The Reaction of Arylidenemalonodinitriles with 1-Arylethylideneaminobenzenes. A New Synthesis of 5'-Amino-1,1':3',1''-terphenyl-2',6'-dicarbonitriles

Piotr Milart* and Janusz Sepiol*

Department of Organic Chemistry, Jagiellonian University, Karasia 3, 30000 Krakow, Poland

Z. Naturforsch. 41b, 371 — 376 (1986); received October 3, 1985

Arylidenemalonodinitriles, Schiff Bases, 5'-Amino-1,1':3',1''-terphenyl-2',6'-dicarbonitriles

The reaction of arylidenemalonodinitriles with a variety of acetophenone anils leading to 5'-amino-1,1':3',1''-terphenyl-2',6'-dicarbonitriles has been investigated. The mechanism of the exchange reaction between arylidenemalonodinitriles and 1-arylethylideneaminobenzenes is proposed.

The reaction of arylidenemalonodinitriles 1 with 1-arylethylideneaminobenzenes 2 gives rise to substituted cyclohexadiene derivatives 3 which then undergo elimination of hydrogen cyanide and afford 3,5-diaryl-2,6-dicyano-aminobenzenes 4. This reaction is a modification of more general dimerization reaction involving ylidenemalonodinitriles synthesized from a variety of ketones. These typical dimers, easily obtained under basic conditions, have found limited applications due to difficult aromatization of a substituted cyclohexadiene system. The structure of “mixed dimers” 3 obtained from ylidenemalonodinitriles 1 and 2 facilitates aromatization of the cyclohexadiene system, and in fact the aromatization in some instances is so spontaneous that only o-aminonitriles 4 are isolated. The reaction of ylidenemalonodinitriles 1 and 2 leading to o-aminonitriles 4 has been investigated by Gewald and Schill [1] and Shararin et al. [2] and has been the subject of a recent review [3].

Recently, we discovered that heating of o-aminonitriles 4 in an autoclave in ethanolic sodium hydroxide solution for several hours caused elimination of both cyano groups from 4 [4]. Aromatic amines 5 were obtained in most cases in excellent yields. The reaction of 1 and 2 leading to 4 although complex from mechanistic point of view, can be carried out in such manner that o-aminonitriles 4 are obtained in a simple step. Thus, 5'-amino-m-terphenyls 5 and certain 3,5-diaryl-aminobenzenes are available by this strategy in essentially two steps from easily accessible synthetic precursors 1 and 2 (Scheme 1). We extended this synthetic approach to the preparation of some polyphenyl systems having m-diarylmethane units [4].

Synthesis of substituted m-terphenyls received recently renewed attention in connection with synthetic routes leading to functionalized spherand systems [5]. Appropriately functionalized m-terphenyls are important building blocks for synthesis of some spherands.

Results and Discussion

Our efficient synthesis of amino-m-terphenyls and 3,5-diaryl-aminobenzenes is connected with convenient preparation of starting o-aminonitriles 4. In an effort to explore further synthetic applications of

Scheme 1.

* Reprint requests and correspondence either to Dr. P. Milart or Dr. J. Sepiol.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0340–5087/86/0300–0371/$ 01.00/0
ylidenemalonodinitriles 1 and 2 we investigated the reaction of arylidenemalonodinitriles 1 with a variety of 1-arylethylideneaminobenzenes 6 (Scheme 2).

1-Arylethylideneaminobenzenes reveal considerable reactivity towards the addition to double bonds in conjugated unsaturated systems. Under conditions of Lewis acid catalysis they form Michael adducts with acrylic acid derivatives. These adducts may undergo cyclization which results in the formation of 2-pyridone derivatives [6].

We have attempted to carry out the base-catalyzed addition of acetophenone anils 6 to arylidenemalonodinitriles 1 assuming that the cyclization of the addition products may lead to N-arylpyridine derivatives 7 (Scheme 2, path a). This reaction was catalyzed by piperidine and was carried out in acetonitrile. Crystalline products were obtained in moderate to good yields. However, their spectral properties were not consistent with the structure of pyridine derivatives 7. Infrared spectra of these products revealed the absorption of the amino group in the 3250–3500 cm⁻¹ region and of the cyano group at 2220 cm⁻¹. The mass spectra of obtained products showed intense molecular ion peaks corresponding to molecular ions of o-aminonitriles 8. The IR spectra of these compounds were identical with infrared spectra of o-aminonitriles 4 which were obtained earlier by an alternative route [4]. Apparently, the reaction of 1 and 6 proceeded along proposed here path b (Scheme 2).

The unexpected course of the reaction between arylidenemalonodinitriles 1 and anils 6 encouraged us to investigate this reaction more systematically. For these purposes we synthesized several ylideneamino-
benzenes 6 having a limited variety of substituents in the aromatic ring of the amine moiety (Table I). The reaction of arylidenemalonodinitrile 1 with ylideneaminobenzenes 6 which were obtained from the same ketone and several derivatives of aniline, gave identical o-aminonitriles 8. In terms of yields of o-aminonitriles 8, the most effective appear to be ylideneaminobenzenes 6 having electron-releasing substituents in the aromatic amine moiety.

The presumed mechanism of the reaction of 1 and 6 is outlined in Scheme 3. We assume that the exchange reaction between 6 and 1 proceeds through the intermediate four-center complex 9a, 9b which collapses to 1-arylethylidenemalonodinitrile 10 and a new Schiff base 11. Newly formed ylideneamalonodinitrile 10 reacts with arylidenemalonodinitrile 1 in the usual manner resulting in the formation of o-aminonitrile 8 (Scheme 4). It was established earlier that the exchange reaction between certain aromatic Schiff bases such as 1-phenylethylideneaminobenzene and benzylidene-(4-methoxy)aminobenzene proceeds via the cyclic four-member intermediate product [7]. Thermally induced [2+2] cycloaddition reaction of tetracyanoethylene with electron rich olefins, also has been investigated [8].

Under these circumstances our conclusions concerning the base catalyzed exchange reaction between 1-arylethylidenemalonodinitriles and ylideneaminobenzenes seems justified.

In an afford to support proposed here mechanism we attempted to isolate compounds 11. However, several attempts to separate 11 from the solutions in acetonitrile using a variety of techniques were unsuccessful. The Schiff bases 11 are either decomposed under reaction conditions or react further to give complex products.

We are currently investigating the scope of this new reaction and its application for the preparation of m-terphenyl and polyphenyl derivatives.

**Experimental**

Melting points were determined in open capillary tubes and are uncorrected. The IR spectra were obtained on a UR-10 (Carl Zeiss, Jena) spectrometer. The mass spectra were obtained on a LKB-9000s instrument at 70 eV ionizing energy. 1-Arylthiolenideaminobenzenes 6 and arylidenemalonodinitriles 1 were prepared by reported in the literature procedures. Their physical and spectral properties were in agreement with the reported data.
Table I. The reaction of arylidene malonodinitriles with 1-arylethylideneaminobenzenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>1-Arylethylideneaminobenzene (6)</th>
<th>Arylidene-malonodinitrile (1)</th>
<th>5'-Amino-1,1':3',1''-terphenyl-4',6'-dicarbonitrile (8)</th>
<th>Yield* [%]</th>
<th>m.p. [°C]</th>
<th>MS [M+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td><img src="image" alt="Structure a" /></td>
<td><img src="image" alt="Structure a" /></td>
<td><img src="image" alt="Structure a" /></td>
<td>38</td>
<td>226</td>
<td>295</td>
</tr>
<tr>
<td>b</td>
<td><img src="image" alt="Structure b" /></td>
<td><img src="image" alt="Structure b" /></td>
<td><img src="image" alt="Structure b" /></td>
<td>43</td>
<td>225</td>
<td>295</td>
</tr>
<tr>
<td>c</td>
<td><img src="image" alt="Structure c" /></td>
<td><img src="image" alt="Structure c" /></td>
<td><img src="image" alt="Structure c" /></td>
<td>57</td>
<td>226</td>
<td>295</td>
</tr>
<tr>
<td>d</td>
<td><img src="image" alt="Structure d" /></td>
<td><img src="image" alt="Structure d" /></td>
<td><img src="image" alt="Structure d" /></td>
<td>69</td>
<td>226</td>
<td>295</td>
</tr>
<tr>
<td>e</td>
<td><img src="image" alt="Structure e" /></td>
<td><img src="image" alt="Structure e" /></td>
<td><img src="image" alt="Structure e" /></td>
<td>32</td>
<td>209</td>
<td>309</td>
</tr>
<tr>
<td>f</td>
<td><img src="image" alt="Structure f" /></td>
<td><img src="image" alt="Structure f" /></td>
<td><img src="image" alt="Structure f" /></td>
<td>41</td>
<td>210</td>
<td>309</td>
</tr>
<tr>
<td>g</td>
<td><img src="image" alt="Structure g" /></td>
<td><img src="image" alt="Structure g" /></td>
<td><img src="image" alt="Structure g" /></td>
<td>52</td>
<td>208</td>
<td>309</td>
</tr>
</tbody>
</table>
Table I (Fortsetzung).

<table>
<thead>
<tr>
<th>Entry</th>
<th>1-Arylethylideneanilines (acetophenone anils)</th>
<th>5'-Amino-1,1',3',3'-terphenyl-4',6'-dicarbonitrile (8)</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>m.p.</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>h</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>46</td>
<td>254 (Lit. [2] 250–251)</td>
<td>329</td>
</tr>
<tr>
<td>i</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>58</td>
<td>253 (Lit. [2] 250–251)</td>
<td>329</td>
</tr>
<tr>
<td>j</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>36</td>
<td>209 (Lit. [2] 207)</td>
<td>309</td>
</tr>
<tr>
<td>k</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>53</td>
<td>252 (Lit. [2] 250–251)</td>
<td>329</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yield of isolated and purified product.

Arylidemalonodinitriles 1; general procedure

Equimolecular amounts of the malonodinitrile (6.6 g, 0.1 mol) and the appropriate aldehyde are refluxed in ethanol (50 ml) with a few drops of piperidine for 10 min. After cooling the precipitate is filtered off and recrystallized from ethanol. Benzylidenemalonodinitrile (la); yield 95%; m.p. 86 °C (Lit. [9] m.p. 86.5–87 °C).

(4-Methyl)benzylidenemalonodinitrile (lj); yield 93%; m.p. 135 °C (Lit. [10] m.p. 134 °C).

(4-Chloro)benzylidenemalonodinitrile (lk); yield 92%; m.p. 162 °C (Lit. [11] m.p. 162–163 °C).

1-Arylethylideneanilines (acetophenone anils) 6; general procedure

A mixture of the appropriate acetophenone (0.1 mol) and aniline derivative (0.12 mol), and aniline/zinc chloride complex (0.5 g) is heated at 150–160 °C for 1 h. In the case of electron-releasing substituents in aniline (–OCH<sub>3</sub> or –N(CH<sub>3</sub>)<sub>2</sub>) the reaction is carried out at 120–130 °C. The products are purified by distillation under reduced pressure or by recrystallization from ethanol.

1-Phenylethylideneaniline (6a); yield 59%; m.p. 42 °C; b.p. 158 °C/8 torr (Lit. [12] m.p. 42 °C; b.p. 171 °C/14 torr).

1-Phenylethylidene-(4'-methyl)aniline (6b); yield 62%; m.p. 30 °C; b.p. 181–185 °C/7 torr (Lit. [12] m.p. 31 °C; b.p. 181–185 °C/7 torr).

1-Phenylethylidene-(4'-methoxy)aniline (6c); yield 79%; m.p. 85 °C (Lit. [12] m.p. 86 °C).

1-Phenylethylidene-(4'-N,N-dimethylamino)aniline (6d); yield 86%; m.p. 94–95 °C (Lit. [13] m.p. 92 °C).

1-(4-Methyl)phenylethylideneaniline (6e); yield 57%; m.p. 47 °C; b.p. 185–190 °C/7 torr (Lit. [12] m.p. 48–50 °C; b.p. 220–240 °C/53 torr).
1-(4-Methyl)phenylethylidene-(4'-methoxy)-aniline (6f); yield 80%; m.p. 79 °C (Lit. [12] m.p. 79–80 °C).

1-(4-Methyl)phenylethylidene-(4'-N,N-dimethylamino)aniline (6g); yield 84%; m.p. 105 °C (Lit. [14] m.p. 104–106 °C).

1-(4-Chloro)phenylethylideneaniline (6h); yield 83%; m.p. 94 °C (Lit. [12] m.p. 94–95 °C).

1-(4-Chloro)phenylethylidene-(4'-methoxy)aniline (6i); yield 82%; m.p. 93 °C (Lit. [12] m.p. 94 °C).

5'-Amino-1,1',3',1''-terphenyl-2',6'-dicarbonitriles (8)

To the solution of the anil 6 (0.01 mol) and the arylidenemalonodinitrile 1 (0.02 mol) in acetonitrile (10 ml) piperidine (0.3 ml) is added. The mixture is stirred and refluxed for 3 h. After cooling the precipitate is filtered off, washed with ethanol and recrystallized from nitromethane. When ethanol or n-butanol are employed as solvents the yields of 8 are significantly lower.