

Facile and Convenient Synthesis of Triazolopyridazine Derivatives via 1,3-Dipolar Cycloaddition Reaction of Organic Azides†

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1,3-Dipolar cycloaddition reactions of substituted benzyl azides **1a-t** and bis (azidomethyl) benzenes **2a-c** with dibenzoylacetylene **3** afforded the corresponding 1H-1,2,3-triazole derivatives **4a-t** and **7a-c** respectively. Reaction of these triazoles **4a-t** and **7a-c** with hydrazine hydrate in ethanolic solution was found to produce in high yield the corresponding triazolopyridazine and bis (triazolopyridazine) derivatives **6a-t** and **9a-c** respectively. The structures of the newly synthesized products **4**, **6**, **7** and **9** were confirmed from their spectral and analytical data.

INTRODUCTION

The chemistry of 1,2,3-triazoles has received much attention because of their large variety of applications. These compounds have been used as fungicides, herbicides, light stabilizers, fluorescent whiteners, optical brightening agents and corrosion retardants¹⁻⁸. Moreover 1,2,3-triazole derivatives show significant antimicrobial cytostatic, virostatic and antiinflammatory characters⁹. The thermal 1,3-dipolar, cycloaddition reaction of organic azides with acetylenic compounds was proved to be the most important route for the synthesis of 1H-1,2,3-triazoles¹⁰⁻¹⁴. Although this method can in principle be applied to different combinations of azides and acetylenes, it requires elevated temperatures which may cause a decomposition of the azides. In order to overcome such problems, such reactions should be carried out on a small scale and at high dilution. On the other hand, the reaction with unsymmetrical acetylenes with azides can in principle give rise to two isomeric triazoles. A comprehensive review on the 1,3-dipolar cycloaddition reaction of azides with different substituted acetylenes can be found in Padwa's work¹⁴.

We have been interested in these reactions since 1986 and few publications concerning the reaction of these azides appeared in the literature¹⁵⁻¹⁹.

In the present paper, we describe the cycloaddition reaction of substituted benzyl azides **1a-t** and bis(azidomethyl) benzenes **2a-c** with dibenzoylacetylene

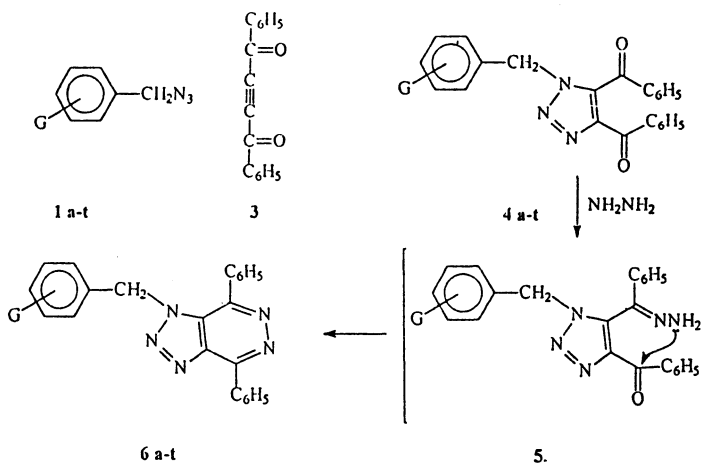
†Based in part on the M.Sc. Thesis of K.H. Abu-Shandi (1995), Yarmouk University, Irbid, Jordan.

3 to form the corresponding triazole derivatives and the reaction of these triazoles with hydrazine to form the triazolopyridazine. To the best of our knowledge, this method of synthesis represents a unique and convenient one for the synthesis of compounds containing the two moieties 1H-1,2,3-triazole and pyridazine in a fused form through the 1,3-dipolar cycloaddition reaction.

RESULTS AND DISCUSSION

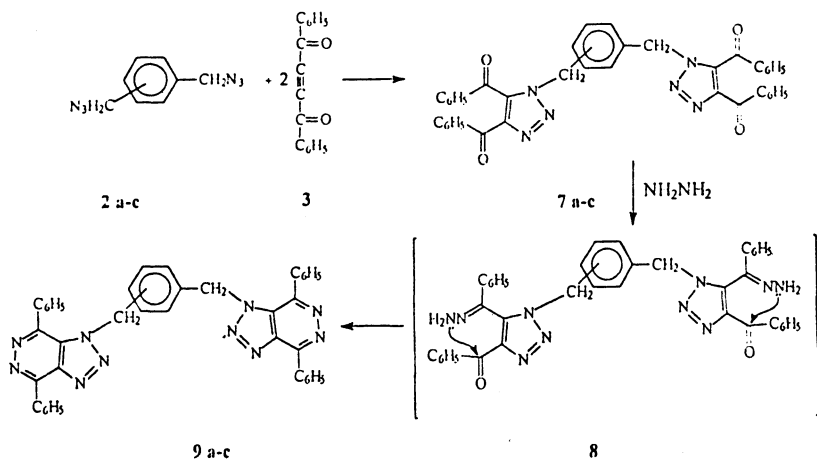
The reaction of substituted benzyl azides **1a-t** and bis (azidomethyl) benzenes **2a-c** with dibenzoylacetylene **3** in boiling ethanol produce the corresponding triazoles **4a-t** and **7a-c** in good yields as shown in schemes 1 and 2 respectively. The completion of the reaction was monitored by the disappearance of the azide infrared absorption band in the range 2220–2170 cm^{-1} in the reaction mixture.

The triazole compounds **4** and **7** were found to be good precursors for the synthesis of triazolopyridazine. Therefore, compounds **4** and **7** when reacted with hydrazine in refluxing ethanol, afforded the corresponding triazolopyridazine and bis(triazolopyridazine) compounds **6** and **9** in excellent yields as shown in schemes 1 and 2. The structures of the newly synthesized products **4**, **6**, **7** and **9**



were elucidated from their spectral data. The IR spectra of triazoles **4a-t** and **7a-c** showed a strong absorption in the range 1650–1640 cm^{-1} due to the (C=O) stretching frequency and a band in the range 1440–1420 cm^{-1} attributed to N=N stretching frequency. The lower C=O frequency value can be attributed to the conjugation of this group with the phenyl and triazole rings.

In the $^1\text{H-NMR}$ spectra of these triazoles **4a-t** and **7a-c**, the benzylic protons appeared as a singlet in the range 5.44–6.04 ppm, the aromatic protons appeared as two sets of multiplets in the range 6.63–8.09 ppm and 8.12–8.65 ppm integrating for fourteen and twentyfour protons corresponding to compounds **4a-t** and **7a-c** respectively. On the other hand, in the $^{13}\text{C-NMR}$ spectra the two



Scheme 2

carbonyl carbons appeared as two singlets at about 186.7 ppm and 184.7 ppm; the benzylic carbon appeared in the range from 50.9–52.9 ppm. furthermore C-4 in the triazole ring appeared in the range 147.0–147.4 ppm. The signal of the vinylic carbon (C-5) could not be assigned since it overlapped with the carbons of the phenyl groups. The analytical and spectral data for the triazoles **4a–t** and bis-triazoles **7a–c** are given in Tables 1 and 3.

Likewise, the IR spectra of triazolopyridazine **6a–t** and bis(triazolopyridazine) **9a–c** showed a strong absorption band in the range of 1610–1580 cm^{-1} assigned to the carbon-carbon double bonds stretching frequency and a band in the range of 1440–1420 cm^{-1} due to the (N=N) stretching frequency.

In the $^1\text{H-NMR}$ spectra of compounds **6a–t** and **9a–c**, the aromatic protons appeared as a two sets of multiplets in the ranges 8.83–9.01 ppm and 6.15–7.82 ppm. The benzylic protons appeared as a singlet in the range 5.69–6.18 ppm. The protons of the methoxy group attached to the benzene ring in compounds **6b** and **6c** appeared as a singlet at 3.69 and 3.64 ppm respectively. Whereas the protons of the methyl group in compounds **6d–f** appeared as a singlet in the range 2.22–1.96 ppm. The mass spectrum for bis(triazolopyridazine) **9b** showed the molecular ion peak at m/z : 648 (M^+ , 13%), 620 ($M^+-\text{N}_2$, 25%), 390 ($M^+-\text{C}_{16}\text{H}_{10}\text{N}_4$, 8%) and 189 ($M^+-\text{C}_{32}\text{H}_{20}\text{N}_4$, 100%). The analytical and spectral data for the triazolopyridazines **6a–t** and bis(triazolopyridazines) **9a–c** are given in Tables 2 and 4.

EXPERIMENTAL

Benzyl and substituted benzyl azides **1a–t** were prepared according to the previously published methods^{19,20}. Bis (azidomethyl) benzenes **2a–c** were prepared according to our earlier published method¹⁵. Dibenzoylacetylene **3** was prepared from *trans*-1,2-dibenzoyl ethylene according to previously reported

TABLE-1
ANALYTICAL AND SPECTRAL DATA FOR 1-SUBSTITUTED-4,5-DIBENZOYL-1H-1,2,3-TRIAZOLES (4a-f)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	Elemental analysis (%): found (calcd.)			IR (KBr, cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
					C	H	N		
4a (C ₂₃ H ₁₇ N ₃ O ₂)	H	87	5	149-50	75.33 (75.19)	4.32 (4.66)	11.72 (11.44)	1640, 1590, 1440	8.38-8.26 (m, 2H), 7.56-7.17 (m, 13H), 5.64 (s, 2H)
4b (C ₂₄ H ₁₉ N ₃ O ₃)	4-OCH ₃	86	9	105-07	72.21 (72.53)	4.86 (4.82)	10.44 (10.57)	1650, 1600, 1440	8.38-8.25 (m, 2H), 7.60-7.26 (m, 8H), 7.11 (d, 2H, J = 8.8 Hz), 6.63 (d, 2H, J = 8.8 Hz), 5.57 (s, 2H), 3.65 (s, 3H)
4c (C ₂₄ H ₁₉ N ₃ O ₃)	3-OCH ₃	80	6	101-03	72.68 (72.53)	4.93 (4.82)	10.30 (10.57)	1650, 1600, 1440	8.38-8.25 (m, 2H), 7.60-6.63 (m, 12H), 5.60 (s, 2H), 3.60 (s, 3H)
4d (C ₂₄ H ₁₉ N ₃ O ₂)	4-CH ₃	79	6	133-35	75.46 (75.57)	5.11 (5.02)	11.40 (11.02)	1645, 1590, 1440	8.36-8.26 (m, 2H), 7.56-6.98 (m, 12H), 5.58 (s, 2H), 2.18 (s, 3H)
4e (C ₂₄ H ₁₉ N ₃ O ₂)	3-CH ₃	83	7	104-05	75.23 (75.57)	4.81 (5.02)	11.32 (11.02)	1650, 1600, 1440	8.39-8.27 (m, 2H), 7.60-6.96 (m, 12H), 5.59 (s, 2H), 2.12 (s, 3H)
4f (C ₂₄ H ₁₉ N ₃ O ₂)	2-CH ₃	84	7	149-50	75.83 (75.57)	5.40 (5.02)	10.83 (11.02)	1650, 1600, 1440	8.43-8.31 (m, 2H), 7.62-6.98 (m, 12H), 5.69 (s, 2H), 2.30 (s, 3H)
4g (C ₂₃ H ₁₆ N ₄ O ₄)	4-NO ₂	87	7	167-69	66.70 (66.99)	3.83 (3.91)	13.41 (13.59)	1645, 1600, 1430	8.35-8.12 (m, 2H), 8.02 (d, 2H), 7.63-7.21 (m, 10H) 573 (s, 2H)
4h (C ₂₃ H ₁₆ N ₄ O ₄)	3-NO ₂	78	8	139-40	67.32 (66.99)	4.16 (3.91)	13.39 (13.59)	1640, 1600, 1430	8.38-8.26 (m, 2H), 8.09-8.01 (m, 2H) 7.66-7.27 (m, 10H), 5.75 (s, 2H)
4i (C ₂₃ H ₁₆ N ₄ O ₄)	2-NO ₂	83	9	129-30	66.63 (66.99)	4.01 (3.91)	13.49 (13.59)	1645, 1590, 1425	8.36-8.03 (m, 3H), 7.76-7.19 (m, 11H), 6.04 (s, 2H)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	Elemental analysis (%): found (calcd.)			IR (KBr, cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
					C	H	N		
4j (C ₂₃ H ₁₆ ClN ₃ O ₂)	4-Cl	85	4	120–21	68.90 (68.74)	4.36 (4.01)	10.48 (10.46)	1640, 1600, 1425	8.37–8.25 (m, 2H), 7.60–7.14 (m, 12H), 5.60 (s, 2H)
4k (C ₂₃ H ₁₆ ClN ₃ O ₂)	3-Cl	80	7	124–25	68.71 (68.74)	4.27 (4.01)	19.34 (10.46)	1645, 1590, 1435	8.38–8.26 (m, 2H), 7.61–7.10 (m, 12H), 5.59 (s, 2H)
4l (C ₂₃ H ₁₆ ClN ₃ O ₂)	2-Cl	90	8	145–46	69.00 (68.74)	4.29 (4.01)	10.64 (10.46)	1649, 1590, 1420	8.40–8.28 (m, 2H), 7.67–7.08 (m, 12H), 5.59 (s, 2H)
4m (C ₂₃ H ₁₆ BrN ₃ O ₂)	4-Br	90	5	127–28	61.96 (61.89)	3.64 (3.61)	9.28 (9.42)	1640, 1600, 1420	8.37–8.25 (m, 2H), 7.57–7.01 (m, 12H), 5.58 (s, 2H)
4n (C ₂₃ H ₁₆ BrN ₃ O ₂)	3-Br	85	4	121–22	62.01 (61.89)	3.87 (3.61)	9.43 (9.42)	1640, 1590, 1435	8.39–8.27 (m, 2H), 7.62–7.01 (m, 12H), 5.59 (s, 2H)
4o (C ₂₃ H ₁₆ BrN ₃ O ₂)	2-Br	77	6	156–157	62.11 (61.89)	3.56 (3.61)	9.63 (9.42)	1640, 1590, 1435	8.41–8.29 (m, 2H), 7.65–7.10 (m, 12H), 5.76 (s, 2H)
4p (C ₂₃ H ₁₆ FN ₃ O ₂)	4-F	86	8	114–15	71.93 (71.69)	4.30 (4.16)	10.77 (10.91)	1660, 1590, 1440	8.35–8.27 (m, 2H), 7.58–6.83 (m, 12H), 5.60 (s, 2H)
4q (C ₂₃ H ₁₆ FN ₃ O ₂)	3-F	84	8	111–12	71.89 (71.69)	4.09 (4.16)	10.89 (10.91)	1650, 1600, 1440	8.28–8.22 (m, 2H), 7.59–6.97 (m, 12H), 5.61 (s, 2H)
4r (C ₂₃ H ₁₆ FN ₃ O ₂)	2-F	81	8	159–60	71.60 (71.69)	4.17 (4.16)	10.77 (10.91)	1640, 1590, 1440	8.35–8.29 (m, 2H), 7.47–6.90 (m, 12H), 5.83 (s, 2H)
4s (C ₂₃ H ₁₅ Cl ₂ N ₃ O ₂)	2,6-Dichloro	92	8	190–91	63.34 (63.30)	3.47 (3.44)	9.60 (9.63)	1640, 1590, 1440	8.36–8.26 (m, 2H), 7.44–7.13 (m, 11H), 5.87 (s, 2H)
4t (C ₂₈ H ₂₇ N ₃ O ₂)	2,3,4,5,6-Pentamethyl	83	8	178–79	76.37 (76.89)	6.12 (6.18)	9.53 (9.61)	1730, 1680, 1450	8.65–8.50 (m, 2H), 7.80–7.06 (m, 8H), 5.80 (s, 2H), 2.20 (s, 3H), 1.95 (s, 6H), 1.80 (s, 6H)

TABLE-2
ANALYTICAL AND SPECTRAL DATA FOR 1-SUBSTITUTED BENZYL-4,7-DIPHENYL-1H,1,2,3-TRIAZOLO [4,5-D] PYRIDAZINE (6a-t)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	Elemental analysis (%)			IR (KBr cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
					found (calcd.)	C	H		
6a (C ₂₃ H ₁₇ N ₅)	H	78	6	157-58	75.98 (76.03)	4.80 (4.68)	19.28 (19.28)	1590, 1430	8.92-8.85 (m, 2H), 7.60-6.58 (m, 13H), 5.79 (s, 2H)
6b (C ₂₄ H ₁₉ N ₅ O)	4-OCH ₃	92	6	176-77	73.32 (73.28)	4.97 (4.83)	17.60 (17.81)	1600, 1430	8.91-8.83 (m, 2H), 7.64-6.56 (m, 12H), 5.74 (s, 3H), 3.69 (s, 3H)
6c (C ₂₄ H ₁₉ N ₅ O)	3-OCH ₃	82	5	138-39	73.29 (73.28)	4.96 (4.83)	17.80 (17.81)	1600, 1440	8.92-8.88 (m, 2H), 7.60-6.15 (m, 12H), 5.77 (s, 2H), 3.64 (s, 3H)
6d (C ₂₄ H ₁₉ N ₅)	4-CH ₃	89	5	179-80	76.35 (76.39)	5.10 (5.04)	18.48 (18.57)	1590, 1430	8.96-8.84 (m, 2H), 7.60-6.15 (m, 12H), 5.77 (s, 2H), 2.22 (s, 3H)
6e (C ₂₄ H ₁₉ N ₅)	3-CH ₃	90	5	125-27	76.36 (76.39)	5.27 (5.04)	18.63 (18.57)	1600, 1440	8.92-8.84 (m, 2H), 7.65-6.31 (m, 12H), 5.76 (s, 2H), 2.13 (s, 3H)
6f (C ₂₄ H ₁₉ N ₅)	2-CH ₃	85	5	187-88	76.36 (76.39)	4.90 (5.04)	18.49 (18.57)	1600, 1400	8.99-8.87 (m, 2H), 7.68-7.06 (m, 12H), 5.68 (s, 2H), 1.96 (s, 3H)
6g (C ₂₃ H ₁₆ N ₆ O ₂)	4-NO ₂	74	4	237-39	67.44 (67.65)	4.13 (3.92)	20.36 (20.59)	1600, 1430	9.07-9.01 (m, 2H), 7.61-7.16 (m, 12H), 6.08 (s, 2H)
6h (C ₂₃ H ₁₆ N ₆ O ₂)	3-NO ₂	89	4	193-95	67.47 (67.65)	4.03 (3.92)	20.36 (20.59)	1580, 1430	9.00-8.95 (m, 2H), 7.65-7.03 (m, 12H), 5.96 (s, 2H)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	Elemental analysis (%)			IR (KBR cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
					found (calcd.)	C	H		
6i (C ₂₃ H ₁₆ N ₆ O ₂)	2-NO ₂	94	4	241-42	67.43 (67.65)	3.95 (3.92)	20.43 (20.59)	1580, 1430	9.01-8.89 (m, 2H), 7.68-7.26 (m, 12H), 6.18 (s, 2H)
6j (C ₂₃ H ₁₆ ClN ₅)	4-Cl	81	6	224-25	69.59 (69.43)	4.16 (4.02)	17.46 (17.61)	1590, 1430	8.96-8.90 (m, 2H), 7.60-6.95 (m, 12H), 5.69 (s, 2H)
6k (C ₂₃ H ₁₆ ClN ₅)	3-Cl	71	6	161-62	69.60 (69.43)	4.14 (4.02)	17.61 (17.61)	1590, 3430	8.96-8.87 (m, 2H), 7.60-6.40 (m, 12H), 5.75 (s, 2H)
6l (C ₂₃ H ₁₆ ClN ₅)	2-Cl	71	6	187-88	69.19 (69.43)	3.90 (4.02)	17.43 (17.61)	1590, 1430	9.01-8.92 (m, 2H), 7.67-6.32 (m, 12H), 5.83 (s, 2H)
6m (C ₂₃ H ₁₆ BrN ₅)	4-Br	82	4	227-29	62.44 (62.44)	3.69 (3.62)	15.69 (15.84)	1600, 1440	8.92-8.90 (m, 2H), 7.58-6.37 (m, 12H), 5.76 (s, 2H)
6n (C ₂₃ H ₁₆ BrN ₅)	3-Br	80	4	184-185	62.32 (62.44)	3.55 (3.62)	15.72 (15.84)	1600, 1440	8.96-8.89 (m, 2H), 7.60-6.34 (m, 12H), 5.75 (s, 2H)
6o (C ₂₃ H ₁₆ BrN ₅)	2-Br	77	4	190-91	62.26 (62.44)	3.50 (3.62)	15.64 (15.84)	1580, 1430	9.00-8.89 (m, 2H), 7.67-7.12 (m, 12H), 5.78 (s, 2H)
6p (C ₂₃ H ₁₆ FN ₅)	4-F	85	8	167-68	72.23 (72.44)	4.31 (4.20)	18.10 (18.37)	1600, 1440	9.01-8.85 (m, 2H), 7.64-6.30 (m, 12H), 5.89 (s, 2H)
6q (C ₂₃ H ₁₆ FN ₅)	3-F	79	8	139-41	72.59 (72.44)	4.09 (4.20)	18.12 (18.37)	1610, 1440	8.96-8.87 (m, 2H), 7.66-6.28 (m, 12H), 5.79 (s, 2H)
6r (C ₂₃ H ₁₆ FN ₅)	2-F	79	8	159-60	72.25 (72.44)	4.06 (4.20)	18.39 (18.37)	1580, 1430	9.03-8.90 (m, 2H), 7.70-6.36 (m, 12H), 5.80 (s, 2H)
6s (C ₂₃ H ₁₅ Cl ₂ N ₅)	2,6-Dichloro	88	3	256-57	64.00 (63.89)	3.40 (3.47)	16.32 (16.20)	1590, 1430	8.93-8.86 (m, 2H), 7.82-7.25 (m, 11H), 5.75 (s, 2H)
6t (C ₂₈ H ₂₇ N ₅)	2,3,4,5,6-Pentamethyl	79	5	235-54	77.66 (77.60)	6.12 (6.24)	16.00 (16.18)	1590, 1430	8.96-8.90 (m, 2H), 7.82-7.25 (m, 8H), 5.50 (s, 2H), 2.17 (s, 6H), 2.10 (s, 6H), 2.07 (s, 3H)

TABLE-3
ANALYTICAL AND SPECTRAL DATA FOR 4,4',5,5'-TETRAKIS (BENZOYL-1,1'-[PHENYLENE BIS(METHYLENE) BIS (TRIAZOLE)] (7a-c)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	IR (KBr, cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
7a (C ₄₀ H ₂₈ N ₆ O ₄)	<i>ortho</i>	80	10	142-44	1650, 1440	8.27-8.24 (m, 4H), 7.53-7.04 (m, 20H), 5.44 (s, 4H)
7b (C ₄₀ H ₂₈ N ₆ O ₄)	<i>meta</i>	84	10	87-90	1640, 1440	8.26-8.23 (m, 4H), 7.64-7.06 (m, 20H), 5.50 (s, 4H)
7c (C ₄₀ H ₂₈ N ₆ O ₄)	<i>para</i>	83	10	152-53	1650, 1440	8.35-8.28 (m, 4H), 7.53-7.05 (m, 20H), 5.45 (s, 4H)

TABLE-4
ANALYTICAL AND SPECTRAL DATA FOR 4,4',7,7'-TETRAPHENYL-1,1'-[PHENYLENE BIS (METHYLENE) BIS (1H-1,2,3-TRIZOLO [4,5-D]PYRIDAZINE)] (9a-c)

Product (m.f.)	G	Yield (%)	Reflux time (h)	m.p. (°C)	Elemental analysis (%)			IR (cm ⁻¹)	¹ H-NMR (δ, ppm) CDCl ₃
					found	calcd.			
					C	H	N		
9a (C ₄₀ H ₂₈ N ₁₀)	<i>ortho</i>	85	1	126-28	74.37 (74.07)	4.51 (4.32)	21.34 (21.60)	1600, 1440	8.98-8.90 (m, 4H), 7.60-7.20 (m, 20H), 5.76 (s, 4H)
9b (C ₄₀ H ₂₈ N ₁₀)	<i>meta</i>	87	1	120-22	74.23 (74.07)	4.50 (4.32)	21.50 (21.60)	1610, 1440	9.01-8.87 (m, 4H), 7.67-7.23 (m, 20H), 5.80 (s, 4H)
9c (C ₄₀ H ₂₈ N ₁₀)	<i>para</i>	90	1	304-05	74.22 (74.07)	4.55 (4.32)	21.83 (21.60)	1610, 1440	9.03-8.90 (m, 4H), 7.76-7.31 (m, 20H), 5.81 (s, 4H)

method^{21, 22}. *Trans*-1,2-Dibenzoyl ethylene was purchased from Fluka Company and was used without further purification. Melting points were determined on electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Pye-Unicam SP-300 Spectrophotometer. Proton and carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker WP 80 SY Spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona, USA.

General procedure for the synthesis of triazoles 4a-t

To an ethanolic solution of substituted benzyl azides **1a-t** (5 mmol) in 50 mL ethanol, 1.17 g (5 mmol) of dibenzoylacetylene **3** was added. The resulting mixture was heated under reflux for the time indicated in Table-1. After removal of the solvent under reduced pressure, the residue was recrystallized from ethanol-petroleum ether (60–80°C). All the triazoles obtained **4a-t** are new compounds. (Table-1).

General procedure for the synthesis of triazole 6a-t

To a solution of the triazoles **4a-t** (5 mmol) in 50 mL ethanol, 0.50 g (15 mmol) of hydrazine hydrate was added. The resulting mixture was heated under reflux for the time indicated in Table-3. After the solvent was removed under reduced pressure, the resulting solid was recrystallized from ethanol-petroleum ether (60–80°C). According to this procedure compounds **6a-t** were prepared. (Table-2).

General procedure for the reaction of bis(azidomethyl) benzenes 2a-c with dibenzoylacetylene 3: Synthesis of compounds 7a-c

The bis(azidomethyl) benzenes **2a-c** (0.94 g, 5 mmol) were dissolved in ethanol (50 mL); 2.34 g (10 mmol) of dibenzoylacetylene **3** was added to the solution. The resulting mixture was heated under reflux for 10 h. The solvent was distilled off under reduced pressure. The crude bis(triazoles) were recrystallized from ethanol-petroleum ether (60–80°C). Three bis(triazoles) **7a-c** were prepared. Their analytical and spectral data are presented in Table-3.

General procedure for the reaction of tetrakis (benzoyl) bis (triazoles) 7a-c with hydrazine hydrate: Synthesis of compounds 9a-c

To a solution of bis(triazoles) **7a-c** (1.64 g, 2.5 mmol) excess of hydrazine hydrate was added. The resulting mixture was heated under reflux for 1 h. After the solvent was removed under reduced pressure, the resulting solid was recrystallized from ethanol-petroleum ether (60–80°C). The analytical and spectral data for bis(triazolopyridazines) **9a-c** are listed in Table-4.

ACKNOWLEDGEMENT

We thank Yarmouk University for financial support of this work.

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(Received: 2 December 1998; Accepted: 1 March 1999)

AJC1698