

Novel cycloadducts from the 1,3-dipolar cycloaddition reactions of triazolium-1-imide 1,3-dipoles

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Dedicated to Tony McKervey on the occasion of his 65th birthday

(received 28 Feb 03; accepted 22 Apr 03; published on the web 03 May 03)

Abstract

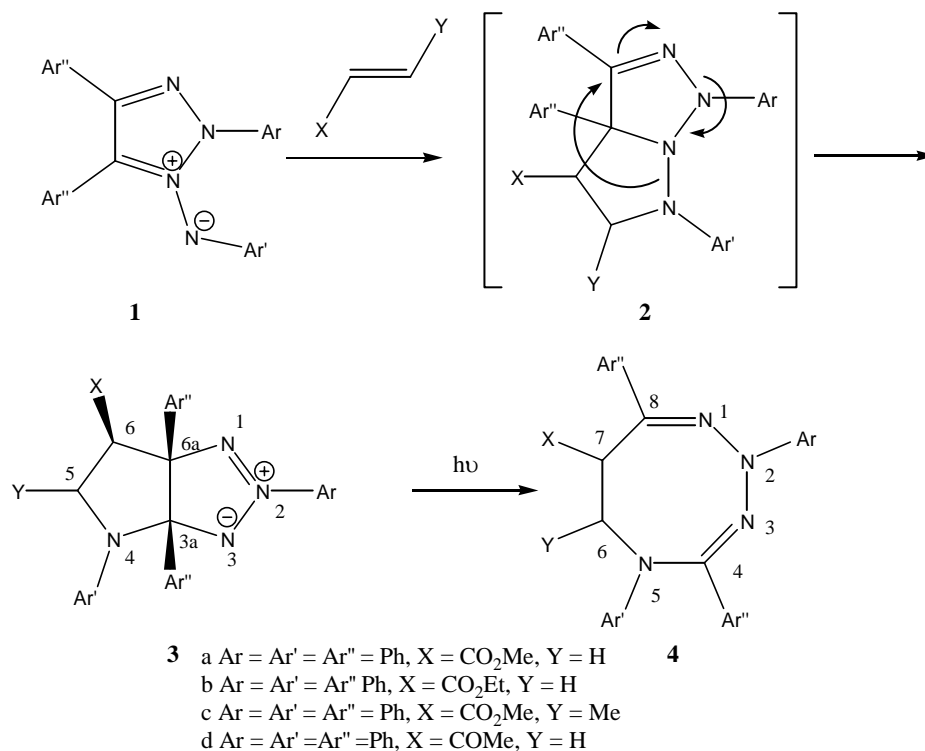
A range of imidazo-1,2,3-triazoles were synthesised by the 1,3-dipolar cycloaddition of triazolium-1-imides with N-sulfonyl imines. Oxazolo-1,2,3-triazoles were identified as side products of this reaction. Benzyne was also used as a 1,3-dipolarophile in the cycloaddition reaction, resulting in a range of tricyclic triazolindoles.

Keywords: 1,3-Dipolar cycloaddition, N-sulfonyl imines, benzyne

Introduction

In work previously carried out by our group 3a,6a-diaryl hexahydropyrrolo-triazoles **3** underwent photoinduced disrotatory ring expansion to the new 2,5,6,7-tetrahydro-1,2,3,5 tetrazocines **4**¹ (Scheme 1). Of key importance in the stability of these tetrazocines was the saturation of the C-6 position, and the nature of the group attached to C-6. Both saturation and electron withdrawing groups were found to initiate rearrangement of the initially formed tetrazocine, by the attack of N-2 on C-6. In searching for new ring systems of this type, and in particular those with a fifth nitrogen in the system, the cycloadditions of triazolium-1-imides **1** with various dipolarophiles were investigated.

The cycloadditions of triazolium-1-imides with various alkene and alkyne dipolarophiles have been extensively studied.² On addition, the initial bicyclic adducts **2** subsequently undergo a 1,4-sigmatropic rearrangement to give the bicyclic 1,2,3-triazoles **3**.



Scheme 1. 1,3-Dipolar cycloaddition of triazolium-1-imides, followed by 1,4-sigmatropic rearrangement. The resulting bicyclic compounds undergo photo-induced ring expansion to give the novel 1,2,3,5-tetrazocines.

Results and Discussion

Benzyne as a Dipolarophile.

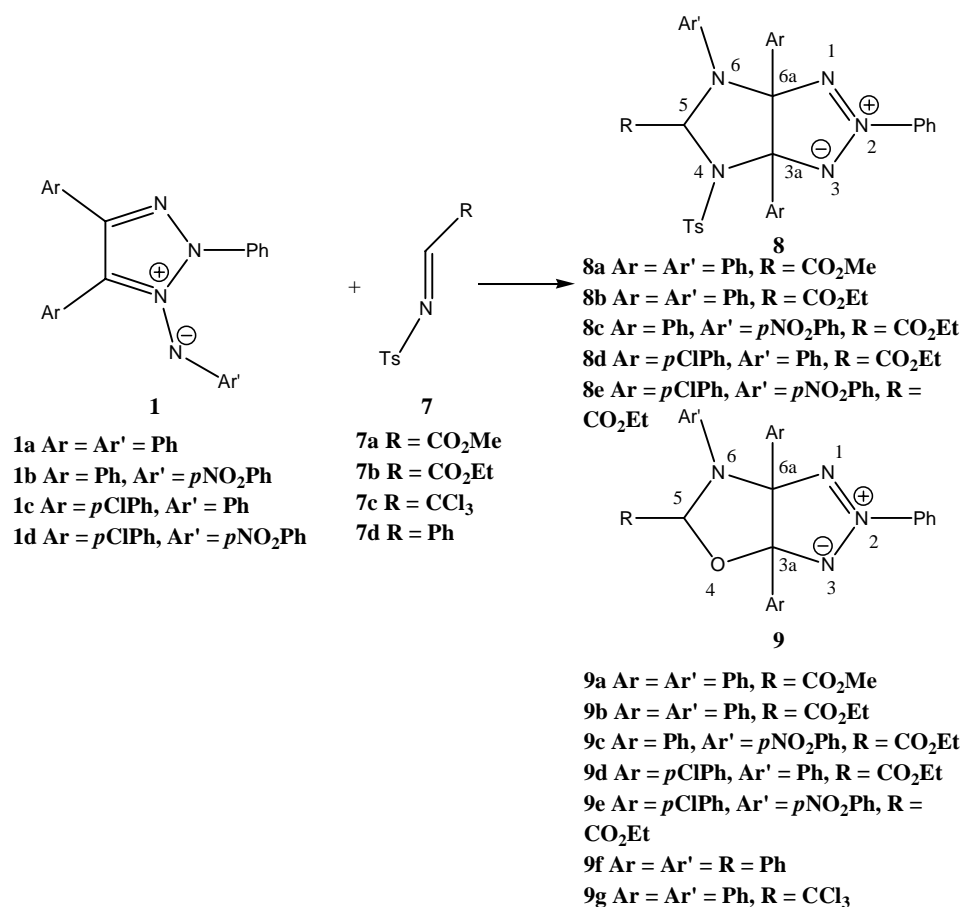
The use of benzyne **5** as a dipolarophile in the cycloaddition with triazolium-1-imide **1** would provide a degree of unsaturation between C-4a and C-8a in the cycloadduct **3** (Scheme 2). Subsequent photochemical induced ring opening would produce a 1,2,3,5-tetrazocine **4** with a C-5a-C-9a double bond, but attack by N-2 on a closed aromatic sextet of electrons would be a highly unfavourable process.

In situ formation of benzyne through diazotisation of anthranilic acid **6** and isoamyl nitrite in 1,2-dimethoxyethane with the 1,3-dipole **1a,b** yielded the cycloadducts **3a,b**. Reaction conditions were optimised by heating a stirred solution of the 1,3-dipole at the reflux temperature of the solvent, thereby increasing the reactivity of the dipole within the short transitory lifetime of benzyne. Similarly, it was observed that yields were maximised by simultaneous addition of solvent solutions of anthranilic acid and isoamyl nitrite every five minutes in 2cm³ aliquots.

Yields of the cycloadduct were increased by introducing a *para* nitro-group on the phenyl ring of the nitrogen terminus of the 1,3-dipole.

trichloroimine **7c** also failed to give the required adduct. However both of the N-sulfonyl imino acetic acid esters **7a,b** successfully added to the triazolium-1-imide **1a-d** to give the novel imidazo-1,2,3-triazoles **8a-e** with a saturated C-5 position (Scheme 3). The success of the addition of the imino acetic acid esters is thought to be due to favourable secondary orbital interactions in the transition state, due to the conjugation of the π -system.

In all cases, oxazolo-1,2,3-triazoles **9a-g** were isolated from the reaction mixtures. These were obtained by the hydrolysis of the N-sulfonyl imines and subsequent cycloaddition of the resulting aldehydes to the triazolium-1-imides. The use of dry solvents in inert atmosphere reduced the yield of the oxazolo-1,2,3-triazoles, but did not improve the yields of the imidazo-1,2,3-triazoles. Cycloadducts of this type were previously synthesised by the cycloaddition of aldehydes with triazolium-1-imides.⁹ Compounds **9a-e**, and **9g** are new derivatives of this ring system.



Scheme 3. 1,3-Dipolar cycladdition of triazolium-1-imides with N-sulfonyl imines, giving novel imidazo-1,2,3-triazoles. Oxazolo-1,2,3-triazoles were identified as side-products of this reaction.

Table 1. Yields and melting points of the novel imidazo-1,2,3-triazoles and oxazolo-1,2,3-triazoles

	Ar	Ar'	R	Yield	M.P. °C
8a	Ph	Ph	CO ₂ Me	15%	197-198
8b	Ph	Ph	CO ₂ Et	26%	206-208
8c	Ph	<i>p</i> NO ₂ Ph	CO ₂ Et	18%	243-244
8d	<i>p</i> ClPh	Ph	CO ₂ Et	10%	228-230
8e	<i>p</i> ClPh	<i>p</i> NO ₂ Ph	CO ₂ Et	20%	168-170
9a	Ph	Ph	CO ₂ Me	22%	220
9b	Ph	Ph	CO ₂ Et	25%	154-156
9c	Ph	<i>p</i> NO ₂ Ph	CO ₂ Et	30%	179-180
9d	<i>p</i> ClPh	Ph	CO ₂ Et	21%	181-182
9e	<i>p</i> ClPh	<i>p</i> NO ₂ Ph	CO ₂ Et	26%	178-180
9f	Ph	Ph	Ph	50%	171-173
9g	Ph	Ph	CCl ₃	46%	163-164

Experimental Section

General Procedures. Infrared spectra were measured on a Perkin-Elmer System 2000 FT-IR. NMR spectra were recorded on a Bruker 400MHz spectrometer. Melting points were recorded on a Griffin apparatus and are uncorrected. Microanalytical data was provided by the Chemistry Department in University College, Dublin. The synthesis of all dipoles^{2,10} and dipolarophiles¹¹ was carried out as described previously.

The following is a typical procedure for the 1,3-dipolar cycloaddition using benzyne as the dipolarophile:

2,3a,4,8b-Tetraphenyl-3,3a,4,6a-tetrahydro-[1,2,3]-triazolo[4,5-b]indole (3a)

1g of the dipole was added to 30cm³ of dimethoxyethane and the solution heated to reflux temperature. 5cm³ of isoamyl nitrite was added to a conical flask containing 15cm³ of dimethoxyethane. Similarly a 20cm³ solution of 3.5g of anthranilic acid in dimethoxyethane was made up. 2cm³ of each solution was added simultaneously to the reaction through the condenser every 5 minutes. When this was complete the reaction was further heated under vigorous stirring for 25 minutes. Excess solvent and isoamyl nitrite were removed under reduced pressure and the remaining oil adsorbed onto 10g of silica. The isolation of the cycloadduct was achieved by flash chromatography. (Pet.ether (60-80) 80%:diethyl ether 20%) to give 3a in 50% yield as a yellow solid. M.p. 142 °C

IR(KBr) (cm⁻¹): 1600, 1588, 1499, 761, 774, 754.

$^1\text{H}(\text{CDCl}_3)$ (ppm): 6.81-6.93 (4H,m), 6.94-7.07 (8H,m), 7.11 (1H,d), 7.15-7.28 (4H,m), 7.44-7.59(5H,m), 8.34(2H,d).

$^{13}\text{C}(\text{CDCl}_3)$ (ppm): 91.40, 105.42, 108.92, 125.42, 123.31, 123.97, 124.05, 127.51, 127.58, 127.80, 127.87, 128.34, 129.94, 129.20, 129.35, 129.64, 131.01, 132.05, 137.99, 139.24, 141.12, 141.56, 150.03.

Microanalysis, found (theory): C 82.56 (82.73), H 4.98 (5.20), N 12.12 (12.05)

4-(4-Nitrophenyl),2,3a,8b-triphenyl-3,3a,4,6a-tetrahydro[1,2,3]-triazolo[4,5-b]indole (3b).

The isolation of the cycloadduct was achieved by flash chromatography. (Pet.ether (80:20) 80%: ether 20%) to give 3b in 70% yield as a yellow solid. M.p. 158 °C

IR(KBr) (cm^{-1}): 1585, 1480, 1468, 1324, 762, 747, .685.

$^1\text{H}(\text{CDCl}_3)$ (ppm):6.84-7.21(10H,m),7.27-7.36(2H,m),7.42-7.68(7H,m),8.08(2H,m), 8.32(2H,d)

$^{13}\text{C}(\text{CDCl}_3)$ (ppm): 120.71, 122.80 ,123.31, 125.25, 127.81, 127.93, 128.07, 128.25, 128.31, 128.38, 128.83, 129.62, 129.83, 132.21, 132.52, 136.94, 138.09, 140.78, 142.01, 147.20, 147.41.

Microanalysis, found (theory): C 75.61 (75.42), H 4.33 (4.54), N 13.51 (13.74)

The following is a typical procedure for the 1,3-dipolar cycloaddition using N-sulfonyl imines as the dipolarophile:

2,3a,6,6a-Tetraphenyl-4-tosyl-5-methylcarbonyl-3,3a,4,5,6,6a-hexahydroimidazo-[4,5-d]-1,2,3-triazole (8a)

1,2-bis(phenylazo)stilbene (0.5g, 0.0013mol) and N-*p*-toluenesulfonyl-2-acetic acid methyl ester (0.35g, 0.0015mol) were stirred under reflux in 25cm³ sodium dried benzene for 24 hours. The hot solution was filtered and the filtrate evaporated to dryness. The residue was purified on a silica gel column (mobile phase, 5:1 pet. ether 40-60: ethyl acetate) yielding 123mg (0.195mmol, 15%) of a yellow solid. M.p. 197-198°C

$^1\text{H}(\text{CDCl}_3)$ (ppm): 1.49 (3H, s, CH₃), 3.47 (3H, s, OCH₃), 5.22 (1H, s, C5-H), 6.80-6.84 (5H, m), 6.96, (1H, t, J=7.2Hz), 7.04, (2H, d, J=8.4Hz), 7.12, (2H, t, J=8.4Hz), 7.23, (3H, d, J=8.0Hz), 7.55-7.59 (6H, m), 7.65, (1H, d, J=7.2Hz), 7.98, (2H, d, J=8.4Hz), 8.45, (2H, d, J=8.0Hz) (all aromatic H).

$^{13}\text{C}(\text{CDCl}_3)$ (ppm): 21.60 (CH₃), 53.00 (OCH₃), 76.70 (C5), 97.87, 97.92 (C3a, C6a), 122.87, 124.24, 125.52, 127.30, 127.65, 127.78, 128.52, 129.03, 129.29, 129.69, 132.81, 136.02, 144.45 (all aromatic C), 164.37 (C=O).

2,3a,6,6a-Tetraphenyl-4-tosyl-5-ethylcarbonyl-3,3a,4,5,6,6a-hexahydroimidazo[4,5-d]-1,2,3-triazole (8b). 26% yield of a yellow solid. M.p. 206-208°CIR (KBr) (cm⁻¹): 1745, 1597, 1505, 1449, 1306, 1263, 1168, 1090, 839, 750, 690.¹H (DMSO-d₆) (ppm): 1.39 (3H, t, J=7.2Hz, OCH₂CH₃), 2.20 (3H, s, CH₃), 4.39-4.43 (2H, m, OCH₂CH₃), 5.21 (1H, s, C5-H), 6.90 (1H, t, J=7.2Hz), 6.98-7.10 (10H, m), 7.13-7.17 (4H, m), 7.45 (2H, d, J=4.8Hz), 7.61 (2H, t, 7.6Hz), 7.3 (1H, t, J=7.6Hz), 7.79 (2H, d, J=8.0Hz), 8.01 (2H, d, J=7.6Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 14.24 (CH₃), 21.31 (OCH₂CH₃), 62.56 (OCH₂CH₃), 75.82 (C5), 100.35, 102.27 (C3a, C6a), 120.56, 122.64, 122.76, 127.29, 127.54, 127.79, 128.03, 128.47, 128.55, 129.14, 129.67, 129.74, 132.88, 135.77, 136.02, 138.09, 139.24, 141.13, 144.27 (all aromatic C), 171.02 (C=O).

Microanalysis, found, (theory): C 69.79 (69.03), H 5.30 (5.17), N 11.16 (10.88)

2,3a,6a-Triphenyl-6-(4-nitrophenyl)-4-tosyl-5-ethylcarbonyl-3,3a,4,5,6,6a**hexahydroimidazo[4,5-d]-1,2,3-triazole (8c).** 18% yield of an orange solid. M.p. 243-244°CIR (KBr) (cm⁻¹): 1739, 1597, 1472, 1450, 1540, 1310, 1175, 859.¹H (DMSO-d₆) (ppm): 1.45 (3H, t, J=7.2Hz, OCH₂CH₃), 1.99 (1H, s, CH₃), 4.48 (2H, m, OCH₂CH₃), 5.55 (1H, s, C5-H), 6.93-6.97 (3H, m), 7.03-7.07 (2H, m), 7.12 (2H, t, J=4.8Hz), 7.29 (2H, t, J=8.8Hz), 7.61 (2H, t, J=8.4Hz), 7.78 (2H, t, J=8.4Hz), 7.85-7.94 (4H, m), 8.03 (2H, t, J=8.0Hz), 8.14 (2H, d, J=9.2Hz), 8.48 (2H, d, J=8.0Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 14.44 (CH₃), 21.42 (OCH₂CH₃), 60.12 (OCH₂CH₃), 73.15 (C5), 96.65, 97.43 (C3a, C6a), 123.12, 124.39, 124.57, 127.40, 127.63, 127.87, 128.31, 128.41, 128.81, 129.00, 129.70, 130.23, 139.22, 144.45 (all aromatic C), 173.26 (C=O).

Microanalysis, found (theory): C 64.08, (64.51), H 4.51 (4.69), N 12.47 (12.20)

2,6-Diphenyl-3a,6a-di-(4-chlorophenyl)-4-tosyl-5-ethylcarbonyl-3,3a,4,5,6,6a-**hexahydroimidazo[4,5-d]-1,2,3-triazole (8d).** 10% yield of an orange solid. M.p. 228-230°CIR (KBr) (cm⁻¹): 1749, 1598, 1492, 1469, 1168, 1092, 855, 669, 768.¹H (DMSO-d₆) (ppm): 1.37 (3H, t, J=7.2Hz, OCH₂CH₃), 2.19 (3H, s, CH₃), 4.38-4.43 (2H, m, OCH₂CH₃), 5.21 (1H, s, C5-H), 6.93 (1H, t, J=7.2Hz), 7.01 (2H, d, J=7.6Hz), 7.07 (2H, d, J=8.8Hz), 7.12-7.20 (6H, m), 7.23, (2H, d, J=8.8Hz), 7.49 (2H, d, J=6.4Hz), 7.60 (2H, t, J=7.6Hz), 7.74 (1H, t, J=7.6Hz), 7.78 (2H, d, J=8.4Hz), 8.05 (2H, d, J=7.6Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 14.21 (CH₃), 21.31 (OCH₂CH₃), 62.77 (OCH₂CH₃), 75.67 (C5), 99.70, 101.77 (C3a, C6a), 120.67, 122.83, 123.01, 127.58, 128.33, 128.54, 129.31, 129.48, 129.67, 129.84, 133.08, 133.44, 134.98, 135.56, 137.19, 139.08, 140.65, 144.49 (all aromatic C), 171.05 (C=O).

Microanalysis, found (theory): C 62.26 (62.36), H 4.47 (4.38), N 9.80 (9.83)

2-Phenyl-3a,6a-di-(4-chlorophenyl)-6-(4-nitrophenyl)-4-tosyl-5-ethylcarbonyl-3,3a,4,5,6,6a-hexahydroimidazo[4,5-d]-1,2,3-triazole (8e). 20% yield of an orange solid. M.p. 168-170°CIR (KBr) (cm⁻¹): 1763, 1598, 1470, 1509, 1323, 1173, 1115, 1092, 834, 685, 749.

^1H (DMSO- d_6) (ppm): 1.45 (3H, t, $J=7.2\text{Hz}$, OCH_2CH_3), 2.28 (3H, s, CH_3), 4.48-4.51 (2H, m, OCH_2CH_3), 5.57 (1H, s, C5-H), 6.92 (2H, d, $J=9.6\text{Hz}$), 7.05-7.09, (2H, m), 7.21 (3H, d, $J=8.8\text{Hz}$), 7.30-7.35 (5H, m), 7.61 (2H, d, $J=8.0\text{Hz}$), 7.72 (1H, t, $J=7.2\text{Hz}$), 7.91 (2H, d, $J=8.4\text{Hz}$), 8.02-8.06 (4H, m)(all aromatic H).

^{13}C (DMSO- d_6) (ppm): 14.23 (CH_3), 21.37 (OCH_2CH_3), 63.44 (OCH_2CH_3), 73.21 (C5), 100.77, 101.25 (C3a, C6a), 115.96, 123.03, 125.21, 127.64, 128.58, 129.22, 129.41, 129.55, 129.74, 129.98, 133.18, 133.29, 133.84, 134.99, 135.12, 136.87, 139.16, 139.96, 144.95, 146.13 (all aromatic C), 170.78 (C=O).

The following is a typical procedure for the 1,3-dipolar cycloaddition with aldehydes acting as the dipolarophile.

2,3a,5,6,6a-Pentaphenyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9f)

1,2-bis(phenylazo)stilbene (0.4g, 0.001mol) and *N-p*-toluenesulfonyl benzaldimine (0.26g, 0.001mol) were stirred under reflux in sodium-dried benzene for 6 hours. After 6 hours a further 0.026g (0.0001mol, 10% excess) of *N-p*-toluenesulfonyl benzaldimine was added and the mixture allowed to reflux for a further 12 hours. The benzene was removed under vacuum and the residue was recrystallised from ethanol, yielding 0.24g (0.0005mol, 50%) of a yellow solid. M.p. 171-173°C (lit. 174-175°C)⁹

IR (KBr) (cm^{-1}): 1602, 1501, 1450, 763, 691.

^1H (DMSO- d_6) (ppm): 6.28 (1H, s, C5-H), 6.78 (3H, t, $J=4\text{Hz}$), 6.99 (2H, t, $J=8\text{Hz}$), 7.14 (6H, t, $J=8\text{Hz}$), 7.21 (2H, t, $J=8\text{Hz}$), 7.47-7.57 (5H, m), 7.68 (2H, t, $J=8\text{Hz}$), 7.76 (1H, t, $J=8\text{Hz}$), 7.93 (2H, d, $J=8\text{Hz}$), 8.25 (2H, d, $J=8\text{Hz}$), (all aromatic H).

^{13}C (DMSO- d_6) (ppm): 91.25 (C5), 98.45, 98.49 (C3a, C6a), 112.24, 120.53, 121.70, 122.96, 126.95, 127.56, 127.77, 128.29, 129.44, 129.28, 129.86, 129.97, 132.89, 137.19, 138.28, 138.89, 140.33, 143.33 (all aromatic C).

2,3a,6,6a-Tetraphenyl-5-methylcarbonyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9a). 22% yield of a pale yellow solid. M.p. 220°C

IR (KBr) (cm^{-1}): 1753, 1598, 1505, 1449, 752, 698.

^1H (DMSO- d_6) (ppm): 3.97 (3H, s, OCH_3), 5.69 (1H, s, C5-H), 6.61 (2H, d, $J=8.4\text{Hz}$), 6.77 (1H, t, $J=7.2\text{Hz}$), 7.05-7.15 (10H, m), 7.45 (2H, d, $J=6.4\text{Hz}$), 7.64 (2H, t, $J=7.2\text{Hz}$), 7.73 (1H, t, $J=7.2\text{Hz}$), 8.22 (2H, d, $J=7.6\text{Hz}$) (all aromatic H).

^{13}C (DMSO- d_6) (ppm): 53.73 (OCH_3), 86.76 (C5), 97.08, 114.78 (C3a, C6a), 115.76, 119.94, 123.01, 126.89, 127.23, 127.85, 128.35, 128.48, 128.79, 129.07, 129.89, 133.04, 136.02, 137.26, 140.22, 141.34 (all aromatic C), 170.40 (C=O).

Microanalysis, found (theory): C 72.79 (73.09), H 5.17 (5.08), N 11.65 (11.76)

2,3a,6,6a-Tetraphenyl-5-ethylcarbonyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole**(9b)**. 25% yield of a yellow solid. M.p. 154-156°CIR (KBr) (cm⁻¹): 1754, 1600, 1505, 1449, 1232, 1203, 1180, 753, 699.¹H (DMSO-d₆) (ppm): 1.37 (3H, t, J=7.2Hz, OCH₂CH₃), 4.41-4.46 (2H, m OCH₂CH₃), 5.65 (1H, s, C5), 6.29 (2H, d, J=8.0Hz), 6.77 (1H, t, J=7.6Hz), 7.08-7.13 (10H, m), 7.46 (2H, d, J=5.2Hz), 7.64 (2H, t, J=8.0Hz), 7.73 (1H, d, J=7.2Hz), 8.22 (2H, d, J=7.2Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 14.32 (OCH₂CH₃), 62.65 (OCH₂CH₃), 86.96 (C5), 97.11, 114.79 (C3a, C6a), 115.73, 119.91, 123.02, 126.91, 127.25, 127.82, 128.31, 128.47, 128.78, 129.05, 129.89, 133.02, 136.09, 137.25, 140.23, 141.33 (all aromatic C), 169.86 (C=O).

Microanalysis, found (theory): C 73.08 (73.45), H 5.69 (5.34), N 10.74 (11.42)

2,3a,6a-Triphenyl-6-(4-nitrophenyl)--5-ethylcarbonyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9c). 30% yield of a yellow solid. M.p. 179-180°CIR (KBr) (cm⁻¹): 1754, 1597, 1449, 1505, 1385, 1314, 1211, 1160, 1134, 1114, 834, 758, 702.¹H (DMSO-d₆) (ppm): 1.41 (3H, t, J=7.2Hz, OCH₂CH₃), 4.48 (2H, m, OCH₂CH₃), 5.95 (1H, s, C5), 6.73 (2H, d, J=9.2Hz), 7.03-7.15 (9H, m), 7.65 (2H, t, J=8.0Hz), 7.73 (1H, d, J=6.8Hz), 8.05 (2H, d, 9.2Hz), 8.25 (2H, d, J=8.0Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 18.90 (OCH₂CH₃), 63.15 (OCH₂CH₃), 86.34 (C5), 96.91, 114.99 (C3a, C6a), 115.20, 123.13, 125.41, 126.77, 127.12, 128.01, 128.58, 128.93, 129.91, 133.23, 135.29, 135.84, 139.51, 140.10, 146.80 (all aromatic C), 168.90 (C=O).

Microanalysis, found (theory): C 67.00 (67.28), H 4.79 (4.71), N 12.87 (13.08)

2,6-Diphenyl-3a,6a-di-(4-chlorophenyl)-5-ethylcarbonyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9d). 21% yield of a yellow solid. M.p. 181-182°CIR (KBr) (cm⁻¹): 1741, 1598, 1492, 1468, 1305, 1236, 1092, 832, 746, 685.¹H (DMSO-d₆) (ppm): 1.35 (3H, t, J=6.8Hz, OCH₂CH₃), 4.37-4.48 (2H, m, OCH₂CH₃), 5.68 (1H, s, C5), 6.61 (2H, d, J=8.8Hz), 6.80 (1H, t, J=7.2Hz), 7.11-7.16 (4H, m), 7.23-7.26 (4H, m), 7.48 (2H, d, J=7.6Hz), 7.64 (2H, t, J=8.0Hz), 7.73 (1H, t, J=6.8Hz), 8.22 (2H, d, J=7.6Hz) (all aromatic H).¹³C (DMSO-d₆) (ppm): 14.29 (OCH₂CH₃), 62.81 (OCH₂CH₃), 86.97 (C5), 96.73, 114.35 (C3a, C6a), 115.89, 120.28, 123.11, 128.12, 128.58, 128.88, 129.20, 129.87, 133.16, 133.28, 133.71, 135.09, 136.29, 140.12, 140.94 (all aromatic C), 169.83 (C=O).

Microanalysis, found (theory): C 64.35 (64.41), H 4.44 (4.32), N 9.76 (10.01)

2-Phenyl-3a,6a-di-(4-chlorophenyl)-6-(4-nitrophenyl)-5-ethylcarbonyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9e). 26% yield of a yellow solid. M.p. 178-180°CIR (KBr) (cm⁻¹): 1747, 1600, 1466, 1509, 1326, 1173, 1137, 1115, 1094, 752, 690.¹H (DMSO-d₆) (ppm): 1.39 (3H, t, J=6.8Hz, OCH₂CH₃), 4.46-4.50 (2H, m, OCH₂CH₃), 5.98 (1H, s, C5), 6.71 (2H, d, J=9.2Hz), 7.08-7.15 (4H, m), 7.25-7.30 (4H, m), 7.65 (2H, t, J=8.0Hz), 7.74 (1H, t, J=7.2Hz), 8.09 (2H, d, J=9.6Hz), 8.24 (2H, d, J=7.6Hz) (all aromatic H).

^{13}C (DMSO- d_6) (ppm): 14.29 (OCH₂CH₃), 62.79 (OCH₂CH₃), 86.97 (C5), 96.74, 114.36 (C3a, C6a), 115.89, 120.25, 123.12, 128.11, 128.58, 128.89, 129.19, 129.85, 133.14, 133.27, 133.70, 135.11, 136.30, 140.13, 140.95 (all aromatic C), 169.83 (C=O).

Microanalysis, found (theory): C 59.72 (59.60), H 4.05 (3.84), N 11.12 (11.59)

2,3a,6,6a-Tetraphenyl-5-trichloromethyl-3,3a,5,6-tetrahydro-oxazolo-[5,4-d]-1,2,3-triazole (9g). 46% yield of an off-white solid. M.p. 163-164°C

IR (KBr) (cm⁻¹): 1589, 1487, 1461, 767, 697.

^1H (DMSO- d_6) (ppm): 6.28 (1H, s, C5-H), 7.05-7.28 (13H, m), 7.50 (2H, d, J=8Hz), 7.68 (2H, d, J=8Hz), 7.76 (1H, t, J=8Hz), 8.24 (2H, d, J=8Hz), (all aromatic H).

^{13}C (DMSO- d_6) (ppm): 97.15 (C5), 102.04, 102.30 (C3a, C6a), 112.50, 124.09, 127.87, 128.63, 128.77, 129.32, 129.55, 130.11, 130.74, 133.86, 137.87, 138.74, 141.35, 144.28 (all aromatic C).

Microanalysis found (theory): C 62.58 (62.76), H 3.93 (3.95), N 10.34 (10.46)

Acknowledgments

M. Sheridan and C. Healy acknowledge Irish government funding.

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