

The Photochemistry of 1-Alkenyl-Substituted-1,2,3-Triazoles Leading to Formation of Pyrrole Derivatives

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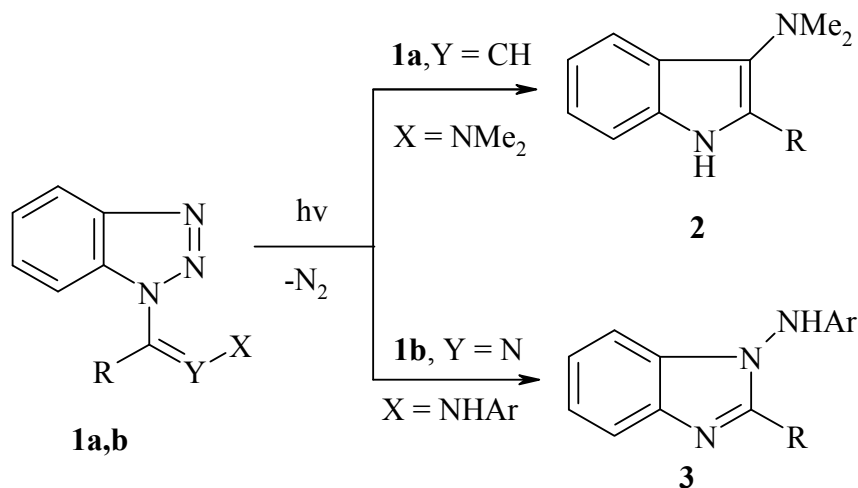
Abstract

Irradiation of 1-alkenyl-substituted-1,2,3-triazoles 5a-d using 16 W low pressure mercury arc-lamp (254 nm) for 16 hrs produced 3-dimethylamino-1H-pyrrole derivatives 9a-d, together with 4-phenyl or (4-ethoxycarbonyl)-1H-1,2,3-triazoles 10a,b.

Keywords: photolysis, 1,2,3-triazoles, pyrrole, microwave

1. Introduction

Previous studies have shown that thermolytic and/or photolytic reactions of 1-substituted benzotriazole derivatives take place with elimination of N₂ followed by subsequent ring closure of the resulting biradical intermediates to form heterocyclic products (Dib, Al-Awadi, Ibrahim, & El-Desoqui, 2003, 2004; H. Al-Awadi, M. Ibrahim, Y. Ibrahim, & N. Al-wadi, 2008; Maerky, Schmid, & Hansen, 1979; Wender & Cooper, 1986). These efficient processes have been described by Katritzky and his coworkers (Katritzky, Lan, Yang, & Denisko, 1998). More recently we have reported the synthesis of indoles **2** and benzimidazoles **3** via photolysis of readily obtainable 1-substituted-1,2,3-benzotriazoles **1a,b** (Scheme 1) (Al-Jalal, Al-Awadi, Ibrahim, & Elnagdi, 2011a, 2011b).



Scheme 1. Photolysis of 1-substituted benzotriazoles **1a,b** to indoles and benzimidazoles

However, literature survey indicated that little investigation have been made on thermolytic and/or photolytic behavior of 1-alkenyl-substituted-1,2,3-triazoles (Boyer & Silvarajan, 1969; Burgess, Carithers, & McCullagh, 1968; Michell & Rees, 1987; Ogata, Takaji, & Hayashi, 1977; Silvarajan & Boyer, 1972; Wender & Cooper, 1969). In the light of the established pharmaceutical activity of 3-dimethylaminopyrrole which is reported as an analgesics and anticonvulsants agent (Bellina & Rossi, 2006; Rochais, Lisowski, Dallemagne, & Rault, 2004;

Liebscher et al., 1992) we became interested in developing photoinduced synthetic route to such compounds via photolysis of suitably 1-substituted-1,2,3-triazole.

In this work we report the first successful photochemical conversion of various 1-alkenyl-substituted-1,2,3-triazoles into polysubstituted pyrrole derivatives by elimination of N₂ followed by ring closure of the resulting biradical intermediates.

2. Experimental

General: Melting points were recorded on a Gallenkamp apparatus. IR spectra were recorded in KBr disks on a Perkin Elmer System 2000 FT-IR spectrophotometer. ¹H- and ¹³C- NMR spectra were recorded on a Bruker DPX 400 MHz NMR spectrometer with proton spectra measured at 400 MHz and carbon spectra at 100 MHz. Mass spectra were measured on a VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer. The UV-visible absorption spectra were scanned using Varian Cary 5 instrument in the wave length range 200-450 Explorer. Microwave experiments were carried out using a CEM Corporation, NC, USA microwave apparatus. X-ray analysis was performed using a Rigaku Rapid II and Bruker X8 Prospector diffractometer. A photochemical reactors limited fitted with a 16 W low pressure mercury arc-lamp was used for the irradiation.

2.1 Click Synthesis of 1-Alkyl Substituted-1,2,3-Triazoles 4a-f

General procedure: A mixture of terminal alkynes (2.50 g, ≈ 25 mmole), sodium azide (1.95 g, 30 mmole), alkyl halide derivatives (25 mmol), copper sulfate pentahydrate (0.6225 g, 0.01 equiv) and sodium ascorbate (0.99 g, 0.02 equiv) in a mixture solvent of tertiary butanol and water (1:1v/v, 50 ml), was stirred at room temperature for 3-12 hrs. After the color of the mixture was changed to yellow brown it was poured on to ice water (150 ml), filtered, washed with water to give compounds 4a-f.

2.1.1 1-(4-Phenyl-1,2,3-Triazol-1-yl)Propan-2-One 4a

Colorless solid from ethanol, yield 4.0 g (80%), mp. 142-144 °C. LCMS (*m/z*) = 202 (*M* + 1). ¹H NMR (400 MHz, CDCl₃): δ 8.89-8.86 (m, 3H), 7.46 (td, 2H, *J* = 7.4, 1.6 Hz), 7.37 (tt, 1H, *J* = 7.6, 1.6 Hz), 5.29 (s, 2H), 2.32 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆): δ 200.9, 146.2, 130.7, 128.9, 127.9, 125.1, 122.7, 58.4, 27.1 (HRMS = 201.0896, requires C₁₁H₁₁N₃O 201.0902).

2.1.2 4-Phenyl-1,2,3-Triazol-1-yl-acetic Acid Isopropyl Ester 4b

Colorless solid from benzene, yield 4.0 g (78%), mp. 130-132 °C. MS: *m/z* (%) = 245 (*M*⁺, 30), 175 (100), 116 (100). IR (KBr, cm⁻¹): 3087, 2987, 1789, 1463, 1443, 1379, 1259, 1105, 1045, 765, 694. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (s, 1H), 7.88 (dd, 2H, *J* = 7.8, 1.2 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.38 (tt, 1H, *J* = 7.8, 1.2 Hz), 5.20 (s, 2H), 5.16 (sex, 1H, *J* = 6.4 Hz), 1.32 (d, 6H, *J* = 6.4 Hz, 2CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 165.8, 148.3, 130.4, 128.9, 128.3, 125.8, 120.9, 70.6, 51.2, 21.7 (2C) (HRMS = 245.1164, requires C₁₃H₁₅N₃O₂ 245.1157).

2.1.3 1-(2-Oxo-2-phenyl-ethyl)-1*H*-1,2,3-triazole-4-carboxylic Acid Ethyl Ester 4c

Colorless solid from ethanol, yield 4.5 g (69%), mp. 170-172 °C. MS: *m/z* (%) = 259 (*M*⁺, 10), 202 (50). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 8.02 (dd, 2H, *J* = 7.6, 1.2 Hz), 7.72 (t, 1H, *J* = 7.6 Hz), 7.59 (t, 2H, *J* = 7.6 Hz), 5.95 (s, 2H), 4.46 (q, 2H, *J* = 7.2 Hz), 1.44 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 189.4, 160.6, 140.7, 134.9, 133.6, 129.5, 129.3, 128.2, 61.4, 55.5, 14.5 (HRMS = 259.0951, requires C₁₃H₁₃N₃O₃ 259.0957).

2.1.4 4-Phenyl-1,2,3-Triazol-1-yl-acetic Acid Methyl Ester 4d

Yellow solid from ethanol, yield 7.5 g (88%), mp. 82-83 °C (lit. mp 81-82 °C, Kumar, Patel, & Reddy, 2009).

2.1.5 1-Allyl-4-phenyl-1*H*-1,2,3-triazole 4e

Colorless solid from benzene, yield 3.6 g (78%), mp. 110-112 °C (lit. mp. 112-113 °C, Kidwai & Jain, 2011).

2.1.6 Trans 1-(2-Ethoxycarbonylvinyl)-1*H*-1,2,3-Triazole-4-Carboxylic Acid Ethyl Ester 4f

This compound was prepared from ethyl propiolate (2.0 g, 20.0 mmol) and sodium azide (0.78 g, 12.0 mmol) after stirring at room temperature for 3 hrs at the same condition of general procedure as colorless crystals from benzene, (*R_f* 0.5, EtOAc: petroleum b.p. 60-80, 1:2v/v), yield 1.2 g (50%), mp. 93-95 °C. MS: *m/z* (%) = 239 (*M*⁺, 10), 194 (60), 138 (100). IR (KBr, cm⁻¹): 3103, 3051, 2980, 1735, 1713, 1663, 1539, 1447, 1373, 1305, 1210, 1157, 1049, 961, 864, 781. ¹H NMR (400 MHz, CDCl₃): δ 8.38 (s, 1H), 8.23 (d, 1H, *J* = 14.4 Hz), 6.67 (d,

1H, $J = 14.4$ Hz), 4.47 (q, 2H, $J = 7.2$ Hz), 4.32 (q, 2H, $J = 7.2$ Hz), 1.45 (t, 3H, $J = 7.2$ Hz), 1.37 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 164.6, 160.0, 141.1, 135.3, 126.0, 113.0, 61.8, 61.5, 14.3, 14.2 (HRMS = 239.0900, requires $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_4$ 239.0906).

2.1.7 Cis 1-(2-Ethoxycarbonylvinyl)-1H-1,2,3-Triazole-4-Carboxylic Acid Ethyl Ester **4f**

White solid from petroleum b.p. 60-80, (R_f 0.65, EtOAc: petroleum b.p. 60-80 °C, 1:2v/v), yield 0.5 g (20%), mp. 66-68 °C. MS: m/z (%) = 239 (M^+ , 10), 194 (60), 138 (100). IR (KBr, cm^{-1}): 3103, 3052, 2980, 1735, 1713, 1663, 1539, 1447, 1373, 1304, 1208, 1157, 1048, 961, 781. ^1H NMR (400 MHz, CDCl_3): δ 9.69 (s, 1H), 7.65 (d, 1H, $J = 10.8$ Hz), 5.83 (d, 1H, $J = 10.8$ Hz), 4.46 (q, 2H, $J = 7.0$ Hz), 4.29 (q, 2H, $J = 7.0$ Hz), 1.44 (t, 3H, $J = 7.0$ Hz), 1.36 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 163.7, 160.2, 140.2, 133.0, 130.0, 109.6, 61.5 (2C), 14.3, 14.0 (HRMS = 239.0900, requires $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_4$ 239.0906).

2.2 Synthesis of 1-Alkenyl substituted-1,2,3-Triazole Derivatives **5a-d**

General procedure: A mixture of each of compounds **4a-d** (10 mmol) and dimethylformamidedimethyleacetal (DMF-DMA) (3 ml, 25 mmol) in xylene (3 ml) was introduced in a microwave oven and irradiated at 150 °C for 3 minutes. The mixture was cooled and poured on petroleum ether p.b. 60-80 °C (50 ml), filtered, and crystallized from ethanol to give compounds **5a-d**.

2.2.1 4-Dimethylamino-3-(4-Phenyl-1,2,3-Triazol-1-yl)but-3-en-2-one **5a**

White solid, yield 2.0 g (78%), mp. 160-162 °C. MS: m/z (%) = 256 (M^+ , 5), 228 (100), 185 (25). IR (KBr, cm^{-1}): 3132, 3047, 2929, 1656, 1600, 1425, 1311, 1217, 1114, 1033, 923, 769. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, 2H, $J = 7.6, 1.2$ Hz), 7.87 (s, 1H), 7.73 (s, 1H), 7.48 (t, 2H, $J = 7.4$ Hz), 7.39 (t, 1H, $J = 7.8$ Hz), 3.20 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.91 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 192.3, 147.9, 146.4, 130.2, 129.0, 128.4, 125.7, 125.1, 108.2, 47.9, 36.7, 24.6 (HRMS = 256.1319, requires $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}$ 256.1324).

2.2.2 3-Dimethylamino-2-(4-Phenyl-1,2,3-Triazol-1-yl)acrylic Acid Isopropyl Ester **5b**

White solid, yield 2.1 g (70%), mp. 155-156 °C. MS: m/z (%) = 300 (M^+ , 5), 229 (100), 201 (25). IR (KBr, cm^{-1}): 3091, 2976, 2967, 1694, 1623, 1465, 1428, 1348, 1285, 1226, 1108, 1085, 1046, 768, 694. ^1H NMR (400 MHz, CDCl_3): δ 7.90 (dd, 2H, $J = 7.6, 1.2$ Hz), 7.86 (s, 1H), 7.63 (s, 1H), 7.46 (t, 2H, $J = 7.6$ Hz), 7.36 (t, 1H, $J = 7.8$ Hz), 5.06 (quin, 1H, $J = 6.4$ Hz), 2.97 (br, 3H, NCH_3), 2.42 (br, 3H, NCH_3), 1.20 (d, 6H, $J = 6.4$ Hz, 2CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 147.0, 146.5, 130.5, 128.9, 128.2, 125.9, 125.7, 97.3, 67.7, 47.6, 36.9, 22.0 (2C) (HRMS = 300.1580, requires $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2$ 300.1586).

2.2.3 1-(1-Benzoyl-2-Dimethylamino-vinyl)-1H-1,2,3-Triazole-4-Carboxylic Acid Ethyl Ester **5c**

Colorless solid, yield 2.3 g (73%), mp. 132-134 °C. LCMS: (m/z) = 315 ($\text{M} + 1$). MS: m/z (%) = 314 (M^+ , 15), 286 (15), 213 (40), 105 (100%). IR (KBr, cm^{-1}): 3132, 3047, 2929, 1656, 1600, 1425, 1311, 1217, 1114, 1033, 923, 769. ^1H NMR (400 MHz, CDCl_3): δ 8.13 (s, 1H), 7.56 (s, 1H), 7.47 (d, 2H, $J = 7.6$ Hz), 7.44 (t, 1H, $J = 7.6$ Hz), 7.39-7.35 (m, 2H), 4.43 (q, 2H, $J = 7.2$ Hz), 3.17 (br, 3H, NCH_3), 2.38 (br, 3H, NCH_3), 1.42 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 188.7, 160.7, 150.2, 140.0, 138.5, 133.2, 130.7, 128.4, 127.9, 108.3, 61.4, 48.2, 38.0, 14.3 (HRMS = 314.1373, requires $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_3$ 314.1379).

2.2.4 3-Dimethylamino-2-(4-Phenyl-1,2,3-Triazol-1-yl)acrylic Acid Methyl Ester **5d**

Colorless solid, mp. 118-120 °C, yield 2.0 g (73%). MS: m/z (%) = 272 (M^+ , 5), 244 (50), 229 (100). IR (KBr, cm^{-1}): 3133, 2948, 1698, 1640, 1468, 1430, 1402, 1327, 1294, 1223, 1158, 1109, 1082, 1023, 764. ^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, 2H, $J = 7.6$ Hz), 7.84 (s, 1H), 7.65 (s, 1H), 7.44 (t, 2H, $J = 7.8$ Hz), 7.34 (t, 1H, $J = 7.2$ Hz), 3.66 (s, 3H, OCH_3), 3.13 (br, 3H, NCH_3), 2.34 (br, 3H, NCH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 166.2, 146.9, 146.1, 130.4, 128.8, 128.2, 125.7, 125.5, 96.7, 51.6, 47.6, 36.2 (HRMS = 272.1268, requires $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_2$ 272.1273).

2.3 Synthesis of 1-Arylhydrazono-1,2,3-Triazole Derivatives **6a-c**

General procedure: To a cooled solution (0 °C) of compound **4a** (2.01 g, 10 mmol), sodium acetate (1.64 g, 20 mmol) in ethanol (100 ml) was gradually added with stirring in about 30 min cooled solution of appropriate aromatic diazonium chloride (10 mmol). The mixture was stirred for 24 hours at room temperature. The yellow solid so formed was filtered and crystallized from ethanol to give compounds **6a-c**.

2.3.1 1-(Phenylhydrazono)-1-(4-Phenyl-1,2,3-Triazol-1-yl)propan-2-one **6a**

Yield 2.3 g (75%), mp. 155-156 °C. MS: m/z (%) = 305 (M^+ , 5), 277 (40), 92 (100). IR (KBr, cm^{-1}): 3179, 3162, 3038, 1668, 1562, 1552, 1510, 1378, 1355, 1257, 1238, 1210, 1142, 1078, 1012, 763, 690. ^1H NMR (400 MHz, CDCl_3): δ 12.23 (s, 1H), 9.05 (s, 1H), 7.95 (dd, 2H, $J = 8.4, 1.2$ Hz), 7.49 (t, 2H, $J = 7.6$ Hz), 7.44-7.37 (m, 5H),

7.16-7.12 (m, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 190.6, 146.1, 142.0, 129.6, 129.0, 128.8 (2C), 126.1, 124.2, 123.9, 120.8, 115.1, 26.1. Anal. Calc. for $\text{C}_{17}\text{H}_{15}\text{N}_5\text{O}$ (305.34): C, 66.87; H, 4.95; N, 22.94. Found: C, 66.79; H, 5.01; N, 22.84.

2.3.2 1-*p*-Chlorophenylhydrazono-1-(4-Phenyl-1,2,3-Triazol-1-yl)propan-2-one **6b**

Yield 2.5 g (73%), mp. 158-160 °C. MS: m/z (%) = 339 (M^+ , 10), 311 (40), 126 (100). IR (KBr, cm^{-1}): 3271, 3149, 3058, 3038, 1673, 1564, 1488, 1397, 1258, 1231, 1083, 1011, 821, 760, 691. ^1H NMR (400 MHz, CDCl_3): δ 12.26 (s, 1H), 9.04 (s, 1H), 7.92 (dd, 2H, J = 8.4, 1.6 Hz), 7.48 (dt, 2H, J = 8.0, 1.2 Hz), 7.41 (tt, 1H, J = 8.0, 1.2 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.0 Hz), 2.71 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 190.5, 146.1, 140.6, 129.7, 129.5, 129.1, 129.0, 128.8, 126.0, 124.1, 120.8, 116.2, 26.1. Anal. Calc. for $\text{C}_{17}\text{H}_{14}\text{ClN}_5\text{O}$ (339.79): C, 60.09; H, 4.15; N, 20.61. Found: C, 60.02; H, 4.24; N, 20.49.

2.3.3 1-(4-Phenyl-1,2,3-Triazol-1-yl)-1-*p*-Tolylhydrazono-propan-2-one **6c**

Yield 2.4 g (75%), mp. 164-166 °C. MS: m/z (%) = 319 (M^+ , 5), 291 (70), 106 (100). IR (KBr, cm^{-1}): 3268, 3171, 3038, 1661, 1552, 1506, 1402, 1265, 1145, 1013, 818, 760, 687. ^1H NMR (400 MHz, CDCl_3): δ 12.21 (s, 1H), 9.07 (s, 1H), 7.95 (dd, 2H, J = 8.4, 1.2 Hz), 7.50 (t, 2H, J = 7.6 Hz), 7.42 (t, 1H, J = 7.6 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.4 Hz), 2.73 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 190.4, 146.0, 139.7, 133.9, 130.2, 129.7, 129.0, 128.7, 126.0, 123.7, 120.8, 115.1, 26.0, 20.9. Anal. Calc. for $\text{C}_{18}\text{H}_{17}\text{N}_5\text{O}$ (319.37): C, 67.70; H, 5.37; N, 21.93. Found: C, 67.72; H, 5.34; N, 21.80.

2.4 Photolysis of Compounds **4e,f**, **5a-d** and **6a-c**

Irradiation using (16 w) low pressure mercury arc-lamp. Each of the substrates **4e,f**, **5a-d** and **6a-c** (1.0 mmol) was dissolved in acetonitrile (25 mL) in quartz tubes and irradiated using (16 W) low pressure mercury arc-lamp for 16 hrs at room temperature. The progress of the reaction was monitored by TLC and the formation of products was detected with LCMS. The solvent was removed in *vacuo* and the resulting residue was subjected to column chromatography on silica gel using ethyl acetate/petroleum ether b.p. 60-80 °C the % yield in (Table 1).

2.4.1 2-Acetyl-3-Dimethylamino-4-Phenyl-1*H*-Pyrrole **9a**

Yellow solid, (R_f 0.55, EtOAc: petroleum b.p. 60-80 °C, 1:4v/v). mp. 158-160 °C. MS: m/z (%) = 228 (M^+ , 100), 211 (55), 169 (30). IR (KBr, cm^{-1}): 3276, 3070, 2927, 1614, 1550, 1458, 1398, 1286, 1122, 973, 919, 763. ^1H NMR (400 MHz, CDCl_3): δ 9.39 (br, 1H, NH), 7.40-7.28 (m, 5H), 6.89 (d, 1H, J = 3.6 Hz), 2.79 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.61 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 188.5, 135.1, 129.6 (2C), 128.2, 127.0, 125.6, 123.7, 122.6, 45.6 (2C), 26.4 (HRMS = 228.1257, requires $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$ 228.1263).

2.4.2 3-Dimethylamino-4-Phenyl-1*H*-Pyrrole-2-Carboxylic Acid Isopropyl Ester **9b**

Colorless solid, (R_f 0.70, EtOAc: petroleum b.p. 60-80 °C, 1:4v/v). mp. 150-152 °C. MS: m/z (%) = 272 (M^+ , 90), 212 (100), 169 (55). IR (KBr, cm^{-1}): 3476, 3088, 2986, 1753, 1560, 1465, 1378, 1334, 1223, 1191, 1106, 1082, 846, 766. ^1H NMR (400 MHz, CDCl_3): δ 8.82 (br, 1H), 7.55 (d, 2H, J = 7.6 Hz), 7.38 (t, 2H, J = 7.6 Hz), 7.29 (t, 1H, J = 7.4 Hz), 6.90 (d, 1H, J = 3.2 Hz), 5.31-5.25 (m, 1H), 2.85 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 128.3, 128.2, 126.3, 126.2, 125.3, 122.3, 119.7, 115.8, 67.6, 44.2, 34.4, 22.3 (2C) (HRMS = 272.1519, requires $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ 272.1525).

2.4.3 5-Benzoyl-3-Dimethylamino-1*H*-Pyrrole-3-Carboxylic Acid Ethyl Ester **9c**

Yellow solid, (R_f 0.95, EtOAc: petroleum b.p. 60-80, 1:4v/v). mp. 138-140 °C. LCMS = 287 ($\text{M} + 1$). MS: m/z (%) = 286 (M^+ , 100), 269 (60), 225 (35). IR (KBr, cm^{-1}): 3262, 2979, 2928, 1714, 1600, 1534, 1446, 1401, 1374, 1273, 1184, 1093, 1032, 736. ^1H NMR (400 MHz, CDCl_3): δ 9.30 (br, 1H, NH), 7.71 (d, 2H, J = 7.8 Hz), 7.56 (s, 1H), 7.54 (t, 1H, J = 7.4 Hz), 7.47 (t, 2H, J = 7.8 Hz), 4.30 (q, 2H, J = 7.2 Hz), 2.61 (s, 6H, 2CH_3), 1.37 (t, 3H, J = 7.2 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 185.5, 163.4, 146.3, 139.4, 131.6, 129.6, 128.6, 128.1, 122.9, 111.4, 59.8, 44.1 (2C), 14.5 (HRMS = 286.1314, requires $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$ 286.1317).

2.4.4 3-Dimethylamino-4-Phenyl-1*H*-Pyrrole-2-Carboxylic Acid Methyl Ester **9d**

Colorless solid, (R_f 0.9, EtOAc: petroleum b.p. 60-80, 1:3v/v). mp. 142-144 °C. LCMS = 245 ($\text{M} + 1$). MS: m/z (%) = 244 (M^+ , 45), 229 (100), 201 (25). IR (KBr, cm^{-1}): 3329, 2957, 2928, 1717, 1691, 1556, 1447, 1437, 1383, 1282, 1259, 1138, 1059, 914. ^1H NMR (400 MHz, CDCl_3): δ 8.81 (br, 1H, NH), 7.52 (d, 2H, J = 7.6 Hz), 7.38 (t, 2H, J = 8.0 Hz), 7.28 (t, 1H, J = 7.2 Hz), 6.90 (d, 1H, J = 3.6 Hz), 3.91 (s, 3H, OCH_3), 2.84 (s, 6H, 2CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 160.4, 134.9, 128.34, 128.28, 128.15, 126.4, 122.0, 120.4, 114.7, 51.3, 44.3 (HRMS = 244.1206, requires $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ 244.1212).

2.4.5 4-Phenyl-1*H*-1,2,3-Triazole **10a**

White solid, mp. 146-148 °C (lit. mp 147-147.4 °C, Zhang, Kung, & Yang, 2010).

2.4.6 Ethyl-1*H*-1,2,3-Triazole-4-Carboxylate **10b**

Colorless solid, mp. 103-104 °C (lit. mp 102-103 °C, Avat-Arman & Khojasteh, 2009).

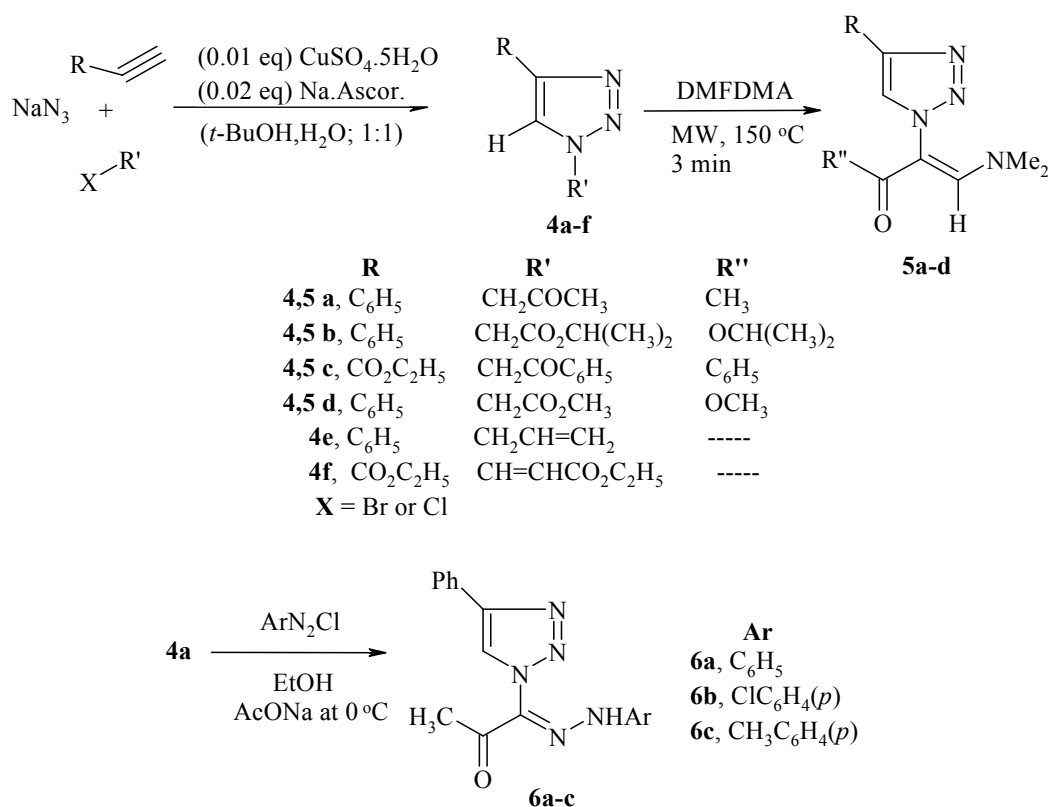
2.4.7 4-Allyl-5-Phenyl-4*H*-1,2,3-Triazole **13**

Colorless oil, (*R_f* 0.85, EtOAc: petroleum b.p. 60-80 °C, 1:3v/v). MS: *m/z* (%) = 185(*M*⁺, 10), 157 (20), 116 (100). IR (KBr, cm⁻¹): 3081, 3032, 2924, 1495, 1454, 1275, 1076, 995, 925, 754, 699. ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.28 (m, 5H), 5.88-5.78 (m, 1H), 5.22 (t, 2H, *J* = 7.2 Hz), 3.88 (t, 1H, *J* = 7.2 Hz), 2.72-2.61 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 135.2, 132.5, 129.0, 128.1, 127.3, 120.3, 119.3, 39.8, 37.5 (HRMS = 185.0947, requires C₁₁H₁₁N₃ 185.0940).

3. Results and Discussion

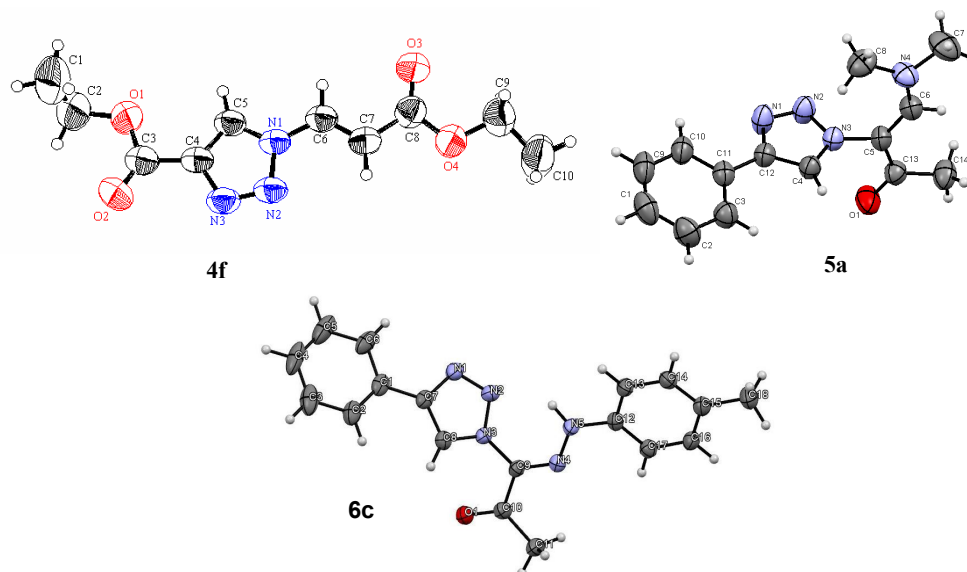
3.1 Synthesis

1-Alkyl substituted-1,2,3-triazoles **4a-f** were prepared from terminal alkynes, sodium azide and alkyl halides using CuSO₄·5H₂O and Na-ascorbate in *ter*-butanol/water mixture solvent after stirring at room temperature for 3-12 hrs some of which are new compounds (click chemistry, Liu & Reiser, 2011). Condensation of **4a-d** with dimethylformamide dimethyl acetal (DMFDMA) in a microwave oven (M.W.) at 150 °C for 3 min. produced 1-alkenyl substituted-1,2,3-triazoles **5a-d**. Coupling of **4a** with the appropriate aromatic diazonium chloride in ethanol and sodium acetate produced 1-arylhydrazono-1-(4-phenyl-1,2,3-triazole-1-yl)propan-2-ones **6a-c** (Scheme 2). The UV spectrum of these compounds shows absorption maxima in the region 248-312 nm (Table 1).



Scheme 2. Synthesis of 1-substituted-1,2,3-triazoles **4a-f**, **5a-d** and **6a-c**

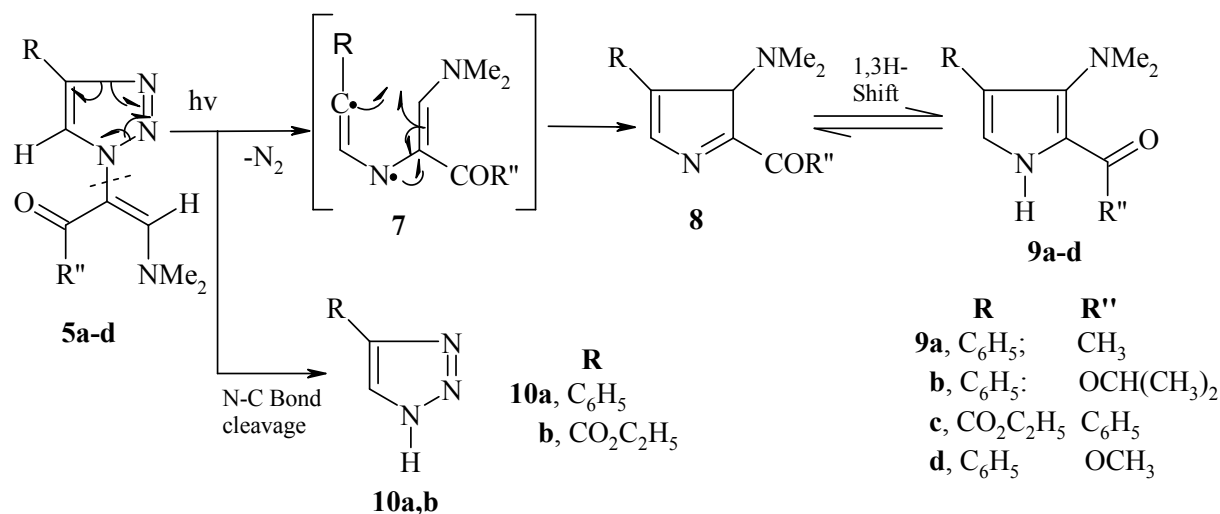
The structure of compounds **4a-f**, **5a-d** and **6a-c** were well established based on full data of ¹H, ¹³C and 2D-NMR, GC-MS, LCMS (see Experimental section) and moreover X-ray crystal structures of compounds **4f**, **5a** and **6c** were determined (Figure 1).

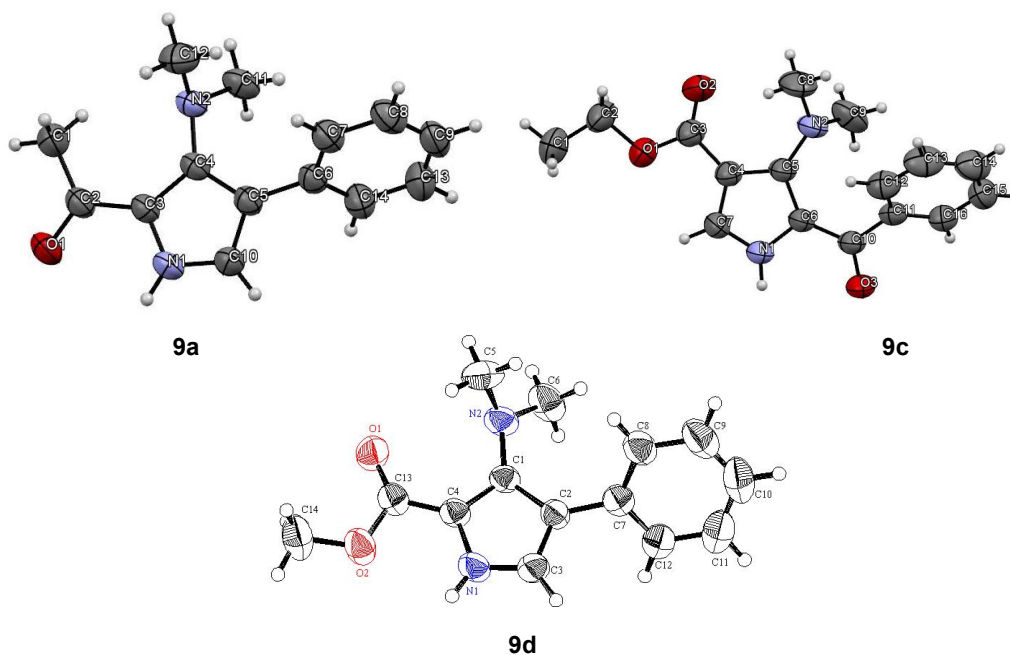
Figure 1. ORTEP drawing of compounds **4f**, **5a** and **6c**

3.2 Photolysis

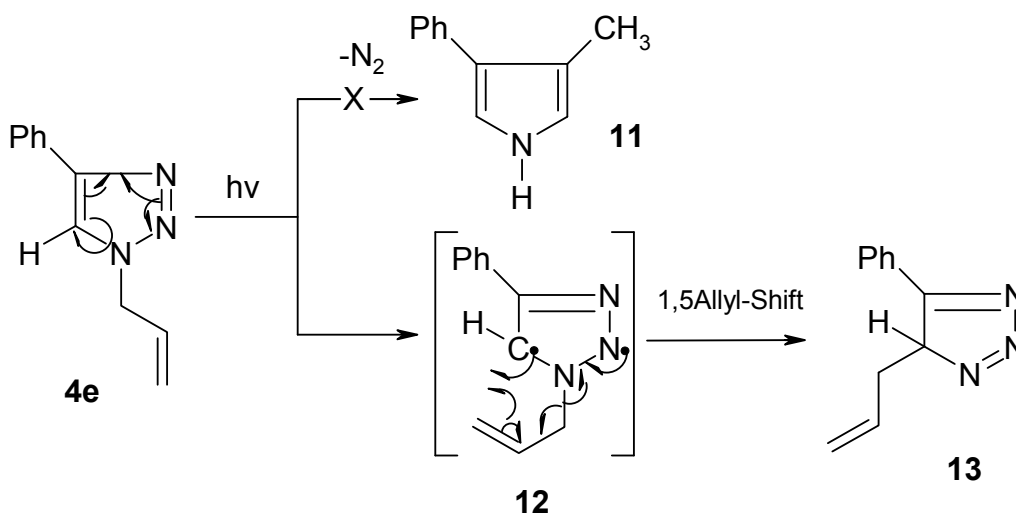
Irradiation of 1-alkenyl substituted-1,2,3-triazoles **5a-d** using 16 W low pressure mercury arc-lamp for 16 hrs produced 3-dimethylamino-1*H*-pyrrole derivatives **9a-d**, in 34-38% yield together with 4-phenyl or (4-ethoxycarbonyl)-1*H*-1,2,3-triazoles **10a,b** in 25-35% yield. The formation of these photoproducts can be explained through extrusion of N_2 molecule to form the corresponding 1,3-diradical intermediate **7** which cyclized to **8** followed by 1,3H-shift produced **9a-d**. Formation of **10a,b** can be explained by photo-hydrolysis of N1-C bond (Scheme 3).

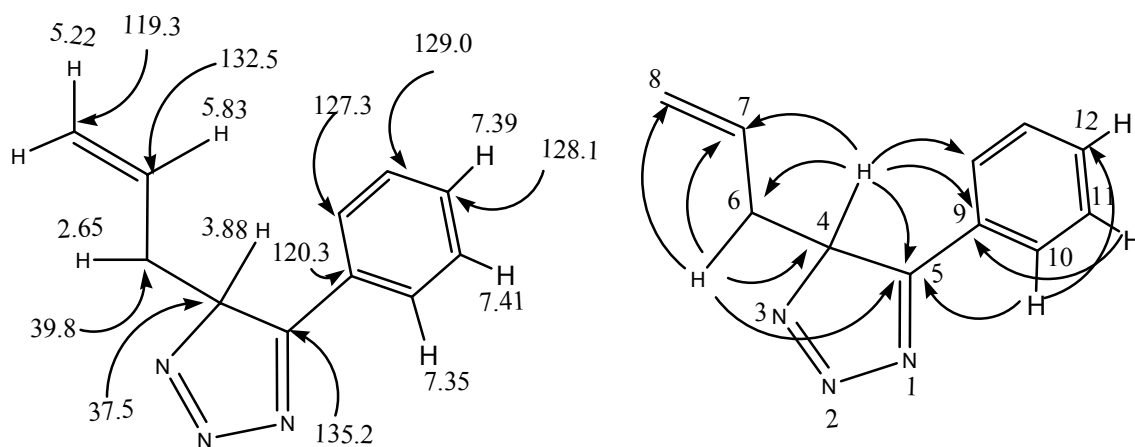
The structure of the new pyrrole derivatives **9a-d** were established based on full data 1H , ^{13}C -NMR, GC-MS and X-ray crystal structures of compounds **9a,c,d** (Figure 2).

Scheme 3. Photoproducts of compounds **5a-d**

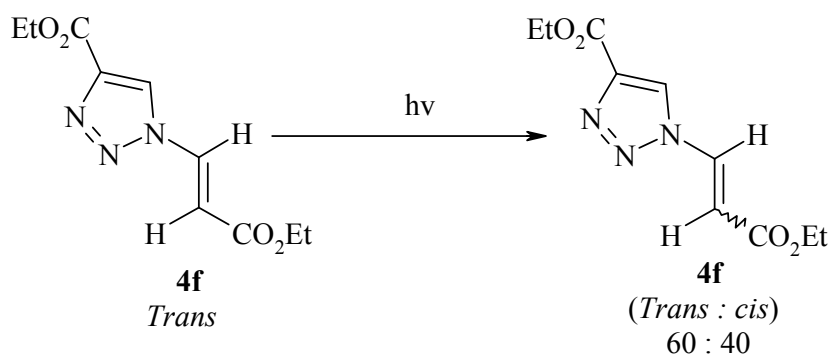
Figure 2. ORTEP drawing of compounds **9a**, **9c** and **9d**

Irradiation of compound **4e** under the same conditions produced 4-allyl-5-phenyl-4*H*-1,2,3-triazole **13** in 38 % yield through 1,5-allyl shift, and not the expected pyrrole **11** (Scheme 4). The structure of photoproduct **13** was suggested by 2D NMR, HSQC, H,H-COSY and HMBC, 2-D experiments (Figure 3).

Scheme 4. Photoproduct of compound **4e**

Figure 3. Important HMBC, H-C correlation of compound **13**

Irradiation of compounds **4f** (*trans*) under the same condition afforded formation of photo-stationary *E-Z* photo-isomerization mixture (*trans/cis*, 60 : 40%) isomers of **4f** (Scheme 5). Moreover irradiation of the isolated *cis* isomers **4f** yielded *trans/cis*, 60: 40% mixture. The two isomers were separated and fully characterized by ^1H , ^{13}C -NMR (see Experiment section).

Scheme 5. *Trans/Cis* photoisomerisation of compound **4f**

Irradiation of 1-arylhydrazono-1,2,3-triazole derivatives **6a-c** in an attempt to prepare the corresponding 1-anilino-imidazole derivatives **14a-c** through loss of molecular nitrogen did not produce any photoproducts (Scheme 6). Table 1 shows the absorption maxima (λ_{max}) and % yield of photoproducts **4e,f** and **5a-d**.

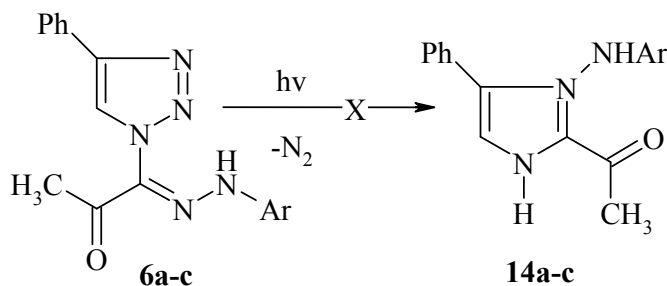
Scheme 6. Photolysis of compounds **6a-c**

Table 1. Photoproducts of compounds **4e,f** and **5a-d**

Substrat	λ max	Irradiation condition	Irradiation time (h)	Photoproducts and Yield %
4e	248	16 W	16 h	13 (38)
4f	260	16 W	16 h	4f (60 <i>trans</i> : 40 <i>cis</i>)
5a	287	16 W	16 h	9a (36), 10a (35)
5b	296	16 W	16 h	9b (34), 10a (28)
5c	312	16 W	16 h	9c (35), 10b (25)
5d	284	16 W	16 h	9d (38), 10a (30)

4. Conclusions

1-alkenyl substituted-1,2,3-triazoles **5a-d** were photochemically converted into 3-dimethylamino-1*H*-pyrrole derivatives **9a-d** together with 4-phenyl or (4-ethoxycarbonyl)-1*H*-1,2,3-triazoles **10a,b**. The photochemical behavior of 1-substituted-1,2,3-triazoles **5a-d** is similar to those of benzotriazoles (Al-Jalal, Al-Awadi, Ibrahim, & Elnagdi, 2011). However 1-allyl-4-phenyl-1*H*-1,2,3-triazole **4e** produced upon irradiation 4-allyl-5-phenyl-4*H*-1,2,3-triazole **13**, while *trans* 1-(2-ethoxycarbonyl-vinyl)-1*H*-1,2,3-triazole-4-carboxylic acid ethyl ester **4f** produced *trans/cis* photo-isomerization mixture.

Supplementary Material

Crystallographic data of (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 928598 (**4f**), CCDC 928127 (**5a**) and CCDC 928599 (**6c**), CCDC 929700 (**9a**), CCDC 929701 (**9c**) and CCDC 939635 (**9d**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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