[4+2] CYCLOADDITION REACTIONS OF NEUTRAL 2-AZADIENES WITH ELECTRON-DEFICIENT DIENOPHILES

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Abstract- A method for the preparation of functionalized tetrahydropyridine and triazine derivatives is described, based on aza Diels-Alder reaction of neutral 2-aza-1,3-dienes with electron-poor dienophiles as tetracyanoethylene and N-phenyl-1,2,4-triazoline-3,5-dione.

INTRODUCTION

The Diels-Alder reaction has both enabled and shaped the art and science of synthesis in recent years and 2-azabutadiene systems have proved to be efficient heterodiienes in Aza Diels-Alder processes.1,2 Most 2-azadienes studied are substituted with electron donating groups and are excellent reagents in normal Diels-Alder reactions.1,2b-e,3 Among them, neutral azadienes have been used as heterodiienes, not only in inverse-electron demand Diels-Alder reactions with electron-rich dienophiles4 but also in normal Diels-Alder reactions with electron-poor dienophiles1c,f and with heterodiienes5a for the preparation of nitrogen containing heterocycles. These experimental results are corroborated by theoretical studies.5b The presence or absence of substituents especially in 3-position seems to play an important role in the reactivity of 2-azadienes.6

Given the above, we have been involved in the synthesis of electron-poor azadienes derived from aminophosphorus derivatives7 and β-amino esters8 as well as of neutral azadienes with electron-rich olefins and carbonyl compounds9 and in the preparation of nitrogen containing heterocycles.10 As a continuation of our work in the cycloaddition chemistry of neutral 2-azadienes,9 here we aim to explore whether azadienes with aromatic substituents could react with electron-deficient dienophiles such as tetracyanoethylene (TCNE) and 4-phenyl-1,2,4-triazolin-3,5-dione (4-PTAD).
RESULTS AND DISCUSSION

Aza Diels-Alder Reaction of 2-Azadienes (1) with Tetracyanoethylene (2). We first investigated the Diels-Alder reaction of 1E-2-azadiene (1a) (R¹=Ph, R²=2-furyl), easily prepared by aza-Wittig treatment of N-vinyl phosphazenes and aldehydes,9c with tetracyanoethylene (TCNE) (2) as electron-deficient alkene in CHCl₃ or toluene at room temperature, leading to the formation of only the polysubstituted tetrahydropyridine (3a) with substituents R¹ and Ph in anti configuration (Scheme 1, Table 1, Entry 1), in a stereoselective fashion. Compound (3a) was characterized on the basis of its spectroscopic data. Thus, the ¹³C NMR spectrum for compound (3a) showed absorptions for the corresponding quaternary carbons substituted with two nitrile groups. In order to study the stereochemistry of the process, azadiene (1b) containing phenyl substituents (R¹=R²=Ph) isolated as a mixture of E- and Z-imine isomers (1E/1Z=70/30),9c was used affording 3b as a mixture of isomeric tetrahydropyridines (3b₁) and (3b₂) in similar proportion to those presented in the precursor azadiene (1b) (Scheme 1, Table 1, Entry 2).

![Scheme 1](image)

The relative configuration of hydrogens at C-3 and C-6 in both isomers was clarified by NOE difference experiments, which confirmed the proposed structure as no interaction was observed between hydrogens...
at C-3 and C-6 in \textit{trans} configuration in compound (3\textsubscript{b1}) of higher abundance, and as a significant integral enhancement was seen between protons at C-3 and C-6 in \textit{cis} configuration in the compound (3\textsubscript{b2}) obtained in lower proportion (Figure 1). These results suggest that the formation of tetrahydropyridine derivatives (3) could be explained by [4+2] cycloaddition of the azadienes (1) and tetrasubstituted alkene (2). However, we were unable to obtain pure samples of compounds (3) by crystallization or by chromatographic purification on silica gel, given that when the purification of compounds (3) was attempted, tautomeric tetrahydropyridines (4) (Scheme 1, Table 1, Entries 3, 4) were isolated instead.

\begin{table}[h]
\centering
\caption{Diels-Alder adducts (3) and (4) obtained.}
\begin{tabular}{cccccccc}
\hline
Entry & Compound & R\textsuperscript{1} & R\textsuperscript{2} & T(°C) & time (h) & yield(%) & mp [°C]\textsuperscript{b} \\
\hline
1 & 3a & phenyl & 2-furyl & 25 & 0.5 & 93 & 127-128 \\
2 & 3b & phenyl & phenyl & 25 & 0.5 & 89 & -c \\
3 & 4a & phenyl & 2-furyl & - & - & 73\textsuperscript{a} & 130-131 \\
4 & 4b & phenyl & phenyl & - & - & 75\textsuperscript{a} & 154-155 \\
\hline
\end{tabular}
\textsuperscript{a} Purified by chromatography. \textsuperscript{b} After recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/Hexane. \textsuperscript{c} Evaporation of solvent under reduced pressure and crystallization in hexanes gave a mixture of 3\textsubscript{b1} and 3\textsubscript{b2} (70/30) as a white solid
\end{table}

Next, the effect of absence of substituents in position 3 of the heterodiene was explored. No cycloaddition was observed when azadiene (5a) (R\textsuperscript{1}= p-NO\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}, 3E/3Z = 40/60) reacted with tetracyanoethylene

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{Scheme2}
\caption{Scheme 2}
\end{scheme}
at room temperature and over a long period (10 days), recovering the starting reagents, while in refluxing toluene a very complex reaction mixture was obtained, in a similar way to that reported for simple heterodienes.\textsuperscript{11} Taking into account that Lewis Acids can activate Diels-Alder reactions,\textsuperscript{8,12} we attempted the process in the presence of ethylaluminium dichloride (EtAlCl\textsubscript{2}). However, the treatment of azadiene (5a)(120 h, room temperature) with this Lewis Acid (EtAlCl\textsubscript{2}) gave pyridine (6) (Scheme 2, 63\% yield). The formation of compound (6) can be explained by a [4+2] cycloaddition in which one molecule of 2-azadiene (5a) acts as the dienophile and the other as heterodiene to afford the dimeric tetrahydropyridine (7), which then loses a molecule of imine followed by aromatization, in a similar way to the dimerization of other neutral azadienes, previously observed by us\textsuperscript{9a,b} and others.\textsuperscript{2a,11,13}

**Aza Diels-Alder Reaction of 2-Azadienes (1) and (5) with N-phenyl-1,2,4-triazoline-3,5-dione (8).** The Diels-Alder methodology for the preparation of pyridine derivatives was further extended to a typical electron-poor dienophile such as N-phenyl-1,2,4-triazoline-3,5-dione (PTAD) (8). The reaction of heterodienes containing aromatic and heteroaromatic substituents (1a) (R\textsubscript{1}=Ph, R\textsubscript{2}=2-furyl, 1E) and 1c (R\textsubscript{1}=3-pyridyl, R\textsubscript{2}=2-thienyl, 1E), with the azodienophile (8) in mild conditions gave the corresponding Diels-Alder cycloadducts (9a,c) (Scheme 3, Table 2, Entries 1, 2) in a stereoselective fashion.

![Scheme 3](image)

**Table 2:** Diels-Alder adducts (9) and (10) obtained.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>R\textsubscript{1}</th>
<th>R\textsubscript{2}</th>
<th>T(°C)</th>
<th>time (h)</th>
<th>yield(%)</th>
<th>mp [°C]\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9a</td>
<td>phenyl</td>
<td>2-furyl</td>
<td>25</td>
<td>1</td>
<td>69a</td>
<td>185-186</td>
</tr>
<tr>
<td>2</td>
<td>9c</td>
<td>3-pyridyl</td>
<td>2-thienyl</td>
<td>25</td>
<td>1</td>
<td>70a</td>
<td>147-149</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>p-NO\textsubscript{2}-Ph</td>
<td>---</td>
<td>110</td>
<td>25</td>
<td>70a</td>
<td>oil</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Purified by chromatography. \textsuperscript{b} After recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/Hexane.
The compounds were characterized by their NMR spectral data, where $^1$H NMR spectrum of 9a showed two singlets at 6.29 and 7.06 ppm corresponding to hydrogens at 3 and 6 positions in bicyclic derivative respectively. The structure was finally determined by X-Ray study of 9a (Figure 2), confirming the stereochemistry proposed. The process could be explained through a [4+2] cycloaddition reaction, which is stereoselective and yields only one stereoisomer.

![Figure 2. ORTEP view of compound (9a)](image)

However, when 2-azadiene (5a) ($R^1= p$-NO$_2$-C$_6$H$_4$) with no substituent at C-3 position (Scheme 4) was used, very hard reactions conditions were necessary and in a sealed tube at refluxing toluene for 25 h, bicyclic product (10) was obtained directly (Scheme 4, Table 2, Entry 3). The formation of this compound (10) could be explained by [4+2] cycloaddition reaction followed by loss of an hydrogen molecule.

![Scheme 4.](image)

In summary, electronically neutral 2-aza-1,3-dienes (1) and (5) with aromatic and heteroaromatic substituents, are a class of heterodienes of great interest, owing to their remarkable aza Diels-Alder reactivity. With electron-deficient dienophiles such as tetracyanoethylene (TCNE) and
N-phenyl-1,2,4-triazoline-3,5-dione (PTAD) cycloadducts (3, 4, 9, 10) \textit{(normal} Diels-Alder reaction\textit{)} can be obtained while the presence of a Lewis acid (EtAlCl\textsubscript{2}) catalyzes the dimerization of azadiene (5a), in which one molecule acts as electron-rich dienophile and the other as heterodiene \textit{(inverse} electron demand Diels-Alder reaction\textit{)} to give substituted pyridine (6). Pyridine ring systems have received considerable attention not only for their widespread occurrence in nature\textsuperscript{15} but also for their remarkable versatility in preparative organic synthesis\textsuperscript{15} and in medicinal chemistry.\textsuperscript{16} In addition, the furan substituent can be considered as a synthetic equivalent of carboxylic acid. Therefore, through the strategies reported in this paper new access to polysubstituted pyridines can be designed.

**EXPERIMENTAL**

**General.** All melting points are uncorrected. Analytical TLC was performed on 0.25 mm silica gel plates. Visualization was accomplished by \textit{UV} light and iodine. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: CH\textsubscript{2}Cl\textsubscript{2} (P\textsubscript{2}O\textsubscript{5}); \textit{n-}hexane and ether (sodium benzophenone ketyl); ethyl acetate (K\textsubscript{2}CO\textsubscript{3}). All solvents used in reactions were freshly distilled from appropriate drying agents before use: CHCl\textsubscript{3} (P\textsubscript{2}O\textsubscript{5}); Toluene (CaH\textsubscript{2}); Dioxane (Na, benzophenone). All other reagents were recrystallized or distilled as necessary. Column (flash) chromatography was carried out on silica gel (70-230 mesh). MS (EI) were obtained with a ionization voltage of 70 eV. Data are reported in the form \textit{m/z} (intensity relative to base = 100). IR were taken as neat oils in NaCl, or as solids in KBr. Peaks are reported in cm\textsuperscript{-1}. \textit{H} NMR and \textit{C} NMR spectra were recorded at 300 and 75 MHz, respectively, using tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in CDCl\textsubscript{3} or D\textsubscript{2}O solutions for \textit{H} NMR, or chloroform (77.0 ppm) as an internal reference in CDCl\textsubscript{3} or D\textsubscript{2}O solutions for \textit{C} NMR. \textit{P} NMR spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Chemical shifts are given in ppm (\textit{\delta}). Coupling constants, \textit{J}, are reported in hertz. All reactions were performed in oven (125 °C) or flame-dried glassware under an inert atmosphere of dry N\textsubscript{2}. Azadienes (1) were prepared as described in the literature.\textsuperscript{9c,d}

**General procedure for preparation of azadienes (5).** Aldehyde (2 mmol) was added to a 0-10 °C solution of phosphazene\textsuperscript{17} (2 mmol) in CHCl\textsubscript{3} under N\textsubscript{2}. Then, the mixture was stirred at rt until TLC indicated the disappearance of phosphazene.

**4-Phenyl-1-(4-nitrophenyl)-2-azabuta-1,3-diene (5a)** The general procedure was followed using 4-phenyl-1,1,1-triphenyl-2-aza-1\textlambda\textsubscript{5}-phosphabuta-1,3-diene (0.94 g, 2 mmol) and 4-nitrobenzaldehyde (0.30 g, 2 mmol) for 5 h. Evaporation of solvent under reduced pressure and chromatographic purification on neutral aluminium oxide (1/10, ethyl acetate/hexane) gave 0.32 g (63.5 %) of a 40/60 diastereomeric
mixture of 1E/3Z, 1E/3E of 5a as an orange solid, mp 138-139 °C. IR (KBr) ν 1513, 1348 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.23 (d, 1H, J = 8.3 Hz) for 3Z, 6.97 (d, 1H, J = 8.3 Hz) for 3Z, 7.07 (d, 1H, J = 13 Hz) for 3E, 7.20-7.69 (m, 11H), 7.92 (d, 2H, J = 8.8 Hz) for 3Z, 7.94 (d, 2H, J = 8.8 Hz) for 3E, 8.23 (d, 2H, J = 8.8 Hz) for 3E, 8.25 (d, 2H, J = 8.8 Hz) for 3Z, 8.29 (s, 1H) for 3Z, 8.34 (s, 1H) for 3Z; ¹³C NMR (75 MHz, CDCl₃) δ 124.4-130.9 (m, 11H), 134.2 (for 3E), 135.6, 140.3 (for 3Z), 141.0 (for 3E), 141.8, 142.4, 151.9, 157.9 (for 3E), 159.2 (for 3Z); MS (EI) m/z 252 (M⁺, 85). Anal. Calcd for C₁₅H₁₂N₂O₂: C, 71.42; H, 4.79; N, 11.10. Found: C, 71.40; H, 4.83; N, 11.11.

1-(4-Nitrophenyl)-2-azabuta-1,3-diene (5b) The general procedure was followed using 1,1,1-triphenyl-2-aza-1λ₅-phosphabuta-1,3-diene (0.76 g, 2 mmol) and 4-nitrobenzaldehyde (0.30 g, 2 mmol) for 2 h. The reaction product is unstable to distillation or chromatography and therefore was not isolated and used for the following reactions. ¹H NMR (300 MHz, CDCl₃) of crude reaction mixture (5a+Ph₃PO) δ 5.21 (d, 1H, J = 7.3 Hz), 5.64 (d, 1H, J = 14.6 Hz), 6.76 (dd, 1H, J = 7.3 Hz, J = 14.6 Hz), 7.59-7.89 (m, 15H), 7.91 (d, 2H, J = 8.8 Hz), 8.21 (d, 2H, J = 8.8 Hz), 8.26 (s, 1H).

General procedure for Aza Diels-Alder reactions. Dienophile (5 mmol) was added to a 0-10 °C solution of azadiene (1) or (5) (5 mmol) in CHCl₃ or toluene (15 mL) under N₂. Then, the mixture was stirred at adequate temperature until TLC indicated the disappearance of azadiene.

6-Furan-2-yl-2,5-diphenyl-2,5-dihydropyridine-3,3,4,4-tetracarbonitrile (3a). The general procedure was followed using 1,4-diphenyl-3-furan-2-yl-2-azabuta-1,3-diene (1a) (1.36 g, 5 mmol) and tetracyanoethylene (2) (0.64 g, 5 mmol) in toluene at rt for 0.5 h. Evaporation of solvent under reduced pressure and crystallization of crude reaction in hexane gave 1.86 g (93 %) of 3a as a green solid, mp 127-128 °C. IR (KBr) ν 2203, 1633 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.01 (s, 1H), 5.78 (s, 1H), 6.33 (t, 1H, J = 1.7 Hz), 6.79 (d, 1H, J = 3.6 Hz), 7.13-7.63 (m, 11H); ¹³C NMR (75 MHz, CDCl₃) δ 45.3, 64.2, 107.7, 109.0, 111.0, 111.3, 112.2, 115.3, 125.1-152.9 (m); MS (CI) m/z 402 (M⁺⁺, 100). Anal. Calcd for C₂₅H₁₅N₅O: C, 74.80; H, 3.77; N, 17.45. Found: C, 75.05; H, 4.31; N, 17.16.

6-Furan-2-yl-2,5-diphenyl-1,2-dihydropyridine-3,3,4,4-tetracarbonitrile (4a) After column chromatography (10/1, hexane/ethyl acetate) of compound (3a), compound (4a) was obtained as a green solid, 1.35 g (73 %), mp 130-131 °C (CH₂Cl₂/Hexane). IR (KBr) ν 3400, 1628, 1466 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.56 (s, 1H), 5.08 (s, 1H), 5.25 (d, 1H, J = 3.6 Hz), 6.17 (dd, 1H, J = 3.6 Hz, J = 1.5 Hz), 7.19-7.72 (m, 13H); ¹³C NMR (75 MHz, CDCl₃) δ 59.7, 108.9, 109.9, 110.0, 111.6, 112.7, 114.1, 122.1-152.1 (m); MS (EI) m/z 401 (M⁺, 13). Anal. Calcd for C₂₅H₁₅N₅O: C, 74.80; H, 3.77; N, 17.45. Found: C, 74.85; H, 3.79; N, 17.44.

trans-Triphenyl-2,5-dihydropyridine-3,3,4,4-tetracarbonitrile (3b₁), cis-2,3,6-triphenyl-2,5-dihydropyridine-3,3,4,4-tetracarbonitrile (3b₂) and 2,5,6-triphenyl-1,2-dihydropyridine-3,3,4,4-tetra-
carbonitrile (4b) The general procedure was followed using a 70/30 diastereomeric mixture of 1E/1Z isomers of 3Z-1,3,4-triphenyl-2-azabuta-1,3-diene (1b) (1.41 g) and tetracyanoethylene (2) (0.64 g) in CHCl₃ for 0.5 h. Evaporation of solvent under reduced pressure and crystallization in hexanes gave 1.83 g (89 %) of a mixture of 3b₁ and 3b₂ compounds (70/30) as a white solid, mp 165-168 °C (CH₂Cl₂/Hexane). IR (KBr) ν 2245, 1640 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.02 (d, 1H, J = 3.2 Hz) for 3b₂, 5.12 (d, 1H, J = 1.8 Hz) for 3b₁, 5.78 (d, 1H, J = 3.2 Hz) for 3b₂, 5.84 (d, 1H, J = 1.8 Hz) for 3b₁, 7.14-7.78 (m, 30H); ¹³C NMR (75 MHz, CDCl₃) δ 45.9 for 3b₁, 48.5 for 3b₂, 63.6 for 3b₂, 64.6 for 3b₁, 107.9 for 3b₁, 108.4 for 3b₂, 109.3 for 3b₁, 109.5 for 3b₂, 110.0 for 3b₂, 110.4 for 3b₂, 111.3 for 3b₁, 111.5 for 3b₁, 125.1-135.6 (m), 161.4 for 3b₁, 164.1 for 3b₂; MS (Cl) m/z 412 (M⁺+1, 100). After column chromatography (10/1, hexane/ethyl acetate) of compound (3b), compound (4b) was obtained as a pink solid, 1.37 g (75 %), mp 154-155 °C (CH₂Cl₂/Hexane). IR (KBr) ν 2243, 1640 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.60 (s, 1H), 5.21 (s, 1H), 7.20-7.77 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 59.7, 108.7, 109.7, 109.1, 111.8, 127.4-135.6 (m), 145.8; MS (Cl) m/z 412 (M⁺+1, 100). Anal. Calcd for C₂₇H₁₇N₅: C, 78.81; H, 4.16; N, 17.02. Found: C, 78.88; H, 4.08; N, 16.96.

2-(4-Nitrophenyl)-3,5-diphenylpyridine (6) The general procedure was followed using a 40/60 diastereomeric mixture of 3Z/3E isomers of 1E-1-(4-nitrophenyl)-4-phenyl-2-azabuta-1,3-diene (5a) (1.25 g) and EtAlCl₂ (0.5 mL, 97%, 5 mmol). After stirring at rt during 120 h, the mixture was neutralized with 6 mL of NaOH (3 N) and stirred at rt for 3 h. Filtration over Al₂O₃, extraction with CH₂Cl₂, dried (MgSO₄) and evaporation of solvent under reduced pressure afforded an oil which was chromatographed on silicagel (10/1, hexane/ethyl acetate) giving 0.22 g (63%) of 6 as a yellow solid, mp 143-144 °C (CH₂Cl₂/Hexane). IR (KBr) ν 1520, 1347 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.14-7.49 (m, 10H), 7.52 (d, 2H, J = 8.8 Hz), 7.90 (d, 1H, J = 2.1 Hz) 8.04 (d, 2H, J = 8.8 Hz), 8.89 (d, 1H, J = 2.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 123.1-138.9 (m), 146.3, 147.0, 147.2, 153.2; MS (EI) m/z 352 (M⁺, 72). Anal. Calcd for C₂₃H₁₆N₂O₂: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.43; H, 4.50; N, 7.98.

7-Furan-2-yl-2,5,8-triphenyl-5,8-dihydro-[1,2,4]-triazolo[1,2-a][1,2,4]triazine-1,3-dione (9a) The general procedure was followed using 1E/3Z-1,4-diphenyl-3-furan-2-yl-2-azabuta-1,3-diene (1a) (1.36 g) and N-phenyl-1,2,4-triazoline-3,5-dione (8) (0.90 g, 5 mmol) in toluene at reflux for 1 h. Evaporation of solvent under reduced pressure and chromatographic separation (5/1, hexane/ethyl acetate) gave 1.54 g (69 %) of 9a as a yellow solid, mp 185-186 °C (CH₂Cl₂/Hexane). IR (KBr) ν 1726 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.23 (s, 1H), 6.40-6.43 (m, 1H), 6.87 (d, 1H, J = 3.5 Hz), 7.12-7.54 (m, 16H); ¹³C NMR (75 MHz, CDCl₃) δ 58.9, 73.3, 112.0, 114.3, 125.1-152.4 (m); MS (EI) m/z 448 (M⁺, 50). Anal. Calcd for C₂₇H₂₀N₄O₃: C, 72.31; H, 4.49; N, 12.49. Found: C, 72.21; H, 4.37; N, 12.41.
2,8-Diphenyl-5-yl-2-thien-2-yl-5,8-dihydro[1,2,4]triazolo[1,2-a][1,2,4]triazine-1,3-dione (9c) The general procedure was followed using 3-thien-2-yl-4-phenyl-1-pyridin-3-yl-2-azabuta-1,3-diene 1c (1.45 g) and N-phenyl-1,2,4-triazoline-3,5-dione (8) (0.90 g, 5 mmol) in toluene at rt for 1 h. Evaporation of solvent under reduced pressure and chromatographic separation (5/1, hexane/ethyl acetate) gave 1.63 g (70 %) of 9c as a white solid, mp 147-149 °C (CH₂Cl₂/Hexane). IR (KBr) ν 1719 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.29 (s, 1H), 6.97-7.00 (m, 1H), 7.06 (s, 1H), 7.13-7.56 (m, 13H), 7.78-7.82 (m, 1H), 8.65 (dd, 1H, J = 4.9 Hz, J = 1.2 Hz), 8.77 (d, 1H, J = 2.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 60.1, 71.2, 123.5-156.5 (m); MS (Cl) m/z 466 (M⁺+1, 100). Anal. Calcd for C₂₆H₁₉N₅O₂S: C, 67.08; H, 4.11; N, 15.04. Found: C, 66.99; H, 4.00; N, 14.96.

2,8-Diphenyl-5-(p-nitrophenyl)[1,2,4]triazolo[1,2-a][1,2,4]triazine-1,3-dione (10) The general procedure was followed using 1-(p-nitro-phenyl)-4-phenyl-2-azabuta-1,3-diene (5a) (1.27 g) and N-phenyl-1,2,4-triazoline-3,5-dione (8) (0.90 g, 1 mmol) in toluene at reflux for 25 h. Evaporation of solvent under reduced pressure and chromatographic separation (15/1, hexane/ethyl ether) gave 0.88 g (70 %) of 10 as an orange oil, Rf = 0.59 (1/2, ethyl acetate/hexane). IR (KBr) ν 1600, 1520 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.18-7.69 (m, 10H), 8.01 (d, 2H, J = 8.8 Hz), 8.26 (d, 2H, J = 8.8 Hz), 8.49 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 120.9-150.9 (m), 157.3; MS (EI) m/z 425 (M⁺, 11). Anal. Calcd for C₂₃H₁₅N₅O₄: C, 64.94; H, 3.55; N, 16.46. Found: C, 64.97; H, 3.50; N, 16.49.

ACKNOWLEDGEMENTS

The present work has been supported by the Universidad del País Vasco (UPV-GC/2002) and by the Dirección General de Investigación Científica of the Ministerio de Ciencia y Tecnología (Madrid DGI-MCYT, BQU2000-0217) and C.A. thanks the Departamento de Educación, Universidades e Investigación of Gobierno Vasco for a Postdoctoral Fellowship.

REFERENCES


14. CCDC-214529 contains the supplementary crystallographic data for this paper. These data can by obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

