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DECOMPOSITION OF ARYLAZIDES BY THF/n-BUTYLLITHIUM-II-
-ISOLATION OF 1-ARYL-4,5-DIHYDRO-5-HYDROXY-1H-1,2,3-TRIAZOLES

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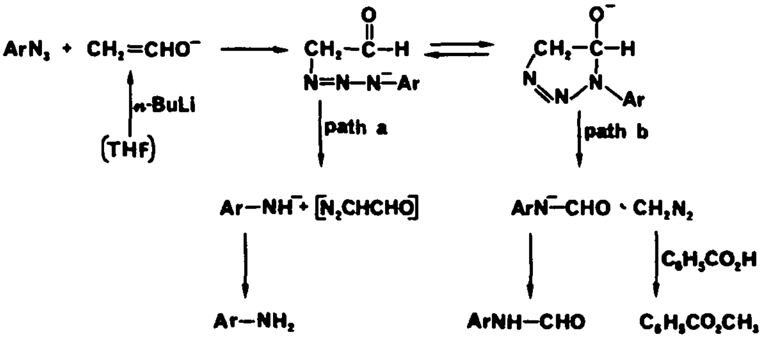
Abstract - By reaction of arylazides having no electron-withdrawing groups with the enolate ion of the acetaldehyde (formed by cycloreversion of THF in the presence of n-butyllithium), 1-aryl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazoles could be isolated and then characterized. Further reaction of such hydroxytriazolines with the same enolate ion afforded substantial amounts of the corresponding N-formylanilines, confirming their intermediacy in the previously reported decomposition of arylazides by THF/n-butyllithium. On the other hand, using alkoxides as bases, the preferred scheme of conversion of the hydroxytriazolines was found to be the known dehydration to 1-aryl-1H-1,2,3-triazoles.

In a recent paper[1] we showed that, by allowing to react a number of arylazides (as well as p-tosylazide) with THF previously treated with n-butyllithium (ca. 16 hrs at room temperature), the corresponding anilines and N-formylanilines are formed, together with diazomethane. This "diazo transfer with deformylation"[2] reaction was thought to be due to the interaction of arylazides with the enolate ion of the acetaldeyde, quantitatively generated by the known cycloreversion of THF in the presence of n-butyllithium.[3] Thus, by analogy with other known diazo transfer with deformylation reactions,[2,4] and at least concerning the formation of N-formylanilines and diazomethane, the formation as intermediates of 1-aryl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole salts was postulated (Scheme 1).

SCHEME 1



Only one of the possible electromeric structures is indicated in each case.

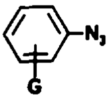
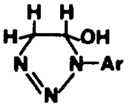
In the present paper we report the isolation and characterization of such arylhydroxytriazolines (from now on, for the sake of simplicity, this and similar termes will be often employed in the text), by using unsubstituted phenylazide as well as arylazides provided of electron-donating groups, and a different procedure of separation and purification of the reaction products (chromatographic techniques using silica gel must be avoided). In addition, the behaviour of a number of arylhydroxytriazolines so isolated with the enolate ion of acetaldehyde as well as with other bases is also reported.

RESULTS AND DISCUSSION

Some attempts to isolate 1-aryl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazoles from the reaction of the enolate ion of the acetaldehyde (obtained as above described) with arylazides provided of electron-withdrawing groups (*o*-nitro-phenylazide, *o*-methylsulphonylphenylazide) failed. On the other hand, when such groups are absent or, on the contrary, electron-donating groups are present in the starting arylazide, the reaction can be stopped before the arylhydroxytriazolines further react, so that the latter can be isolated in high to nearly quantitative yields (Table 1).

TABLE 1

Yields of 1-aryl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazoles isolated from the reaction of arylazides and the lithium enolate of the acetaldehyde (see Discussion) in THF at room temperature.

G in 		Reaction time, h	m.p. °C	Recryst. solvent
H	99	4	102-104	CCl_4
o-SMe	82	1.5	131-133	EtOH
o-OMe	94	2	98-100	$EE/CHCl_3$
m-OMe	97	3.5	96-98	CCl_4
p-OMe	70	24	131-132	EtOH
p-Me	97	5	108-111	CCl_4
o-S-Et	96	1.2	118-119	EtOH

This favourable substituent effect of electron-donating groups can be rationalized by considering both the lower rate of further decomposition of the corresponding arylhydroxytriazolines, and the fact that the equilibrium between the ketotriazene and hydroxytriazoline salts would be more shifted towards the latter (Scheme I). Concerning the dependence of the position of the above equilibrium on the substituent effect, a similar conclusion has already been reported.[4b,5] In all cases any treatment with silica gel (separation and purification by chromatographic technique) must be avoided because it causes decomposition of the hydroxytriazolines.

On the other hand, in order to further confirm that the isolated arylhydroxytriazolines are the actual intermediates in the diazomethane and formanilides formation (Scheme 1), we treated them with the enolate ion of the acetaldehyde, in conditions identical to those used for their obtainment, but for longer times of reaction and/or at higher temperatures. In all cases together with the corresponding anilines and/or 1-aryl-1H-1,2,3-triazoles, substantial (and in one case almost quantitative) yields of N-formylanilines were isolated (Table 2). As previously reported,[1] comparable amounts of diazomethane would also be formed; however, because of the relatively high temperature of reaction (THF boiling point) which would favour its decomposition, only very low yields of diazomethane could be trapped as methyl benzoate. On the other hand, by using n-BuLi not allowed to stand in THF for 16^h (i.e., when the reagent is for the most part n-BuLi itself instead of the lithium enolate of the acetaldehyde), an increase of the reactivity of the hydroxytriazolines was observed, while the same products as from the reaction with the enolate ion of the acetaldehyde, though in different relative amounts, were isolated. In particular, an increase of arylamines seemingly at the expense of formanilides is observed in some cases. This could be really due to some deformylation of formanilides by n-butyllithium, as indicated by separate experiments (reaction of N-formyl-o-methylthioaniline with n-butyllithium in THF).

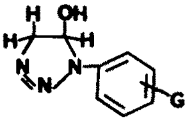
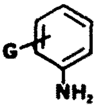
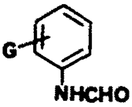
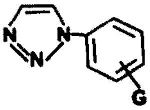
On the contrary, by treating the same arylhydroxytriazolines with either sodium methoxide in methanol or potassium t-butoxide in t-butanol, no appreciable amounts of both anilines and formanilides were isolated, but only the corresponding 1-aryl-1H-1,2,3-triazoles in good to nearly quantitative yields. This behaviour is consistent with that previously reported for the reactions of phenylazide with some ketones in the presence of alkoxides (where 5-hydroxytriazolines are formed as intermediates), or of 5-hydroxytriazolines themselves with alkoxides.[6] However, it is in contrast with the behaviour observed with the enolate ion of the acetaldehyde (as well as with n-BuLi), indicating that the general behaviour of hydroxytriazolines with bases is not only controlled by structural factors,[4] but also by the nature of the base.

The different behaviour observed with the alkoxides in the corresponding alcohols compared to lithium enolate of the acetaldehyde (and n-BuLi) in THF could be related, at least in part, to the different position of the equilibrium between the hydroxytriazoline and the corresponding anionic form:

In particular, with alkoxides this equilibrium would be less shifted towards the anion of the hydroxytriazoline, so that the dehydration (following an "irreversible" E_1CB or an E_2 mechanism, as previously proposed)[6b] to 1,2,3-triazole is the main or the only reaction. On the contrary, with stronger bases (like the enolate ion of the acetaldehyde, and even more n-butyllithium), because of a lower concentration of the undissociated hydroxytriazole likely involved in the dehydration pathway, formation of triazole would be more difficult, so that alternative or competitive pathways (in our case the decomposition affording formanilides and anilines) are observed. Further studies are in progress on this point.

TABLE 2

Products isolated by decomposition of 1-Aryl-4,5-dihyro-5-hydroxy-1H-1,2,3 triazoles with bases.

						
G =		Yield%	Yield%	Yield%	Temp. °C	Reaction time
	A(2)	-	54	34	refl.	5'
H	C(3)	-	--	98	r.t.	5^h
	D(2)	-	--	90	"	40'
o-SMe	A(2)	54	31	--	60	30'
	B(2)	91	8	--	r.t.	1^h15'
	C(3)	--	--	65	"	60^h
	D(2)	--	--	87	"	1.5^h
o-OMe	A(2)	--	97	--	60	5'
	B(2)	83	14	--	r.t.	30'
	C(3)	--	--	100	"	10^h
	D(2)	--	--	100	"	2^h
m-O-Me	A(2)	42	25	26	refl.	24^h
	B(2)	10	89	--	r.t.	1.5^h
	C(2)	--	--	100	"	6.5^h
	D(2)	--	--	100	"	2.5^h
p-OMe	A(2)	26	14	51	refl.	20^h
	C(2)	--	--	100	r.t.	5^h
	D(2)	--	--	100	"	1.5^h
p-Me	A(2)	--	39	56	refl.	23^h
	B(2)	1	74	22	r.t.	1.5^h
	C(3)	--	--	96	"	22^h
	D(2)	--	--	96	"	2^h
o-S-Et	A(2)	29	65	--	refl.	4^h
	B(2)	44	42	--	r.t.	1.5^h
	C(3)	--	--	87	"	9^h
	D(2)	--	--	78	"	1^h

[*] A= $CH_2{=}CHOLi$/THF; B= n-BuLi/THF: only cases where cycloreversion of THF during reaction is presumably not greatly advanced[3] (room temp. and time of reaction ≤1.5 hrs) are reported; C = MeONa/MeOH; D = t-BuOK/t-BuOH. Values in parentheses refer to (Base)/(hydroxytriazoline) ratios.

EXPERIMENTAL

MPS taken on an Electrothermal apparatus were uncorrected. ^1H NMR spectra were recorded on a Varian EM 360A or a Varian EM 390 spectrometer and chemical shifts are reported in parts per million (δ) from internal Me_4Si. IR spectra were recorded on a Perkin-Elmer 681 spectrometer. Thin-layer chromatography (TLC) was performed on silica gel sheets with fluorescent indicator (stratocrom SIF, Carlo Erba). Column chromatography was carried out by using 70-230 mesh silica gel from Merck. Flash chromatography was conducted by using silica gel: average particle size 60 µm, particle size distribution 40-63 µm, 230-400 ASTM.

Materials. Tetrahydrofuran (THF) from commercial source (RS, Carlo Erba) was purified by distillation (twice) from sodium wire in a N_2 atmosphere. Standardized (1.3 M) n-butyllithium in hexane was from Aldrich Chemical Co.. All other chemicals were commercial grade further purified by distillation or crystallization prior to use.

Organic azides. The synthesis was accomplished in all cases from the arylamines through the corresponding diazonium salts.[8]

Phenylazide and p-tolylazide were prepared according to the reported procedures.[8,9]

o-Methoxyphenylazide, m.p. 82-84°C (lit[10] 84.5°C); IR (CH_2Cl_2): 2150 cm^{-1}; ^1H NMR ($CDCl_3$, δ): 6.87 (m, 4H), 3.81 (s,3H).

m-Methoxyphenylazide, m.p. 40-42°C (lit[11] 42°C); IR (neat): 2111 cm^{-1}; ^1H NMR($CDCl_3$, δ): 6.91 (m, 4H), 3.73 (s, 3H).

p-Methoxyphenylazide, m.p. 32-35°C (lit[12] 36°C); IR (CH_2Cl_2): 2130 cm^{-1}; ^1H NMR($CDCl_3$, δ): 6.80 (s, 4H), 3.70 (s, 3H).

o-Methylthiophenylazide, m.p. 51-52°C; IR(CH_2Cl_2): 2150 cm^{-1}; ^1H NMR($CDCl_3$, δ): 6.93 (m, 4H); 2.32 (s, 3H).(Found: C, 50.9; H, 4.3; N, 25.4. Calc. for $C_7H_7N_3S$: C, 50.91; H, 4.28; N, 25.43).

o-Ethylthiophenylazide, m.p. 30-31°C; IR (neat): 2150 cm^{-1}; ^1H NMR($CDCl_3$, δ): 6.95 (m, 4H), 3.79 (q,2H), 1.18 (t, 3H). (Found: C, 53.6; H, 5.0; N, 23.4. Calc. for $C_8H_9N_3S$: C, 53.63; H, 5.07; N, 23.46).

Reactions of arylazides with the enolate ion of the acetaldehyde: general procedure.

A mixture containing lithium enolate of the acetaldehyde (24 mmole) in anhydrous THF (40 ml), prepared by allowing to stand THF in the presence of n-butyllithium as previously reported,[1] is added dropwise and at ca. 15°C to a solution of arylazide (12 mmole) in THF, using a nitrogen-flushed, three necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a dropping funnel. After the reaction was completed, the reaction mixture was quenched by adding aqueous NH_4Cl, the organic layer separated and the aqueous layer extracted with ethyl ether. The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure, affording crude 5-hydroxytriazolines which were purified by recrystallization (Table 1).

Reactions of 1-Aryl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazoles:

a) Reactions with the enolate ion of the acetaldehyde

Lithium enolate of the acetaldehyde (9.6 mmole) in THF (15 ml), prepared as previously described,[1] is added dropwise to a solution of hydroxytriazoline (4.8 mmole), using a nitrogen-flushed, 100 ml, three necked flask, equipped with a nitrogen inlet, a dropping funnel, and a reflux condenser. The reaction mixture is then heated to reflux and, after the reaction is completed, is quenched with aqueous NH_4Cl. Organic layer is then separated and aqueous layer extracted with ethyl ether. The combined extracts were then dried over Na_2SO_4 and evaporated under reduced pressure giving a products mixture which was separated by flash chromatography (ether-petrol 7:3 as eluent).

b) Reactions with n-butyllithium

These reactions were carried out using a procedure similar to that above described, with the following exceptions:

i) n-butyllithium in THF was immediately added to the hydroxytriazoline solution, without allowing it to stand for 16^h at room temperature;

ii) the reactions were performed in all cases at room temperature;

iii) ether-petrol 8:2 was used as eluent in the flash chromatography.

c) Reactions with alkoxides:

These reactions were performed at room temperature, by adding sodium methoxide or potassium t-butoxide (11 mmole) in the respective alcohols (20 ml) to a solution of hydroxytriazoline (5.5 mmole) in the same alcohols (20 ml). When the reaction was completed, the reaction mixture was quenched with aqueous NH_4Cl and then subjected to the work-up above described for the reactions with the enolate ion, using ethyl ether as eluent in the flash chromatography.

Products

1-Phenyl-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 102-104°C dec. (CCl_4 or ether); IR (CH_2Cl_2): υ_{OH}=3590 cm^{-1}, 3500-3120 cm^{-1}; ^1H NMR(DMSO-d_6,δ): 7.30(m, 5H); 6.40 (d, 1H: exchange with D_2O); 5.60 (m, 1H); 4.15 (d, 2H). (Found: C, 58.9; H, 5.5; N, 25.7. Calc. for $C_8H_9N_3O$: C, 58.90; H, 5.52; N, 25.77).

1-(p-Tolyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 108-111°C dec. (CCl_4); IR (CH_2Cl_2): υ_{OH} = 3600 cm^{-1}, 3520-3170 cm^{-1}; ^1H NMR(DMSO-d_6,δ): 7.10 (m,4H); 6.30 (d, 1H: exchange with D_2O); 5.50 (m,1H); 4.09 (d, 2H); 2.18 (s, 3H). (Found: C, 60.8; H,6.2; N, 23.7. Calc. for $C_9H_{11}N_3O$: C, 61.02; H, 6.21; N, 23.73).

1-(o-Methylthiophenyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 131-133°C dec. (ethanol); IR (KBr): υ_{OH} = 3600-3010 cm^{-1}; ^1H NMR(DMSO-d_6,δ): 7.25 (m, 4H); 6.28 (d, 1H: exchange with D_2O); 5.55 (m, 1H); 4.20 (m, 2H); 2.42 (s,3H). (Found: C, 51.6; H, 5.2; N, 20.1 . Calc. for $C_9H_{11}N_3OS$: C,51.67; H, 5.26; N, 20.10).

1-(o-Ethylthiophenyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 118-119°C dec. (ethanol); IR (KBr): υ_{OH} = 3600-3110 cm^{-1}; ^1H NMR($(CD_3)_2CO$,δ): 7.30 (m, 4H); 5.80 (m, 1H); 5.25 (d, 1H: exchange with D_2O); 4.25 (t, 2H); 2.91 (q, 2H); 1.26(t, 3H). (Found: C, 53.8; H, 5.8; N, 18.8. Calc. for $C_{10}H_{13}N_3OS$: C, 53.81; H, 5.83; N, 18.83).

1-(o-Methoxyphenyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 98-100°C dec. (ethyl ether-chloroform); IR (CH_2Cl_2): ν_{OH}=3580 cm^{-1}, 3500-3110 cm^{-1}; ^{1}H NMR(DMSO-d$_6$,δ): 7.10 (m, 4H); 6.10 (d, 1H: exchange with D_2O); 5.45 (t, 1H); 4.10 (m, 2H); 3.82 (s, 3H). (Found: C, 55.9; H, 5.7; N, 21.7. Calc. for $C_9H_{11}N_3O_2$: C, 55.96; H, 5.70; N, 21.76).

1-(m-Methoxyphenyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 96-98°C dec. (CCl_4); IR (KBr): ν_{OH} = 3500-3090 cm^{-1}; ^{1}H NMR(DMSO-d$_6$,δ): 6.85 (m, 4H); 6.45 (d, 1H: exchange with D_2O); 5.54 (m, 1H); 4.18 (d, 2H); 3.74 (s, 3H). (Found: C, 55.9; H, 5.7; N, 21.7. Calc. for $C_9H_{11}N_3O_2$: C, 55.96; H, 5.70; N, 21.76).

1-(p-Methoxyphenyl)-4,5-dihydro-5-hydroxy-1H-1,2,3-triazole, m.p. 131-132°C dec. (ethanol); IR (KBr): ν_{OH}=3500-3100 cm^{-1}; ^{1}H NMR(DMSO-d$_6$,δ): 6.95 (m, 4H); 6.25 (d, 1H: exchange with D_2O); 5.40 (m, 1H); 4.01 (d, 2H); 3.60 (s, 3H). (Found: C, 55.9; H, 5.7; N, 21.7. Calc. for $C_9H_{11}N_3O_2$: C, 55.96; H, 5.70; N, 21.76).

1-Phenyl-1H-1,2,3-triazole, m.p. 50-52°C (lit^{13} 56°) (ether-petrol); ^{1}H NMR ($CDCl_3$,δ): 8.03 (d, 1H; J=1Hz, lit^{6b} 1Hz); 7.90 (d, 1H; J≈1Hz, lit^{6b} 1Hz); 7.43 (m, 5H). (Found: C, 66.2; H, 4.8; N, 28.9. Calc. for $C_8H_7N_3$: C, 66.21; H, 4.83; N, 28,96).

1-(p-Tolyl)-1H-1,2,3-triazole, m.p. 85-86°C (ether-petrol); ^{1}H NMR ($CDCl_3$,δ): 7.92 (d, 1H; J≈1Hz); 7.80 (d, 1H; J=1Hz); 7.47 (m, 4H); 2.40 (s, 3H). (Found: C, 67.9; H, 5.6; N, 26.4. Calc. for $C_9H_9N_3$: C, 67.92; H, 5.66; N, 26.41).

1-(o-Methylthiophenyl)-1H-1,2,3-triazole, oil; ^{1}H NMR(CCl_4,δ): 7.80 (d, 1H; J≈1Hz); 7.68 (d, 1H; J≈1Hz); 7.22 (m, 4H); 2.29 (s, 3H). (Found: C, 56.5; H, 4.7; N, 21.8. Calc. for $C_9H_9N_3S$: C, 56.54; H, 4.71; N, 22.00).

1-(o-Ethylthiophenyl)-1H-1,2,3-triazole, oil; ^{1}H NMR($CDCl_3$,δ): 7.90 (d, 1H; J≈1Hz); 7.75 (d, 1H; J ≈ 1Hz); 7.37 (m, 4H); 2.76 (q, 2H); 1.25 (t, 3H). (Found: C, 58.5; H, 5.3; N, 20.4. Calc. for $C_{10}H_{11}N_3S$: C, 58.54; H, 5.37; N, 20.49).

1-(o-Methoxyphenyl)-1H-1,2,3-triazole, oil; ^{1}H NMR($CDCl_3$,δ): 7.98 (d, 1H; J≈1Hz), 7.61 (d, 1H; J=1 Hz); 7.00 (m, 4H); 3.78 (s, 3H).(Found: C, 61.7; H, 5.1; N, 24.0. Calc. for $C_9H_9N_3O$: C, 61.71; H, 5.14; N, 24.00).

1-(m-Methoxyphenyl)-1H-1,2,3-triazole, oil; ^{1}H NMR($CDCl_3$,δ): 7,92 (d, 1H; J=1Hz); 7.69 (d, 1H; J≈ 1Hz); 7.08 (m, 4H); 3.79 (s, 3H). (Found: C, 61.7; H, 5.1; N, 23.9. Calc. for $C_9H_9N_3O$: C, 61.71; H, 5.14; N, 24.00).

1-(p-Methoxyphenyl)-1H-1,2,3-triazole, oil; ^{1}H NMR($CDCl_3$,δ): 7.85 (d, 1H; J≈1Hz); 7.71 (d, 1H; J≈ 1Hz); 7.21 (m, 4H); 3.79 (s, 3H). (Found: C, 61.7; H, 5.1; N, 24.0. Calc. for $C_9H_9N_3O$: C, 61.71; H, 5.14; N, 24.00).

Formanilide, m.p. 46-47° (lit^{14} 47°) (ether-petrol) and N-formyl-p-toluidine, m.p. 51-52° (lit^{15} 52°) (ether-petrol), were identical to authentic samples (mixed m.p.s and IR spectra).

N-formyl-o-thioanisidine, m.p. 52-54° (lit^{15} 53-54°)(CCl_4); IR (CH_2Cl_2): ν_{NH}=3340 cm^{-1}; $\nu_{C=O}$=1700 cm^{-1}; ^{1}H NMR($CDCl_3$, δ): 8.72-8.43 (bs, 1H: exchange with D_2O); 8.15 (m, 1H); 7.00 (m, 4H); 2.29 (s, 3H).

N-formyl-o-thiophenetidine, m.p. 29-30° (ether-petrol); IR (CH_2Cl_2): ν_{NH}=3340 cm^{-1}; $\nu_{C=O}$=1700 cm^{-1}; ^{1}H NMR($CDCl_3$,δ): 8.41 (m, 1H); 8.05-7.90 (bs, 1H: exchange with D_2O); 7.15 (m, 4H); 2.68 (q, 2H); 1.12 (t, 3H). (Found: C, 59.6; H, 6.1; N, 7.7. Calc. for $C_9H_{11}NOS$: C, 59.67; H, 6.08; N, 7.73).

N-formyl-o-anisidine, m.p. 82-83° (lit^{15} 83.5°) (CCl_4); IR (CH_2Cl_2): ν_{NH}=3400 cm^{-1}; $\nu_{C=0}$=1700 cm^{-1}; ^{1}H NMR($CDCl_3$,δ): 8.33 (m, 1H) 8.14-7.92 (bs, 1H: exchange with D_2O); 6.90 (m, 4H); 3.83 (s, 3H).

N-formyl-m-anisidine, m.p. 55-57° (lit^{14} 57°) (CCl_4); IR (CH_2Cl_2): ν_{NH}=3421 cm^{-1}; $\nu_{C=0}$=1702 cm^{-1}; ^{1}H NMR($CDCl_3$,δ): 9.28-8.97 (bs, 1H: exchange with D_2O); 8.44 (m, 1H); 6.78 (m, 4H); 3.72 (s, 3H).

N-formyl-p-anisidine, m.p. 80-81° (lit^{15} 81°) (CCl_4); IR (CH_2Cl_2):ν_{NH}=3430 cm^{-1};$\nu_{C=0}$=1700 cm^{-1}; ^{1}H NMR($CDCl_3$,δ): 8.37 (m, 1H); 8.20-7.90 (bs, 1H: exchange with D_2O); 7.20 (m, 4H); 3.75 (s, 3H).

All the isolated anilines were identical (IR, NMR) to authentical samples, i.e. to those used for the synthesis of the starting arylazides.

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