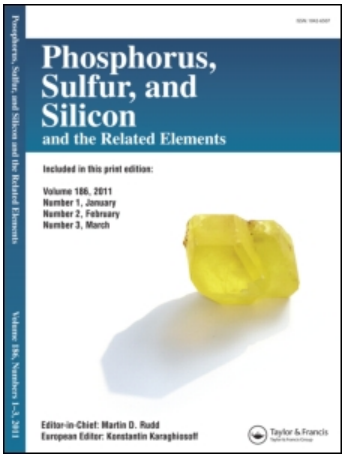

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SYNTHESIS AND REACTIONS OF TRIPHENYLPHOSPHONIMINOGLYOXALIC ACID ANILIDE ARYLHYDRAZONES

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SYNTHESIS AND REACTIONS OF TRIPHENYLPHOSPHONIMINOGLYOXALIC ACID ANILIDE ARYLHYDRAZONES

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A series of α-azidoglyoxalic acid anilide arylhydrazones **2** were prepared and converted to the corresponding phosphonimines **6** by reaction with triphenylphosphine. Treatment of the latter with acyl chlorides yielded the phosphonium salts **9** which afforded, upon treatment with triethylamine, 1,5-disubstituted 1H-1,2,4-triazole-3-carboxylic acid anilides **11**. Acid hydrolysis of **6** yielded the amidrazones **8**.

Key words: 1H-1,2,4-Triazoles; hydrazonyl chlorides; phosphonimines; amidrazones; azidoglyoxalic acid anilide arylhydrazones.

Although *N*-aryl-C-phenylaminocarbonylmethanohydrazonyl chlorides **1** have been known[1] since 1924, their reaction with the azide ion has not yet been reported. In the light of the known versatile reactivity of the azido group,[2] it was thought that hydrazonyl azides of type **2** would be useful intermediates in heterocyclic synthesis.

RESULTS AND DISCUSSION

In this report the previously unknown azidohydrazones **2a–e** were prepared in good yield by reaction of the corresponding hydrazonyl chlorides **1a–e** with sodium azide under phase transfer conditions. Thus, when a mixture of the hydrazonyl chloride **1** and sodium azide was stirred in a tetrahydrofuran-water mixture (4:1 v/v) in the presence of tetrabutylammonium iodide at room temperature, the corresponding *N*-aryl-C-phenylaminocarbonylmethanohydrazonyl azide **2** was obtained in 80% yield (Scheme 1). Attempts to prepare **2** by reacting sodium azide with **1** in 80% aqueous dioxan at 25° as previously described for the synthesis of *N*-arylbenzohydrazonyl azides[3] afforded **2** in lower yields.

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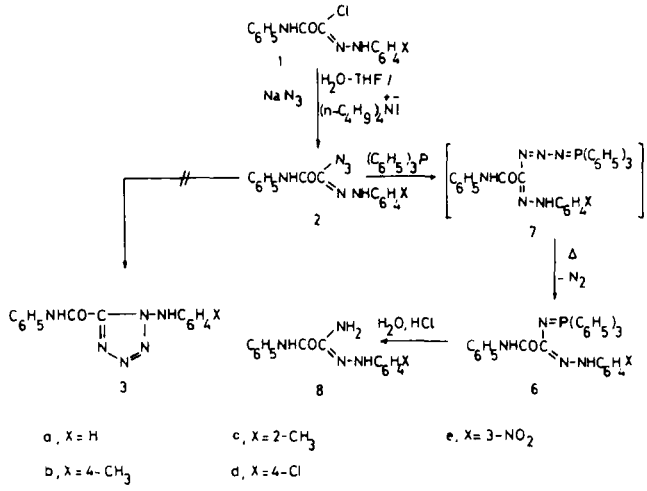


SCHEME 1

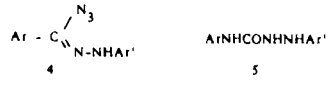


TABLE I

Melting points and analytical data of products **2**, **6** and **8**

Compound no.	M.P. C°	Formula (M.W)	Analysis calculated (found)		
			C, %	H, %	N, %
2a	106	$C_{14}H_{12}N_6O$ (280.292)	60.0 (60.1)	4.3 (4.1)	29.9 (29.7)
2b	107	$C_{15}H_{14}N_6O$ (294.319)	61.2 (61.4)	4.8 (4.6)	28.5 (28.7)
2c	96	$C_{15}H_{14}N_6O$ (294.319)	61.2 (61.1)	4.8 (4.7)	28.5 (28.4)
2d	120	$C_{14}H_{11}ClN_6O$ (314.754)	53.4 (53.5)	3.5 (3.5)	26.7 (26.8)
2e	151	$C_{14}H_{11}N_7O_3$ (325.291)	51.7 (51.5)	3.4 (3.4)	30.1 (29.8)
6a	190	$C_{32}H_{27}N_4OP$ (514.566)	74.7 (74.6)	5.3 (5.4)	10.9 (10.8)
6b	184	$C_{32}H_{29}N_4OP$ (528.593)	75.0 (75.1)	5.5 (5.6)	10.6 (10.4)
6c	198	$C_{33}H_{29}N_4OP$ (528.593)	75.0 (75.2)	5.5 (5.4)	10.6 (10.8)
6d	212	$C_{32}H_{26}N_5O_3P$ (549.028)	70.0 (70.1)	4.7 (4.9)	10.2 (10.0)
6e	205	$C_{32}H_{26}N_5O_3P$ (533.357)	68.6 (68.4)	4.6 (4.7)	12.5 (12.4)
8a	216	$C_{14}H_{14}N_4O$ (254.294)	66.1 (65.9)	5.5 (5.6)	22.0 (21.8)
8b	224	$C_{15}H_{16}N_4O$ (268.321)	67.1 (67.0)	6.0 (6.1)	20.9 (20.7)
8c	230	$C_{14}H_{13}ClN_4O$ (288.756)	58.2 (57.9)	4.5 (4.7)	19.3 (19.5)
8d	200	$C_{14}H_{13}N_5O_3$ (299.293)	56.1 (55.9)	4.3 (4.2)	23.3 (23.1)

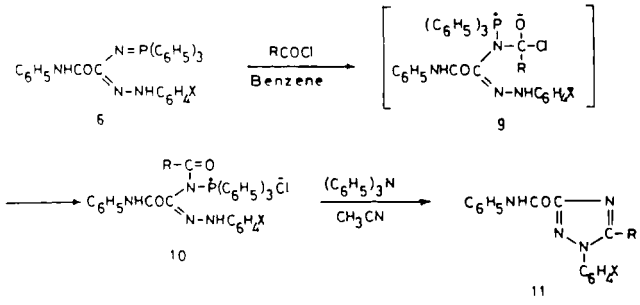
The novel azidohydrazones **2a–e** were characterized by the strong azide absorption at 2120–2130 cm^{-1} in their infrared spectra (Table 1). This finding excludes the isomeric tetrazole structure **3** for the products isolated. Attempts to cyclize the azides **2** to the isomeric tetrazoles **3** by warming them in an inert solvent[4] were not successful, the azides **2** being recovered.

Furthermore, it was reported[5] that *N*-arylbenzohydrazonyl azides **4** undergo acid catalyzed rearrangement to the semicarbazides **5** by suspending the azide in 2.2 M sulfuric acid at room temperature. Similar treatment of the azides **2** at room temperature for one month gave no rearranged products and the starting material was recovered unchanged (Scheme 1).

Treatment of **2a–e** with triphenylphosphine in ether gave after 1 h reflux the phosphonimines **6a–e** respectively in more than 90% yield (Scheme 1). The structure of **6** was confirmed by the absence of the azide absorption band in 2120–2130 cm^{-1} region and the appearance of a P=N stretching band in the 1200–1300 cm^{-1} region in their infrared spectra.[6,7] The results of their elemental analyses and their chemical reactions outlined below are also compatible with their assigned structure.

Although no mechanistic study of this reaction was carried out, it is not unreasonable to assume that the reaction between **2** and triphenylphosphine would follow the same reaction sequence postulated for the phosphonimine formation from triphenylphosphine and alkyl or aryl azides[8] (Scheme 1). The intermediacy of linear adducts of type **7** has been formulated in analogous reactions[9–11] between azides and triphenylphosphine. Chemical evidence for the linear structure of phosphazides has been reported.[12]

The phosphonimines **6** were found to exhibit reactions similar to those of phosphorous yields. For example, it was found that **6a–e** are susceptible to hydrolysis when treated with aqueous hydrochloric acid in ethanol. The reaction products were triphenylphosphine oxide and the amidrazones **8a–e**, respectively (Scheme 2). The ease of acid hydrolysis of **6** seems to be related to their basicity.



11	X/R	11	X/R
a	H/$C_6H_5CH{=}CH$	h	2-CH_3/$C_6H_5CH{=}CH$
b	H/C_6H_5	i	2-CH_3/$C_6H_4CH_3$-4
c	H/$C_6H_4NO_2$-m	j	4-Cl/$C_6H_5CH{=}CH$
d	4-CH_3/$C_6H_5CH{=}CH$	k	4-Cl/C_6H_5
e	4-CH_3/C_6H_5	l	4-Cl/$C_6H_4CH_3$-4
f	4-CH_3/$C_6H_4NO_2$-m	m	4-Cl/$C_6H_4NO_2$-3
g	2-CH_3/CH_3	n	3-NO_2/C_6H_5

SCHEME 2

The most plausible mechanism for this acid hydrolysis is the one that involves initial protonation of nitrogen followed by the attack of oxygen on the phosphorous atom.[13] The structure of the amidrazones **8** was elucidated on the basis of their IR spectra and elemental analyses. In their IR spectra each of these amidrazones exhibits characteristic —NH_2 bands in the 3100–3400 cm^{-1} region.

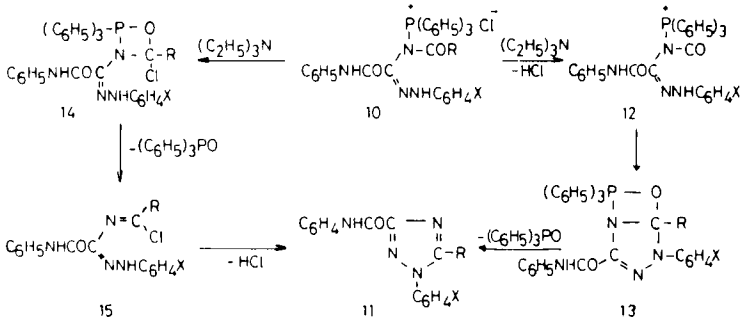
Treatment of **6** with excess of acyl chloride in benzene at room temperature led to the phosphonium salts **10** which were usually isolated as crystalline compounds of analytical purity (Scheme 2). The yields of **10** were almost quantitative. Their assigned structures were compatible with their IR and ^1H NMR spectral data together with their elemental analyses (Tables II and IV). A plausible rationale for the formation of **10** is shown in Scheme 2. The phosphonimine **6** being a nucleophilic reagent can attack the acyl carbon to give the corresponding tetrahedral addition intermediate **9**. Decomposition of the latter would yield the corresponding phosphonium salts **10**.

Treatment of **10** with triethylamine in acetonitrile afforded the triazole derivatives **11** along with triphenylphosphine oxide (Scheme 3). Two possible mechanistic sequences can account for this reaction (Scheme 3). In the first sequence it is assumed that **10** are dehydrochlorinated by triethylamine to give the betaine intermediate **12.** Subsequent nucleophilic attack by the basic centre of

TABLE II

Melting points and analytical data of compounds **10a–n**

Compound No.	M.P. C°	Formula (M.W.)	Analysis calculated (found)		
			C, %	H, %	N, %
10a	146	$C_{41}H_{34}ClN_4O_2P$ (681.191)	72.3 (72.2)	5.0 (4.8)	8.2 (8.1)
10b	100	$C_{39}H_{32}ClN_4O_2P$ (655.153)	71.5 (71.4)	4.9 (5.0)	8.5 (8.4)
10c	110	$C_{39}H_{32}ClN_3O_4P$ (673.146)	68.6 (68.7)	4.5 (4.6)	10.3 (10.1)
10d	102	$C_{42}H_{36}ClN_4O_2P$ (695.218)	72.5 (72.2)	5.2 (5.3)	8.0 (7.8)
10e	185	$C_{40}H_{34}ClN_4O_2P$ (669.180)	71.7 (71.6)	5.1 (5.1)	8.4 (8.3)
10f	142	$C_{40}H_{33}ClN_5O_4P$ (714.179)	67.3 (67.5)	4.6 (4.5)	9.8 (9.6)
10g	210	$C_{35}H_{32}ClN_4O_2P$ (607.109)	69.2 (69.2)	5.3 (5.4)	9.2 (9.1)
10h	173	$C_{42}H_{36}ClN_4O_2P$ (695.218)	72.5 (72.4)	5.2 (5.4)	8.0 (8.1)
10i	135	$C_{41}H_{36}ClN_4O_2P$ (683.207)	72.1 (72.0)	5.3 (5.6)	8.2 (8.2)
10j	199	$C_{41}H_{33}Cl_2N_4O_2P$ (715.653)	68.8 (68.6)	4.6 (4.4)	7.8 (7.7)
10k	96	$C_{39}H_{31}Cl_2N_4O_2P$ (689.615)	67.9 (68.0)	4.5 (4.6)	8.1 (8.3)
10l	199	$C_{40}H_{33}Cl_2N_4O_2P$ (703.642)	68.3 (68.4)	4.7 (4.5)	7.9 (7.8)
10m	154	$C_{39}H_{30}Cl_2N_5O_4P$ (734.614)	63.7 (63.6)	4.1 (4.2)	9.5 (9.4)
10n	102	$C_{39}H_{31}ClN_5O_4P$ (700.172)	66.9 (66.9)	4.5 (4.6)	10.0 (9.8)



SCHEME 3

the hydrazone moiety on the acyl carbon atom would afford the bicyclic derivative **13**. Decomposition of the latter would yield triphenylphosphine oxide and the triazole derivative **11**. Alternatively, nucleophilic addition of the chloride ion to the acyl carbon atom, followed by the decomposition of the formed addition intermediate **14** would lead to the formation of the imidoyl chloride derivative **15** (Scheme 3). The latter then undergoes intramolecular nucleophilic substitution to give **11**. The intermediacy of **15** is a plausible mechanistic option in view of the known formation of imidoyl chlorides upon reaction of phosphonimines with acyl chlorides.[14]

EXPERIMENTAL SECTION

Melting points were taken on a Gallenkamp apparatus and are uncorrected. Infrared spectra were determined on a Pye Unicam SP-3-300 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Varian T-60 instrument with TMS as internal standard. Element analysis were carried out at microanalytical laboratory at University of Cairo, Giza, Egypt. *N*-Aryl-C-phenylaminocarbonylmethanohydrazonyl chlorides **1a–e** were prepared by a literature method.[15]

α-Azidoglyoxalic acid anilide arylhydrazones (**2a–e**). *Method A.* A solution of the appropriate **1** (4 mmol) in tetrahydrofuran (60 ml) was treated with a solution of sodium azide (0.33 g, 5 mmol) and tetrabutylammonium iodide (0.4 mmol) in water (60 ml). The mixture was vigorously stirred for 1 h at room temperature. The organic layer was then collected, washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure the oily residue solidified on trituration with methanol. The crude product was filtered, recrystallized from ethanol or dioxan to give the corresponding **2** in 80–90% (Table I).

Method B. To a solution of **1** (3 mmol) in dioxan-water mixture (4:1, v/v, 70 ml) was added a solution of sodium azide (0.26 g, 4 mmol) in the same solvent mixture (10 ml). The reaction mixture was stirred at room temperature for 3 h, then diluted with water (100 ml). The solid that precipitated was collected and recrystallized from ethanol or dioxan to give **2** in 60–70% yield. The compounds prepared by this method were identical in all respects (m.p., IR spectra) with those obtained by Method A.

α-Triphenylphosphoniminoglyoxalic acid anilide arylhydrazones (**2a–e**). A solution of the appropriate azidohyrazone **2** (20 mmol) and triphenylphosphine (5.2 g, 20 mmol) in dry ether (100 ml) was refluxed for 1 h and cooled. The solid that precipitated was filtered and washed with ether. The products **6a–e** obtained proved to be analytically pure and were not further crystallized (Table I).

Hydrolysis of the iminophosphoranes **6a–d**. To a solution of the appropriate iminophosphorane **6** (0.5 g) in ethanol-water mixture (4:1 v/v, 20 ml) was added concentrated hydrochloric acid (3 ml). The mixture was refluxed for 2 h during which the iminophosphorane **6** dissolved. Upon cooling the crude amidrazone **8** precipitated. It was collected, washed with dilute solution of sodium bicarbonate and recrystallized from ethanol to give the amidrazone **8** in almost quantitative yield (Table I).

TABLE III

Melting points and analytical data of triazole derivatives **11a–n**

Compound no.	M.P. C°	Formula (M.W.)	Analysis calculated (found)		
			C, %	H, %	N, %
11a	184	$C_{23}H_{18}N_4O$ (366.425)	75.3 (75.6)	5.0 (5.2)	15.3 (15.2)
11b	219	$C_{21}H_{16}N_4O$ (340.387)	74.1 (74.3)	4.7 (4.4)	16.5 (16.4)
11c	212	$C_{21}H_{15}N_5O_3$ (385.386)	65.4 (65.6)	3.9 (3.7)	18.1 (17.9)
11d	180	$C_{24}H_{20}N_4O$ (304.264)	75.7 (75.8)	5.3 (5.2)	14.7 (14.6)
11e	214	$C_{22}H_{18}N_4O$ (354.414)	74.6 (74.6)	5.1 (5.0)	15.8 (15.6)
11f	188	$C_{22}H_{17}N_5O_3$ (399.413)	66.2 (66.6)	4.3 (4.4)	17.5 (17.4)
11g	184	$C_{17}H_{16}N_4O$ (292.343)	69.8 (69.6)	5.5 (5.1)	19.2 (19.0)
11h	190	$C_{24}H_{20}N_4O$ (382.052)	75.7 (75.8)	5.3 (5.4)	14.7 (14.8)
11i	165	$C_{23}H_{20}N_4O$ (370.041)	74.9 (74.8)	5.5 (5.5)	15.2 (15.3)
11j	214	$C_{23}H_{17}ClN_4O$ (400.887)	68.9 (69.0)	4.3 (4.3)	13.9 (13.7)
11k	260	$C_{21}H_{15}ClN_4O$ (374.849)	67.3 (67.3)	4.0 (4.1)	14.9 (14.7)
11l	126	$C_{22}H_{17}ClN_4O$ (388.848)	68.0 (68.2)	4.4 (4.5)	14.4 (14.2)
11m	220	$C_{21}H_{14}ClN_5O_3$ (419.848)	60.1 (60.2)	3.4 (3.3)	16.7 (16.6)
11n	188	$C_{21}H_{15}N_5O_3$ (385.386)	65.4 (65.6)	3.9 (4.1)	18.1 (18.0)

TABLE IV

Characteristic IR spectral data of products **2**, **6**, **8**, **10** and **11**

Compound no.	$\bar{\nu}_{CO}^{Cm^{-1}}$	$\bar{\nu}N_3$ (P=N)	$\bar{\nu}_{NH}$	Compound no.	$\bar{\nu}_{CO}^{Cm^{-1}}$	$\bar{\nu}_{NH}$
2a	1650	2120	3320,	**10h**	1660	3240, 3420
2b	1650	2120	3320, 3360	**10i**	1650	3210, 3400
2c	1650	2122	3310, 3350	**10j**	1660	3200, 3420
2d	1660	2060	3330, 3380	**10k**	1660	3200, 3280
2e	1650	2130	3280, 3370	**10l**	1650	3320, 3400
6a	1650	(1270)	3270, 3500	**10m**	1650	3380, 3420
6b	1650	(1240)	3280, 3310	**10n**	1660	3160, 3340
6c	1650	(1240)	3300, 3340	**11a**	1650	3340
6d	1650	(1230)	3530, 3320	**11b**	1650	3360
6e	1660	(1260)	3330, 3360	**11c**	1690	3180
8a	1650		3200, 3250	**11d**	1660	3360
8b	1660		3150, 3400	**11e**	1650	3340
8c	1660		3230, 3430	**11f**	1670	3360
8d	1650		3200, 3360	**11g**	1650	3260
10a	1650		3420, 3480	**11h**	1650	3340
10b	1650		3280, 3390	**11i**	1660	3320
10c	1660		3200, 3400	**11j**	1650	3350
10d	1650		3300, 3500	**11k**	1650	3240
10e	1650		3300, 3440	**11l**	1650	3320
10f	1650		3340, 3440	**11m**	1670	3340
10g	1650		3300, 3440	**11n**	1660	3310

TABLE V

Characteristic ^{1}H NMR data of products **2**, **6**, **10** and **11**

Compound no.	δ, ppm (multiplicity)
2b	2.15 (s, 3H), 6.8–7.9 (m, 11H)
2c	2.15 (s, 3H), 7.0–7.7 (m, 10H), 8.45 (s, 1H)
6a	7.1–7.8 (m, 25H), 8.5 (s, 1H), 9.1 (s, 1H)
6b	2.25 (s, 3H), 7.0–7.7 (m, 24H), 8.55 (s, 1H), 9.15 (s, 1H)
6c	2.2 (s, 3H), 7.0–7.7 (m, 24H), 8.65 (s, 1H), 9.1 (s, 1H)
6d	7.0–7.7 (m, 24H), 8.6 (s, 1H), 9.0 (s, 1H)
6e	7.1–7.8 (m, 24H), 8.5 (s, 1H), 9.1 (s, 1H)
10d	2.2 (s, 3H), 6.25 (s, 1H), 6.4 (s, 1H), 7.0–7.9 (m, 30H), 9.2 (s, 1H)
10e	2.2 (s, 3H), 7.0–7.7 (m, 30H), 9.15 (s, 1H)
10f	2.25 (s, 3H), 7.0–7.7 (m, 29H), 8.2 (s, 1H)
10g	2.0 (s, 3H), 2.6 (s, 3H), 7.0–7.8 (m, 24H), 11.8 (s, 1H), 12.05 (s, 1H)
10h	2.25 (s, 3H), 6.3 (s, 1H), 6.5 (s, 1H), 7.0–7.9 (m, 30H), 9.15 (s, 1H)
10l	2.3 (s, 3H), 7.0–7.8 (m, 29H), 9.2 (s, 1H)
11a	6.8–7.8 (m, 17H), 9.1 (s, 1H)
11d	2.3 (s, 3H), 7.0–7.8 (m, 16H), 9.1 (s, 1H)
11e	2.3 (s, 3H), 6.9–7.7 (m, 14H), 11.7 (s, 1H)
11f	2.3 (s, 3H), 7.0–7.8 (m, 13H), 8.9 (s, 1H)
11g	1.5 (s, 3H), 2.7 (s, 3H), 7.0–7.9 (m, 9H), 11.7 (s, 1H)
11h	2.3 (s, 3H), 6.8–7.9 (m, 20H), 9.2 (s, 1H)
11i	2.3 (s, 3H), 3.7 (s, 3H), 6.6–7.5 (m, 13H), 9.3 (s, 1H)
11l	2.2 (s, 3H), 7.0–7.6 (m, 9H), 9.4 (s, 1H)

Reaction of the Iminophosphoranes **6** *with Acyl Chlorides.* A mixture of the appropriate iminophosphorane **6** (1 mmol) and acyl chloride (2 mmol) in dry benzene (50 ml) was stirred at room temperature for 3 h. Then the reaction mixture was treated with petroleum ether (50 ml, 40/60°). The crude product that precipitated was filtered and washed with petroleum ether. Crystallization from benzene-petroleum ether mixture gave the corresponding phosphonium chloride **10** (Table II).

1,5-Disubstituted 1H-1,2,4-Triazole-3-carboxanilides (**11a–n**). To a solution of the appropriate phosphonium chloride **10** (2 mmol) in acetonitrile (100 ml) was added triethylamine (6 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was then evaporated and the residue left was triturated with ethanol where it solidified. The crude triazole **11** was filtered and recrystallized from acetonitrile (Table III).

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