# SYNTHESIS OF 1-VINYL 1,2,3-TRIAZOLE DERIVATIVES

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**Abstract:**

Four different α-diazo-β-oxoaldehyde derivatives were condensed with 2-bromoethyl amine to yield 1-bromoethyl-4-acyl-1*H*-1,2,3-triazole derivatives in moderate-to-good yields. Two of these triazoles were converted to their 1-vinyl derivatives by reacting with a base.

**Introduction:**

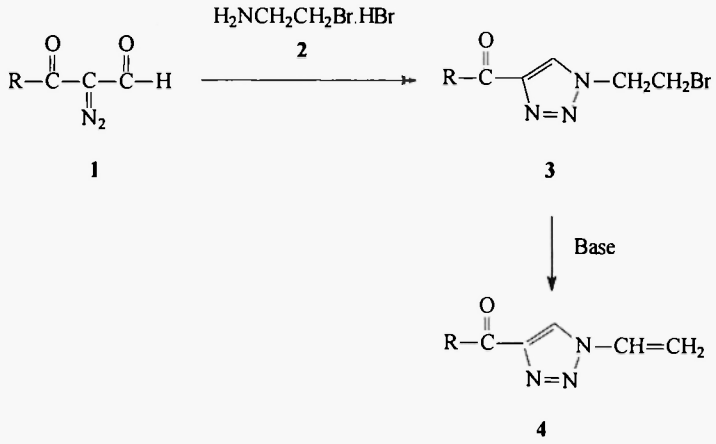
Triazoles, like many other five membered heterocyclic compounds are used very often in the pharmacological and medicinal applications. It is also well known that aromatic polymers containing heterocyclic rings are among the most thermally stable polymers available [1]. Preparation of some N-vinyl-1,2,3-triazoles [2-7] and N-vinyl-1,2,4-triazoles [8-14] are reported in the literature. By the polymerization of vinyl-substituted triazoles, polytriazoles can be obtained with a different physical characteristics [15-16].

1*H*-1,2,3-triazole derivatives are usually prepared by the condensation of amine derivatives with α-diazo-1,3-dicarbonyl compounds [17] or acylacetylene+azide approach [18]. Recently we reported the reactions of α-diazo-β-oxoaldehyde derivatives with several amine derivatives to yield new 4-acyl-1*H*-1,2,3-triazole derivatives [19].

In this work the aim is to synthesize new 1-vinyl-1,2,3-triazole compounds by a new method based on our previous study [19].

**Results:**

Four different α-diazo-β-oxoaldehyde **1** derivatives were condensed with 2-bromoethyl amine **2** to yield 1-bromoethyl-4-acyl-1*H*-1,2,3-triazole derivatives **3** in moderate-to-good yields. Two of these triazoles were converted to their 1-vinyl derivatives **4** by reacting with a base (Scheme) (Table). α-Diazo-β-oxoaldehyde derivatives **1** were synthesised by Vilsmeier-Haack formylation [20, 21].




**Scheme**

**Table.** Synthesized 1,2,3-triazole derivatives **3**, **4**.

| | R | R' | Yield (%) | M.p. (°C) | Ref. |
|---|---|---|---|---|---|
| **3.1** | Thiophene-2-yl | Bromoethyl | 71 | 134-136 | * |
| **3.2** | Furan-2-yl | Bromoethyl | 70 | 156-157 | * |
| **3.3** | 2,5-$Me_2$-furan-3-yl | Bromoethyl | 67 | 124-126 | * |
| **3.4** | EtO | Bromoethyl | 73 | 96-98 | * |
| **4.1** | Thiophene-2-yl | Vinyl | 76 | 126-129 | * |
| **4.2** | EtO | Vinyl | 75 | 47-49 | * |

* This work.

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**Experimental Part:**
*General.* All diazo compounds (**1,5**) and chloromethylene dimethyliminium chloride (**6**) were prepared as described in [21, 22]. M.p.: Electrothermal glass-bath apparatus in capillary tubes. $^1$H-NMR (δ [ppm]): 200-MHz *Bruker* apparatus. $^{13}$C-NMR: at 50 MHz.

*Synthesis of compounds 3:*
4,6 g (22,5 mmol) of 2-bromoethylammonium bromide (**2**) is dissolved in 25 ml of ethyl alcohol. To this solution, 2,2 g (22,5 mmol) of potassium acetate in 25 ml of ethyl alcohol solution is added. After stirring for 10 minutes at room temperature, precipitate is filtered and washed with 10 ml of ethyl alcohol. 15,0 mmol of diazo compound (**1**) is added on this solution and stirred for 4 hours at room temperature. Precipitated product is filtered and recrystallized from ethyl alcohol.

*Synthesis of compound **4.1**:*
90 ml of ethyl alcohol and 0.559 g,13.9 mmol of NaOH is added on 2 g, 6.7 mmol of [1-(2-bromoethyl)-1H-1,2,3-triazol-4-yl](2-thiophenyl)-methanone (**3.1**) and

refluxed for 5 hours. After cooling to room temperature, precipitated product is filtered and recrystallized from ethyl alcohol.

*Synthesis of **4.2**:*
20 mmol of sodium ethoxide is added in 50 ml of dry THF. 10 mmol of **3.4** is added on this mixture and refluxed for 4 hours. Reaction mixture is cooled to room temperature, filtered and solvent is removed under reduced pressure. Product is obtained in pure form.

*[1-(2-bromoethyl)-1H-1,2,3-triazol-4-yl](2-thienyl)-methanone (**3.1**):*
$^1$H-NMR (200 MHz) (DMSO-D6) (9.04 (s, H-C(5)); 8.60 (d, 1H); 8.15 (d, 1H); 7.36 (t, 1H); 4.94 (t, 2H); 4.06 (t, 2H). $^{13}$C-NMR (50 MHz) ( 176.52, 146.01, 141.69, 136.17, 135.65, 129.59, 128.77, 51.18, 30.98. $C_9H_8BrN_3OS$: Calc.; C 37.8 %, H 2.8 %, Br 27.9 %, N 14.7 %, O 5.6 %, S 11.2 %; Found; C 37.6 %, H 2.9 %, N 14.6 %, S 11.0 %.

*[1-(2-bromoethyl)-1H-1,2,3-triazol-4-yl](2-furyl)-methanone (**3.2**):*
$^1$H-NMR (200 MHz) (DMSO-D6) (9.01 (s, H-C(5)); 8.1 (d, 1H); 8.0 (d, 1H); 6.8 (m, 1H); 4.9 (t, 2H); 4.0 (t, 2H). $^{13}$C-NMR (50 MHz) (172.0, 151.1, 149.5, 146.0, 130.2, 122.8, 113.5, 51.9, 31.8). $C_9H_8BrN_3O_2$: Calc.; C 40.0 %, H 3.0 %, Br 29.6 %, N 15.6 %, O 11.8 %; Found; C 40.3 %, H 2.9 % N 15.3 %.

*[1-(2-bromoethyl)-1H-1,2,3-triazol-4-yl](2,5-dimethyl-3-furyl)- methanone (**3.3**):*
$^1$H-NMR (200 MHz) ($CDCl_3$) (8.3 (s, H-C(5)); 7.2 (d, 1H); 4.8 (t, 2H); 3.8 (t, 2H). $^{13}$C-NMR (50 MHz) (181.0, 160.5, 150.2, 149.4, 128.2, 120.5, 107.7, 52.0, 29.2, 14.9, 13.4). $C_{11}H_{12}BrN_3O_2$: Calc.; C 44.3 %, H 4.1 %, Br 26.8 %, N 14.1 %, O 10.7%; Found; C 44.5 %, H 4.0 %, N 14.4 %.

*Ethyl-1-(2-bromoethyl)-1H-1,2,3-triazol-4-carboxylate (**3.4**):*
$^1$H-NMR (200 MHz) ($CDCl_3$) (8.2 (s, H-C(5)); 4.8 (t, 2H); 4.3 (q, 2H); 3.7 (t, 2H); 1.3 (t, 3H);. $^{13}$C-NMR (50 MHz) (160.8, 140.2, 128.7, 61.6, 52.1, 29.5, 14.5). $C_7H_{10}BrN_3O_2$: Calc.; C 33.9 %, H 4.1 %, Br 32.2 %, N 16.9 %, O 12.9 %; Found; C 33.7 %, H 4.3 %, N 16.6 %.

*2-Thienyl-(1vinyl-1H-1,2,3-triazol-4-yl)- methanone (**4.1**):*
$^1$H-NMR (200 MHz) ($CDCl_3$) (8.7 (s, H-C(5)); 8.5 (s, 1H); 7.7 (d, 1H); 7.4 (m, 1H); 7.2 (m, 1H); 5.9 (dd, 1H); 5.3 (dd, 1H);. $^{13}$C-NMR (50 MHz) (177.2, 147.8, 142.4, 136.7, 135.6, 129.9, 128.8, 124.9, 107.5). $C_9H_7N_3OS$: Calc.; C 52.7 %, H 3.4 %, N 20.5 %, O 7.8 %, S 15.6 %; Found; C 52.5 %, H 3.5 %, N 20.3 %.

*Ethyl-1-vinyl-1H-1,2,3-triazol-4-carboxylate (**4.2**):*
$^1$H-NMR (200 MHz) ($CDCl_3$) (8.3 (s, H-C(5)); 7.3 (m, 1H); 5.8 (d, 1H); 5.3 (d, 1H); 4.4 (q, 2H); 1.4 (t, 3H);. $^{13}$C-NMR (50 MHz) (160.7, 140.5, 129.9, 124.6, 116.3, 107.3, 61.7, 14.5). $C_7H_9N_3O_2$: Calc.; C 50.3 %, H 5.4 %, N 25.1 %, O 19.1 %; Found; C 50.0 %, H 5.2 %, N 25.3 %.

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