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles and 1-carbamoyl-3,5-diphenyl-4-arylazopyrazoles have been synthesised by the condensation of the corresponding 1,3-diphenyl-2-arylhydrazono-1,2,3-propanetriones with 2,4-dinitrophenylhydrazine and semicarbazide hydrochloride, respectively.

Keyphrases □ Antidiabetics—synthesis, pyrazoles, isoxazoles □ 1-(2,4-Dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles—synthesis, potential hypoglycemics □ 1-Carbamoyl-3,5-diphenyl-4-arylazopyrazoles—synthesis, potential hypoglycemics

Numerous derivatives of pyrazoles and isoxazoles have been prepared for testing their antidiabetic activity (1–4). The compounds 1-phenyl-3-methyl-4-arylhydrazono-2-pyrazolin-5-ones have shown encouraging antidiabetic activity in experimental animals (5). To examine their hypoglycemic activity, a series of 1-(2,4-dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles and 1-carbamoyl-3,5-diphenyl-4-arylazopyrazoles have been prepared and are reported in the present communication.



R = substituted phenyl
DNP = 2,4-dinitrophenyl

Scheme I

Precursors 1,3-diphenyl-2-arylhydrazono-1,2,3-propanetriones (I) were obtained by coupling diazotized anilines with 1,3-diphenyl-1,3-propanedione (4). 2,4-Dinitrophenylhydrazine and semicarbazide hydrochloride

Table I—Characteristics of 1-(2,4-Dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles

No.	R	Yield, %	M.p.	Color	Formula	Anal., %	
						Calcd.	Found
1	2-Nitrophenyl	55	208–209°	Red crystals	$\text{C}_{27}\text{H}_{17}\text{N}_7\text{O}_6$	N, 18.3	N, 18.0
2	3-Nitrophenyl	65	196–197°	Red crystals	$\text{C}_{27}\text{H}_{17}\text{N}_7\text{O}_6$	N, 18.3	N, 18.1
3	3-Chlorophenyl	60	203°	Orange	$\text{C}_{27}\text{H}_{17}\text{ClN}_6\text{O}_4$	C, 61.8 H, 3.2 N, 15.4	C, 61.6 H, 3.4 N, 15.0
4	4-Chlorophenyl	75	186°	Orange needles	$\text{C}_{27}\text{H}_{17}\text{ClN}_6\text{O}_4$	N, 15.4	N, 15.3
5	2-Methylphenyl	70	228–229°	Orange needles	$\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_4$	N, 16.6	N, 16.4
6	3-Methylphenyl	55	198–199°	Yellow- orange	$\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_4$	N, 16.6	N, 16.3
7	4-Methylphenyl	50	163°	Red crystals	$\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_4$	C, 66.7 H, 4.0 N, 16.6	C, 66.6 H, 4.1 N, 16.1
8	2-Methoxyphenyl	50	233°	Orange-red needles	$\text{C}_{28}\text{H}_{20}\text{N}_6\text{O}_5$	N, 16.1	N, 16.0
9	2-Ethoxyphenyl	60	221–222°	Orange needles	$\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_5$	N, 15.7	N, 15.6
10	4-Ethoxyphenyl	65	132°	Pale- yellow needles	$\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_5$	N, 15.7	N, 15.4
11	4-Sulfamoyl- phenyl	55	132–133°	Orange	$\text{C}_{27}\text{H}_{19}\text{N}_7\text{O}_6\text{S}$	N, 17.2	N, 17.0
12	2,5-Dichloro- phenyl	75	233°	Orange	$\text{C}_{27}\text{H}_{15}\text{Cl}_2\text{N}_6\text{O}_4$	Cl, 12.7	Cl, 12.4
13	2,5-Dimethyl- phenyl	60	238–239°	Orange needles	$\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_4$	N, 16.2	N, 16.0
14	2,5-Dimethoxy- phenyl	55	242–243°	Dark brown	$\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_6$	N, 15.2	N, 15.0
15	2-Chloro-6- methylphenyl	65	224°	Orange	$\text{C}_{28}\text{H}_{19}\text{ClN}_6\text{O}_4$	C, 62.4 H, 3.5 N, 15.6	C, 62.2 H, 3.4 N, 15.1

Table II—Characteristics of 1-Carbamoyl-3,5-diphenyl-4-arylazopyrazoles

No.	R	Yield, %	M.p.	Color	Formula	Anal., %	
						Calcd.	Found
1	2-Nitrophenyl	60	193–194°	Orange fibers	$C_{22}H_{16}N_6O_3$	N, 20.3	N, 20.0
2	3-Nitrophenyl	50	265–266°	Orange	$C_{22}H_{16}N_6O_3$	C, 64.1 H, 3.9 N, 20.3	C, 64.1 H, 4.0 N, 19.9
3	2-Methylphenyl	50	192–193°	Orange	$C_{23}H_{19}N_5O$	C, 72.4 H, 4.9 N, 18.3	C, 72.2 H, 4.8 N, 17.9
4	3-Methylphenyl	45	242–243°	Orange fibers	$C_{23}H_{19}N_5O$	N, 18.3	N, 18.2
5	4-Methylphenyl	65	219–220°	Orange	$C_{23}H_{19}N_5O$	N, 18.3	N, 18.0
6	2-Methoxyphenyl	50	180–181°	Orange	$C_{23}H_{19}N_5O_2$	C, 69.5 H, 4.8 N, 17.6	C, 69.4 H, 4.6 N, 17.2
7	3-Methoxyphenyl	45	157°	Red	$C_{23}H_{19}N_5O_2$	N, 17.6	N, 17.5
8	4-Methoxyphenyl	55	168–171°	Orange fibers	$C_{23}H_{19}N_5O_2$	C, 69.5 H, 4.8 N, 17.6	C, 69.6 H, 4.9 N, 17.1
9	2-Ethoxyphenyl	50	163–165°	Orange	$C_{24}H_{21}N_5O_2$	N, 17.0	N, 17.2
10	4-Sulfamoyl-phenyl	60	250–251°	Orange	$C_{22}H_{18}N_6O_3S$	N, 18.8	N, 18.5
11	2,5-Dichlorophenyl	70	207–209°	Orange	$C_{22}H_{15}Cl_2N_5O$	Cl, 16.2	Cl, 16.0
12	2,6-Dichlorophenyl	75	161–162°	Orange	$C_{22}H_{15}Cl_2N_5O$	Cl, 16.2	Cl, 16.3
13	2,5-Dimethylphenyl	60	186–187°	Orange needles	$C_{24}H_{21}N_5O$	C, 72.9 H, 5.3 N, 17.7	C, 72.8 H, 5.1 N, 17.2

ride react with I to yield 1-(2,4-dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles (II) (Table I) and 1-carbamoyl-3,5-diphenyl-4-arylazopyrazoles (III) (Table II) congeners, respectively. They are all highly colored crystalline compounds and are soluble in common organic solvents.

EXPERIMENTAL

Melting points were taken with a Kofler hot stage apparatus and are uncorrected.

1,3-Diphenyl-2-arylhydrazono-1,2,3-propanetriones (I)—These were prepared by coupling aryldiazonium salts, prepared from anilines, with 1,3-diphenyl-1,3-propanedione (4).

1-(2,4-Dinitrophenyl)-3,5-diphenyl-4-phenylazopyrazole (II, R = C_6H_5)—To 1,3-diphenyl-2-phenylhydrazono-1,2,3-propanetrione (0.82 g., 0.0025 mole) in glacial acetic acid (25 ml.) was added 2,4-dinitrophenylhydrazine (0.50 g., 0.0025 mole) in ethyl alcohol (15 ml.) containing concentrated sulfuric acid (2 ml.). The mixture was refluxed for 8 hr. On cooling, shining crystals separated out which were recrystallized from alcohol (0.60 g., 50%) as yellow-orange crystals, m.p. 136–137°.

Anal.—Calcd. for $C_{27}H_{18}N_6O_4$: N, 17.1. Found: N, 16.8.

The details of the other 1-(2,4-dinitrophenyl)-3,5-diphenyl-4-arylazopyrazoles which were prepared are given in Table I.

1-Carbamoyl-3,5-diphenyl-4-phenylazopyrazole (III, R = C_6H_5)—A solution of 1,3-diphenyl-2-phenylhydrazono-1,2,3-propanetrione

(0.82 g., 0.0025 mole) in alcohol (30 ml.) was treated with an aqueous solution of semicarbazide hydrochloride (0.23 g., 0.0025 mole). This was heated under reflux for 2 hr. On cooling, shining crystals separated out which were recrystallized from alcohol (0.50 g., 65%) as orange fibers, m.p. 215°.

Anal.—Calcd. for $C_{22}H_{17}N_5O$: N, 19.07. Found: N, 18.8.

The details of the other 1-carbamoyl-3,5-diphenyl-4-arylazopyrazoles which were prepared are given in Table II.

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