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Phenyl azide **1** and several substituted benzyl azides **2a-o** underwent 1,3-dipolar cycloaddition reactions with dimethyl acetylenedicarboxylate **3**, phenylacetylene **4** and ethyl propiolate **5** to afford the triazoles **6-13**. The reactions of these azides with ethyl propiolate were found to be completely regioselective.

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Certain 1,2,4- and 1,2,3-triazole derivatives have been reported to possess useful applications. Some are reported as fungicides and plant growth regulators [1] as bactericides and medical fungicides [2], as insecticides and acaricides [3] and in dyeing and color development [4].

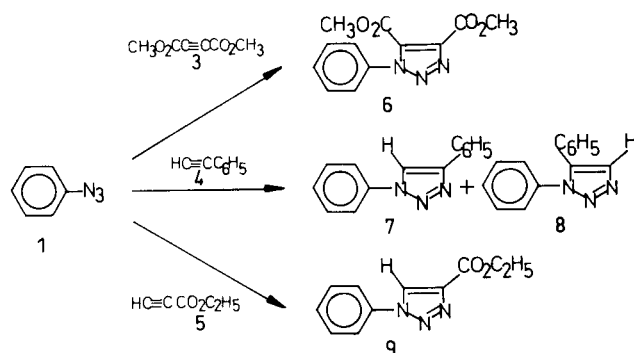
The most common method for the preparation of 1,2,3-triazoles is the 1,3-dipolar cycloaddition reaction of azides with substituted acetylenes [5-13]. Most of the literature on 1,2,3-triazoles, however, is concerned with the synthesis of

the 4,5-dialkyl systems [14-19]. As yet, not much work has been reported on the synthesis of triazoles with other functional groups on the ring. This has prompted us to contribute in that area. Thus, in 1986 we reported the preparation of bis(azidomethyl)benzenes and their reaction with acetylenedicarboxaldehyde bis(diethyl acetal) to form the phenylene bis(methylene) bis(triazole-4,5-dicarboxaldehyde) tetrakis(ethyl acetals) [13]. In the present paper, we describe the reaction of phenyl azide and substituted benzyl azides with some acetylenic esters and with phenylacetylene.

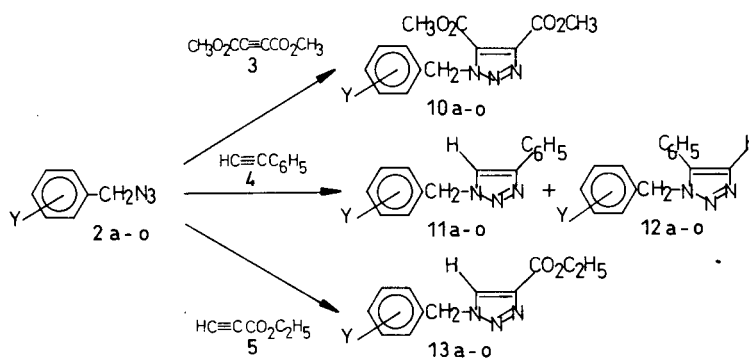
Thus, phenyl, benzyl and substituted benzyl azides **1** and **2a-o** were reacted with dimethyl acetylenedicarboxylate **3** in boiling ethanol to give the corresponding triazoles **6** and **10a-o** in more than 80% yield as shown in Schemes 1 and 2.

All the products **6** and **10a-o** were characterized by ir, ¹H nmr spectroscopy and correct elemental analysis. These compounds exhibited C=O stretching at 1720-1735 and N=N at 1425-1460 cm⁻¹ in their ir spectra. Triazole **6** showed a singlet at 7.55 ppm for the aromatic protons and two singlets at 3.91 and 4.00 ppm for the two methyl

Scheme 1



Scheme 2



| Y | Y | Y | Y | Y |
|------------------------|-----------------------|-----------------------|----------|----------|
| a . H | d . 4-CH ₃ | g . 4-NO ₂ | j . 4-Cl | m . 4-Br |
| b . 4-OCH ₃ | e . 3-CH ₃ | h . 3-NO ₂ | k . 3-Cl | n . 3-Br |
| c . 3-OCH ₃ | f . 2-CH ₃ | i . 2-NO ₂ | l . 2-Cl | o . 2-Br |

Table I
Triazoles 6, 10a-o

| Compound | Y | ¹ H NMR (ppm) deuteriochloroform | IR (cm ⁻¹) | Molecular Formula | Elemental Analysis | | | X |
|----------|--------------------|--|---------------------------|---|--------------------|--------------|----------------|----------------|
| | | | | | C | H | N | |
| 6 | | 7.55 (s, 5H), 4.00 (s, 3H), 3.91 (s, 3H) | 1730, 1620, 1520, 1440 | C ₁₂ H ₁₁ N ₃ O ₄ | 55.17 55.41 | 4.24 4.44 | 16.08 15.89 | |
| 10a | H | 7.33-7.28 (m, 5H), 5.80 (s, 2H), 3.95 (s, 3H), 3.87 (s, 3H) | 1730, 1610, 1540, 1450 | C ₁₃ H ₁₃ N ₃ O ₄ | 56.72 56.70 | 4.76 4.77 | 15.28 15.32 | |
| 10b | 4-OCH ₃ | 7.22 (d, 2H, J = 8.9 Hz), 6.84 (d, 2H, J = 8.9 Hz), 5.72 (s, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), | 1715, 1600, 1510, 1445 | C ₁₄ H ₁₅ N ₃ O ₅ | 55.08 55.15 | 4.95 4.96 | 13.76 13.83 | |
| 10d | 4-CH ₃ | 7.14 (s, 4H), 5.75 (s, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 2.32 (s, 3H) | 1725, 1600, 1540, 1425 | C ₁₄ H ₁₅ N ₃ O ₄ | 58.13 58.15 | 5.19 5.23 | 14.54 14.52 | |
| 10e | 3-CH ₃ | 7.20-7.05 (br, 4H), 5.74 (s, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 2.32 (s, 3H) | 1720, 1600, 1540, 1430 | C ₁₄ H ₁₅ N ₃ O ₄ | 58.13 58.16 | 5.19 5.25 | 14.54 14.44 | |
| 10f | 2-CH ₃ | 7.28-6.93 (m, 4H), 5.79 (s, 2H), 3.95 (s, 3H), 3.80 (s, 3H), 2.33 (s, 3H) | 1730, 1610, 1530, 1440 | C ₁₃ H ₁₂ N ₄ O ₄ | 58.13 58.19 | 5.19 5.39 | 14.54 14.72 | |
| 10g | 4-NO ₂ | 8.21 (d, 2H, J = 8.9 Hz), 7.46 (d, 2H, J = 8.9 Hz), 5.94 (s, 2H), 3.98 (s, 3H), 3.93 (s, 3H) | 1735, 1620, 1540, 1450 | C ₁₃ H ₁₂ N ₄ O ₆ | 48.75 48.75 | 3.78 3.83 | 17.49 17.41 | |
| 10h | 3-NO ₂ | 8.26-7.53 (m, 4H), 5.93 (s, 2H), 3.97 (s, 3H), 3.95 (s, 3H) | 1710, 1600, 1520, 1450 | C ₁₃ H ₁₂ N ₄ O ₆ | 48.75 48.90 | 3.78 3.94 | 17.49 17.37 | |
| 10i | 2-NO ₂ | 8.23-8.11 (m, 1H), 7.62-7.48 (m, 2H), 6.93-6.82 (m, 1H), 6.22 (s, 2H), 3.99 (s, 3H) 3.90 (s, 3H) | 1720, 1600, 1510, 1440 | C ₁₃ H ₁₂ N ₄ O ₆ | 48.75 48.80 | 3.78 3.82 | 17.49 17.27 | |
| 10j | 4-Cl | 7.40-7.14 (m, 4H), 5.78 (s, 2H), 3.96 (s, 3H), 3.90 (s, 3H) | 1705, 1580, 1540, 1420 | C ₁₃ H ₁₂ ClN ₃ O ₄ | 50.42 50.46 | 3.91 4.02 | 13.57 13.51 | 11.45 11.47 |
| 10k | 3-Cl | 7.34-7.21 (m, 4H), 5.78 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H) | 1715, 1590, 1530, 1430 | C ₁₃ H ₁₂ ClN ₃ O ₄ | 50.42 50.68 | 3.91 3.87 | 13.57 13.77 | 11.45 11.19 |
| 10l | 2-Cl | 7.50-7.13 (m, 3H), 6.95-6.83 (m, 1H), 5.93 (s, 2H), 3.98 (s, 3H), 3.89 (s, 3H) | 1720, 1590, 1560, 1430 | C ₁₃ H ₁₂ ClN ₃ O ₄ | 50.42 50.42 | 3.91 3.93 | 13.57 13.67 | 11.45 11.42 |
| 10m | 4-Br | 7.48 (d, 2H, J = 8.6 Hz), 7.15 (d, 2H, J = 8.6 Hz), 5.76 (s, 2H), 3.96 (s, 3H), 3.90 (s, 3H) | 1720, 1590, 1545, 1440 | C ₁₃ H ₁₂ BrN ₃ O ₄ | 44.09 44.05 | 3.42 3.54 | 11.86 11.77 | 22.56 22.78 |

Table I (continued)

| Compound | Y | ¹ H NMR (ppm) deuteriochloroform | IR (cm ⁻¹) | Molecular Formula | Elemental Analysis | | | |
|----------|------|---|---------------------------|---|--------------------|--------------|----------------|----------------|
| | | | | | Calcd./Found | C | H | N |
| 10n | 3-Br | 7.66-7.55 (m, 1H), 7.29-7.16 (m, 2H), 6.86-6.74 (m, 1H), 5.91 (s, 2H), 3.98 (s, 3H), 3.88 (s, 3H) | 1715, 1580, 1540, 1430 | C ₁₃ H ₁₂ BrN ₃ O ₄ | 44.09 44.07 | 3.42 3.47 | 11.86 11.85 | 22.56 22.45 |
| 10o | 2-Br | 7.47-7.42 (m, 2H), 7.24-7.17 (m, 2H), 5.77 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H) | 1705, 1580, 1540, 1415 | C ₁₃ H ₁₂ BrN ₃ O ₄ | 44.09 44.04 | 3.42 3.49 | 11.86 11.90 | 22.56 22.81 |

groups of the diester. Triazoles **10a-o** displayed signals in the range of 8.26-6.82 ppm for the aromatic protons. The methylene benzylic protons appeared as singlets in the range 6.22-5.72 ppm, the methyl attached to the phenyl ring showed as a singlet around 2.32 ppm whereas the methoxy groups appeared at 3.78 ppm. The methyl groups of the diester appeared as two singlets averaged at 3.96 and 3.88 ppm as shown in Table 1.

On the other hand, the reactions of azides **1** and **2a-o** with phenylacetylene **4** afforded a mixture of two isomeric products as expected and revealed by thin layer chromatography in over 85% overall yield. The isomeric triazoles **7, 8** and **11, 12a-o** are shown in Schemes 1 and 2. The product mixtures were separated by preparative thick layer chromatography using silica gel and a toluene-ethyl acetate mixture. The relative ratio of the two isomeric products was found to be in the range 10:90-40:60. Surprisingly, the separated isomers in each reaction gave identical ir and ¹H nmr spectra and melting points. This might be due to the similarity of the chemical environment of the protons in either position 4 or 5 in the triazole ring. The less hindered triazoles **7** and **11a-o** are believed to be the major products on the basis of steric considerations. This assignment is quite compatible with the reported results of Tsylin and Mihelcic and their co-workers on the addition of heterocyclic and aliphatic azides to phenylacetylene [20,21]. The ¹H nmr spectra of triazoles **7, 8** and **11, 12a-o** showed the aromatic protons, including that on the triazole ring, in the range 8.24-7.00 ppm. The spectral and analytical data of the latter triazoles are summarized in Table 2.

Unlike the reactions with phenylacetylene, the reactions of azides **1** and **2a-o** with ethyl propiolate **5** were found to be completely regiospecific. Thin layer chromatography using different solvent systems confirmed the presence of a sole product in each reaction. These products are believed to be triazoles **9** and **13a-o** as depicted in Schemes 1 and 2. This belief is based on the assumption that the attack of the nucleophilic nitrogen of the azide **1** or **2** on the electrophilic β -carbon of the unsaturated ester **5** is both sterically and electronically favored and the assumption that the cycloaddition reaction involves conjugate addition of the azide **1** or **2** to the Michael acceptor **5** followed by cyclization as explained in Scheme 3. The spectral and analytical data for triazoles **9** and **13a-o** are given in Table 3.

EXPERIMENTAL

Phenyl azide **1** was prepared according to the method described by Lindsay and Allen [22]. Benzyl and substituted benzyl azides **2a-o** were prepared from the corresponding chlorides or bromides *via* the reaction with sodium azide following the method reported by Henkel and Weygand [23]. Melting points were determined on an Electrothermal melting point apparatus, and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP-300 spectrophotometer. Proton nuclear magnetic resonance spectra were recorded on a WP 80 SY spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona, U.S.A.

Scheme 3

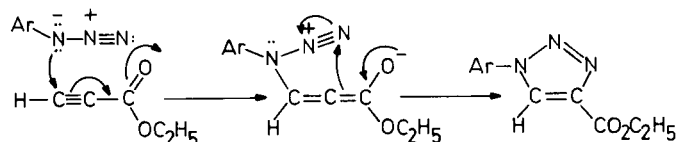


Table 2
Triazoles 7 (8), 11 (12)a-o

| Compound | Y | ¹ H NMR (ppm) deuteriochloroform | IR (cm ⁻¹) | Molecular Formula | Elemental Analysis | | | X |
|----------|--------------------|--|------------------------|---|--------------------|--------------|----------------|----------------|
| | | | | | C | H | N | |
| 7 (8) | | 8.20-7.21 (m, 11H) | 1620, 1530, 1430 | C ₁₄ H ₁₁ N ₃ | 76.00 75.87 | 5.01 5.26 | 18.99 18.85 | |
| 11 (12)a | H | 7.86-7.11 (m, 11H), 5.55 (s, 2H) | 1610, 1530, 1440 | C ₁₅ H ₁₃ N ₃ | 76.60 76.54 | 5.53 5.62 | 17.87 17.75 | |
| 11 (12)b | 4-OCH ₃ | 7.85-6.85 (m, 10H), 5.50 (s, 2H), 3.81 (s, 3H) | 1600, 1500, 1450 | C ₁₆ H ₁₅ N ₃ O | 72.43 72.47 | 5.70 5.84 | 15.84 16.00 | |
| 11 (12)c | 3-OCH ₃ | 7.86-6.83 (m, 10H), 5.53 (s, 2H), 3.78 (s, 3H) | 1590, 1570, 1380 | C ₁₆ H ₁₅ N ₃ O | 72.43 72.64 | 5.70 5.60 | 15.84 15.88 | |
| 11 (12)d | 4-CH ₃ | 7.85-7.00 (m, 10H), 5.51 (s, 2H), 2.35 (s, 3H) | 1630, 1530 1430 | C ₁₆ H ₁₅ N ₃ | 76.87 77.19 | 6.04 6.19 | 16.81 16.65 | |
| 11 (12)e | 3-CH ₃ | 7.86-6.89 (m, 10H), 5.51 (s, 2H), 2.33 (s, 3H) | 1615, 1540 1440 | C ₁₆ H ₁₅ N ₃ | 76.87 77.19 | 6.04 6.14 | 16.81 16.78 | |
| 11 (12)f | 2-CH ₃ | 7.85-7.25 (m, 10H), 5.58 (s, 2H), 2.31 (s, 3H) | 1620, 1540, 1440 | C ₁₆ H ₁₅ N ₃ | 76.87 76.62 | 6.04 6.12 | 16.81 16.87 | |
| 11 (12)g | 4-NO ₂ | 8.24 (d, 2H, J = 8.7 Hz), 7.76 (d, 2H, J = 8.7 Hz), 7.49-7.25 (m, 6H), 5.69 (s, 2H) | 1620, 1540, 1440 | C ₁₅ H ₁₂ N ₄ O ₂ | 64.28 64.35 | 4.32 4.12 | 20.00 19.98 | |
| 11 (12)h | 3-NO ₂ | 8.24-7.35 (m, 10H), 5.69 (s, 2H) | 1590, 1520, 1430 | C ₁₅ H ₁₂ N ₄ O ₂ | 64.28 64.43 | 4.32 4.45 | 20.00 20.06 | |
| 11 (12)i | 2-NO ₂ | 8.21-7.09 (m, 10H), 5.98 (s, 2H) | 1600, 1520, 1440 | C ₁₅ H ₁₂ N ₄ O ₂ | 64.28 64.40 | 4.32 4.27 | 20.00 20.13 | |
| 11 (12)j | 4-Cl | 7.87-7.26 (m, 10H), 5.55 (s, 2H) | 1600, 1530, 1430 | C ₁₅ H ₁₂ ClN ₃ | 66.79 66.33 | 4.48 4.64 | 15.58 15.13 | 13.14 13.43 |
| 11 (12)k | 3-Cl | 7.88-7.22 (m, 10H), 5.55 (s, 2H) | 1610, 1550, 1425 | C ₁₅ H ₁₂ ClN ₃ | 66.79 66.61 | 4.48 4.60 | 15.58 15.50 | 13.14 13.47 |
| 11 (12)l | 2-Cl | 7.88-7.21 (m, 10H), 5.72 (s, 2H) | 1610, 1540, 1425 | C ₁₅ H ₁₂ ClN ₃ | 66.79 66.66 | 4.48 4.56 | 15.58 15.68 | 13.14 13.00 |
| 11 (12)m | 4-Br | 7.85-7.12 (m, 10H), 5.52 (s, 2H) | 1600, 1540, 1415 | C ₁₅ H ₁₂ BrN ₃ | 57.34 57.15 | 3.85 3.87 | 13.37 13.23 | 25.43 25.51 |
| 11 (12)n | 3-Br | 7.87-7.19 (m, 10H), 5.53 (s, 2H) | 1590, 1540, 1420 | C ₁₅ H ₁₂ BrN ₃ | 57.34 57.46 | 3.85 4.00 | 13.37 13.47 | 25.43 25.58 |
| 11 (12)o | 2-Br | 7.89-7.21 (m, 10H), 5.71 (s, 2H) | 1600, 1515, 1430 | C ₁₅ H ₁₂ BrN ₃ | 57.34 57.31 | 3.85 3.96 | 13.37 13.05 | 25.43 25.57 |

Table 3
 Triazoles **9**, **13a-o**

| Compound | Y | ¹ H NMR (ppm) deuteriochloroform | IR (cm ⁻¹) | Molecular Formula | Elemental Analysis | | | X |
|------------|--------------------|---|---------------------------|---|--------------------|------|-------|---|
| | | | | | C | H | N | |
| 9 | | 8.52 (s, 1H), 7.84-7.28 (m, 5H), 4.42 (q, 2H, J = 7.2 Hz), 1.43 (t, 3H, J = 7.2 Hz) | 1730, 1620, 1550, 1430 | C ₁₁ H ₁₁ N ₃ O ₂ | 60.82 | 5.10 | 19.34 | |
| | | | | | 60.40 | 5.10 | 19.48 | |
| 13a | H | 8.01 (s, 1H), 7.38-7.30 (m, 5H), 5.58 (s, 2H), 4.38 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz) | 1730, 1600, 1550, 1440 | C ₁₂ H ₁₃ N ₃ O ₂ | 62.33 | 5.67 | 18.17 | |
| | | | | | 62.15 | 5.75 | 18.25 | |
| 13b | 4-OCH ₃ | 7.92 (s, 1H), 7.25 (d, 2H, J = 8.8 Hz), 6.91 (d, 2H, J = 8.8 Hz) 5.50 (s, 2H), 4.40 (q, 2H, J = 7.1 Hz), 3.81 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz) | 1715, 1600, 1520, 1430 | C ₁₃ H ₁₅ N ₃ O ₃ | 59.76 | 5.79 | 16.08 | |
| | | | | | 59.62 | 5.84 | 16.19 | |
| 13c | 3-OCH ₃ | 7.99 (s, 1H), 7.41-6.80 (m, 4H), 5.54 (s, 2H), 4.40 (q, 2H, J = 7.1 Hz), 3.79 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz) | 1720, 1620, 1530, 1440 | C ₁₃ H ₁₅ N ₃ O ₃ | 59.76 | 5.79 | 16.08 | |
| | | | | | 59.60 | 5.96 | 16.07 | |
| 13d | 4-CH ₃ | 7.95 (s, 1H), 7.19 (s, 1H), 5.53 (s, 2H), 4.39 (q, 2H, J = 7.1 Hz), 2.34 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz) | 1720, 1600, 1550, 1430 | C ₁₃ H ₁₅ N ₃ O ₂ | 63.66 | 6.16 | 17.13 | |
| | | | | | 63.41 | 6.12 | 17.20 | |
| 13e | 3-CH ₃ | 7.97 (s, 1H), 7.30-7.11 (m, 4H), 5.53 (s, 2H), 4.39 (q, 2H, J = 7.1 Hz), 2.34 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz) | 1730, 1620, 1550, 1450 | C ₁₃ H ₁₅ N ₃ O ₂ | 63.66 | 6.16 | 17.13 | |
| | | | | | 63.70 | 5.94 | 17.28 | |
| 13f | 2-CH ₃ | 7.83 (s, 1H), 7.27-7.18 (bs, 4H), 5.59 (s, 2H), 4.39 (q, 2H, J = 7.1 Hz), 2.27 (s, 3H), 1.38 (t, 3H, J = 7.1 Hz) | 1730, 1620, 1550, 1440 | C ₁₃ H ₁₅ N ₃ O ₂ | 63.66 | 6.16 | 17.13 | |
| | | | | | 63.70 | 6.19 | 17.30 | |
| 13g | 4-NO ₂ | 8.25 (d, 2H, J = 8.7 Hz), 8.09 (s, 1H), 7.45 (d, 2H, J = 8.7 Hz), 5.72 (s, 2H), 4.42 (q, 2H, J = 7.1 Hz), 1.40 (t, 3H, J = 7.1 Hz) | 1730, 1620, 1540, 1450 | C ₁₂ H ₁₂ N ₄ O ₄ | 52.17 | 4.38 | 20.28 | |
| | | | | | 51.95 | 4.41 | 20.13 | |

Table 3 (continued)

| Compound | Y | ¹ H NMR (ppm) deuteriochloroform | IR (cm ⁻¹) | Molecular Formula | Elemental Analysis | | | |
|----------|-------------------|---|---------------------------|---|--------------------|--------------|----------------|----------------|
| | | | | | C | H | N | X |
| 13h | 3-NO ₂ | 8.29-8.18 (m, 2H), 8.11 (s, 1H), 7.63-7.57 (m, 2H), 5.72 (s, 2H), 4.40 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1710, 1600, 1530, 1440 | C ₁₂ H ₁₂ N ₄ O ₄ | 52.17 52.23 | 4.38 4.47 | 20.28 20.40 | |
| 13i | 2-NO ₂ | 8.26 (s, 1H), 8.23-8.12 (m, 1H), 7.69-7.54 (m, 2H), 7.24-7.16 (m, 1H), 5.99 (s, 2H), 4.42 (q, 2H, J = 7.1 Hz), 1.40 (t, 3H, J = 7.1 Hz) | 1710, 1600, 1520, 1440 | C ₁₂ H ₁₂ N ₄ O ₄ | 52.17 52.14 | 4.38 4.40 | 20.28 20.32 | |
| 13j | 4-Cl | 8.00 (s, 1H), 7.45-7.17 (m, 4H), 5.57 (s, 2H), 4.41 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1710, 1580, 1530, 1440 | C ₁₂ H ₁₂ ClN ₃ O ₂ | 54.25 54.19 | 4.55 4.68 | 15.82 15.98 | 13.34 13.57 |
| 13k | 3-Cl | 8.05 (s, 1H), 7.37-7.14 (m, 4H), 5.57 (s, 2H), 4.41 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1715, 1590, 1520, 1435 | C ₁₂ H ₁₂ ClN ₃ O ₂ | 54.25 54.35 | 4.55 4.36 | 15.82 15.93 | 13.34 13.45 |
| 13l | 2-Cl | 8.07 (s, 1H), 7.50-7.26 (m, 4H), 5.73 (s, 2H), 4.42 (q, 2H, J = 7.1 Hz), 1.40 (t, 3H, J = 7.1 Hz) | 1715, 1575 1530, 1430 | C ₁₂ H ₁₂ ClN ₃ O ₂ | 54.25 54.30 | 4.55 4.52 | 15.82 16.02 | 13.34 13.23 |
| 13m | 4-Br | 8.00 (s, 1H), 7.53 (d, 2H, J = 8.7 Hz), 7.16 (d, 2H, J = 8.7 Hz), 5.54 (s, 2H), 4.40 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1720, 1590, 1520, 1440 | C ₁₂ H ₁₂ BrN ₃ O ₂ | 46.47 46.68 | 3.99 4.14 | 13.55 13.54 | 25.76 25.86 |
| 13n | 3-Br | 8.03 (s, 1H), 7.57-7.20 (m, 4H), 5.56 (s, 2H), 4.41 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1715, 1590, 1530, 1430 | C ₁₂ H ₁₂ BrN ₃ O ₂ | 46.47 46.56 | 3.90 3.94 | 13.55 13.60 | 25.76 25.93 |
| 13o | 2-Br | 8.07 (s, 1H), 7.71-7.20 (m, 4H), 5.72 (s, 2H), 4.41 (q, 2H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.1 Hz) | 1710, 1590, 1515, 1435 | C ₁₂ H ₁₂ BrN ₃ O ₂ | 46.47 46.63 | 3.90 4.11 | 13.55 13.38 | 25.76 25.59 |

General Procedure for the Reactions of Azides **1** and **2a-o** with Dimethyl Acetylenedicarboxylate **3**, Phenylacetylene **4** and Ethyl Propiolate **5**.

Azide **1** or **2a-o** (10 mmoles) was dissolved in ethanol (50 ml). The acetylene **3**, **4** or **5** (10 mmoles) was added to the solution and the mixture was heated under reflux for the time indicated below. After removing the solvent under reduced pressure the residue

was dissolved and the triazole recrystallized from petroleum ether-methanol mixture.

Dimethyl 1-Phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate **6**.

This compound was obtained in a yield of 92%, mp 108-110°. The reflux time was 20 hours.

Dimethyl 1-Benzyl-1*H*-1,2,3-triazole-4,5-dicarboxylate **10a**.

This compound was obtained in a yield of 91%, mp 45-47°. The reflux time was 10 hours.

Dimethyl 1-(4-Methoxybenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10b**.

This compound was obtained in a yield of 85%, mp 70-71°. The reflux time was 10 hours.

Dimethyl 1-(4-Methylbenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10d**.

This compound was obtained in a yield of 93%, mp 37-39°. The reflux time was 20 hours.

Dimethyl 1-(3-Methylbenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10e**.

This compound was obtained in a yield of 89%, mp 37-39°. The reflux time was 20 hours.

Dimethyl 1-(2-Methylbenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10f**.

This compound was obtained in a yield of 85%, mp 72-74°. The reflux time was 20 hours.

Dimethyl 1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10g**.

This compound was obtained in a yield of 97%, mp 90-92°. The reflux time was 20 hours.

Dimethyl 1-(3-Nitrobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10h**.

This compound was obtained in a yield of 84%, mp 85-86°. The reflux time was 19 hours.

Dimethyl 1-(2-Nitrobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10i**.

This compound was obtained in a yield of 88%, mp 90-91°. The reflux time was 24 hours.

Dimethyl 1-(4-Chlorobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10j**.

This compound was obtained in a yield of 90%, mp 86-88°. The reflux time was 16 hours.

Dimethyl 1-(3-Chlorobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10k**.

This compound was obtained in a yield of 89%, mp 45-46°. The reflux time was 20 hours.

Dimethyl 1-(2-Chlorobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10l**.

This compound was obtained in a yield of 87%, mp 95-96°. The reflux time was 10 hours.

Dimethyl 1-(4-Bromobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10m**.

This compound was obtained in a yield of 90%, mp 89-90°. The reflux time was 20 hours.

Dimethyl 1-(3-Bromobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10n**.

This compound was obtained in a yield of 88%, mp 85-87°. The reflux time was 18 hours.

Dimethyl 1-(2-Bromobenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate **10o**.

This compound was obtained in a yield of 89%, mp 73-74°.

The reflux time was 22 hours.

1,4-Diphenyl-1*H*-1,2,3-triazole **7** and 1,5-Diphenyl-1*H*-1,2,3-triazole **8**.

These compounds were obtained in an overall yield of 93%, mp 184-186°. The reflux time was 36 hours.

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole **11a** and 1-Benzyl-5-phenyl-1*H*-1,2,3-triazole **12a**.

These compounds were obtained in an overall yield of 87%, mp 80-82°. The reflux time was 28 hours.

1-(4-Methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole **11b** and 1-(4-Methoxybenzyl)-5-phenyl-1*H*-1,2,3-triazole **12b**.

These compounds were obtained in an overall yield of 79%, mp 143-144°. The reflux time was 40 hours.

1-(3-Methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole **11c** and 1-(3-Methoxybenzyl)-5-phenyl-1*H*-1,2,3-triazole **12c**.

These compounds were obtained in an overall yield of 94%, mp 114-115°. The reflux time was 38 hours.

1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole **11d** and 1-(4-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazole **12d**.

These compounds were obtained in an overall yield of 84%, mp 95-97°. The reflux time was 40 hours.

1-(3-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole **11e** and 1-(3-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazole **12e**.

These compounds were obtained in an overall yield of 85%, mp 200-202°. The reflux time was 40 hours.

1-(2-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole **11f** and 1-(2-Methylbenzyl)-5-phenyl-1*H*-1,2,3-triazole **12f**.

These compounds were obtained in an overall yield of 86%, mp 92-94°. The reflux time was 48 hours.

1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11g** and 1-(4-Nitrobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12g**.

These compounds were obtained in an overall yield of 89%, mp 157-159°. The reflux time was 30 hours.

1-(3-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11h** and 1-(3-Nitrobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12h**.

These compounds were obtained in an overall yield of 79%, mp 146° dec. The reflux time was 30 hours.

1-(2-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11i** and 1-(2-Nitrobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12i**.

These compounds were obtained in an overall yield of 79%, mp 123-124°. The reflux time was 30 hours.

1-(4-Chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11j** and 1-(4-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12j**.

These compounds were obtained in an overall yield of 78%, mp 146-147°. The reflux time was 30 hours.

1-(3-Chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11k** and 1-(3-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12k**.

These compounds were obtained in an overall yield of 82%, mp 98-99°. The reflux time was 40 hours.

1-(2-Chlorobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11l** and 1-(2-Chlorobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12l**.

These compounds were obtained in an overall yield of 80%, mp 89-90°. The reflux time was 42 hours.

1-(4-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11m** and 1-(4-Bromobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12m**.

These compounds were obtained in an overall yield of 80%, mp 150-152°. The reflux time was 40 hours.

1-(3-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11n** and 1-(3-Bromobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12n**.

These compounds were obtained in an overall yield of 83%, mp 94-95°. The reflux time was 36 hours.

1-(2-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole **11o** and 1-(2-Bromobenzyl)-5-phenyl-1*H*-1,2,3-triazole **12o**.

These compounds were obtained in an overall yield of 78%, mp 105-106°. The reflux time was 44 hours.

Ethyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate **9**.

This compound was obtained in a yield of 95%, mp 84-86°. The reflux time was 20 hours.

Ethyl 1-Benzyl-1*H*-1,2,3-triazole-4-carboxylate **13a**.

This compound was obtained in a yield of 91%, mp 82-84°. The reflux time was 16 hours.

Ethyl 1-(4-Methoxybenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13b**.

This compound was obtained in a yield of 88%, mp 99-100°. The reflux time was 15 hours.

Ethyl 1-(3-Methoxybenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13c**.

This compound was obtained in a yield of 88%, mp 62-64°. The reflux time was 20 hours.

Ethyl 1-(4-Methylbenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13d**.

This compound was obtained in a yield of 84%, mp 72-74°. The reflux time was 16 hours.

Ethyl 1-(3-Methylbenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13e**.

This compound was obtained in a yield of 86%, mp 75-77°. The reflux time was 18 hours.

Ethyl 1-(2-Methylbenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13f**.

This compound was obtained in a yield of 92%, mp 90-92°. The reflux time was 20 hours.

Ethyl 1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13g**.

This compound was obtained in a yield of 94%, mp 135-137°. The reflux time was 28 hours.

Ethyl 1-(3-Nitrobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13h**.

This compound was obtained in a yield of 94%, mp 134-135°. The reflux time was 16 hours.

Ethyl 1-(2-Nitrobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13i**.

This compound was obtained in a yield of 91%, mp 143-144°. The reflux time was 24 hours.

Ethyl 1-(4-Chlorobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13j**.

This compound was obtained in a yield of 93%, mp 129-130°. The reflux time was 4 hours.

Ethyl 1-(3-Chlorobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13k**.

This compound was obtained in a yield of 92%, mp 90-91°. The reflux time was 9 hours.

Ethyl 1-(2-Chlorobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13l**.

This compound was obtained in a yield of 90%, mp 91-93°. The reflux time was 10 hours.

Ethyl 1-(4-Bromobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13m**.

This compound was obtained in a yield of 90%, mp 135-136°. The reflux time was 6 hours.

Ethyl 1-(3-Bromobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13n**.

This compound was obtained in a yield of 92%, mp 108-109°. The reflux time was 5 hours.

Ethyl 1-(2-Bromobenzyl)-1*H*-1,2,3-triazole-4-carboxylate **13o**.

This compound was obtained in a yield of 93%, mp 82-83°. The reflux time was 8 hours.

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