Pergamon

Tetrahedron Vol. 51, No. 1, pp. 235-242, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00937-6

A Non-Obvious Reaction Pathway in the Formation of 2-Aminobenzene-1,3-dicarbonitriles from α,β-Unsaturated Ketones or Aldehydes

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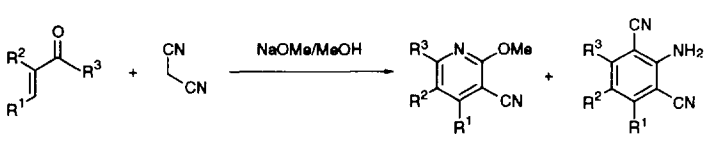
Abstract: Key intermediates demonstrating a non-obvious reaction pathway leading to 2-aminobenzene-1,3-dicarbonitriles from enones have been isolated and characterised in the reaction between (*E*)-4-phenyl-3-butene-2-one and propanedinitrile in a basic hydro-alcoholic medium. (*E*)-4-Phenyl-3-butene-2-one reacts with three molecules of propanedinitrile to give a 6-amino-2-iminobicyclo[2.2.2]-5-octene-1,3,3,5-tetracarbonitrile system which evolves to a substituted cyclohexadiene by elimination of the sodium salt of 1,1,1-tricyanomethane. Further oxidation leads to the final 2-aminobenzene-1,3-dicarbonitrile. The proposed pathway involves more steps and more difficult transformations than previously presented for similar systems. We can not exclude a simpler reaction pathway derived from the double Michael and Knoevenagel adduct of (*E*)-4-phenyl-3-butene-2-one and propanedinitrile, however we have not found any evidence for this simpler process.

INTRODUCTION

Our group recently reported[1,2] that the reaction between propanedinitrile and α,β-unsaturated aldehydes or ketones (these will be abbreviated as enals or enones for simplicity) in boiling sodium methoxide-methanol yields an alkyl or aryl substituted 2-methoxypyridine-3-carbonitrile, **3**. Together with this pyridine system an alkyl or aryl substituted 2-aminobenzene-1,3-dicarbonitrile was also obtained, **4** (Scheme 1). The structure of the later compound was unequivocally established by X-ray analysis.[3] The rate of formation of both compounds varied according to the experimental conditions employed. Upon increasing the amount of propanedinitrile in relation to the carbonyl compound in the reaction medium, the formation of the 2-aminobenzene-1,3-dicarbonitrile was enhanced at the expense of the 2-methoxy-



1 **2** **3** **4**

Scheme 1

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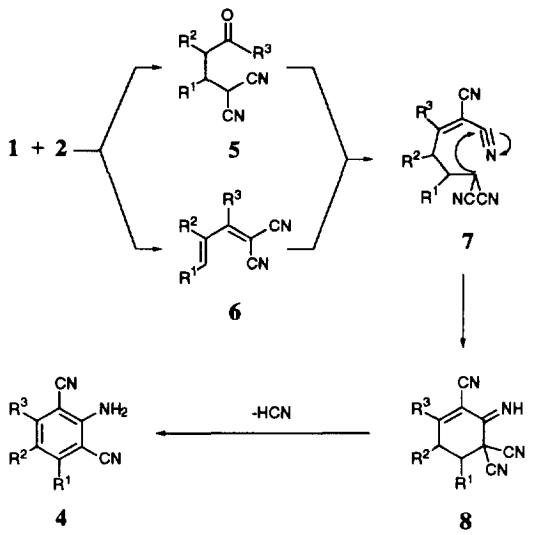
pyridine-3-carbonitrile.[2] **4** was predominantly obtained by using a 2:1 molar ratio between **2** and **1**.

The surprising formation of **4** from enones and enals can be explained by the mechanism depicted in Scheme 2 which would be in agreement with the proposals made by several authors for the formation of **4** by other processes[4] or for the reaction of propanedinitrile and enones with different structural characteristics to the ones used in our group.[5] The reaction starts with Michael addition of **2** to **1** or by Knoevenagel condensation of **2** with **1** yielding **5** or **6** respectively. The reaction of a second molecule of **2** with **5** or **6** leads to **7** which undergoes cyclization to give **8** and HCN elimination to afford the 2-aminobenzene-1,3-dicarbonitrile **4**. In contrast, the systems described in reference 5 can not evolve into 2-aminobenzene-1,3-dicarbonitriles since they present a carbon bearing two alkylic substituents. Its inability to undergo elimination prevents aromatisation in the last step.



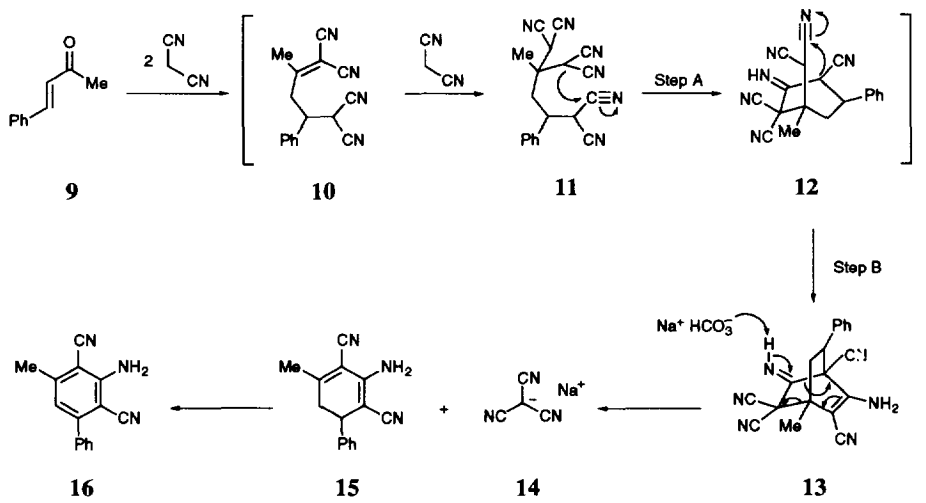
Scheme 2

We have not yet been able to isolate any precursor of **4** for this synthetic pathway which would allow us to confirm the proposed mechanism for the formation of these compounds. This can be attributed to the fact that the reaction is carried out under very drastic conditions (sodium methoxide/methanol at reflux). With the aim of isolating some possible reaction precursors of **4**, it was decided to attempt the reaction between **1** and **2** at room temperature instead of boiling methanol, with a weaker base (sodium bicarbonate in place of sodium methoxide) and in a solvent where the solubility of these type of compounds is lower (water/ethanol).

RESULTS AND DISCUSSION

When (*E*)-4-phenyl-3-butene-2-one, **9**, propanedinitrile and sodium bicarbonate were stirred in ethanol/water at room temperature for 14 h, three new products were isolated from the complex reaction mixture (there was a significant amount of polymeric materials which remained on the top of the column in the chromatographic purification step). Along with the desired 2-aminobenzene-1,3-dicarbonitrile, **16**, and a fraction of (*E*)-4-phenyl-3-butene-2-one that did not react, **9**, two additional products, **13** and **15**, were obtained (Scheme 3).

One of them, **13**, was easily separated from the mixture by filtering. Elemental analyses point to the empirical formula $C_{19}H_{14}N_6$. Mass spectrometry confirmed this by showing the molecular ion at *m/z* 326 (7%). This molecular formula suggests that one molecule of **9** had reacted with three molecules of propanedinitrile and that a molecule of water had been lost in the process. Consequently, it is reasonable to propose that the reaction starts with Michael addition of propanedinitrile followed by Knoevenagel condensation of **2** (or *vice-versa*) with (*E*)-4-phenyl-3-butene-2-one leading to **10**. A third molecule of **2**

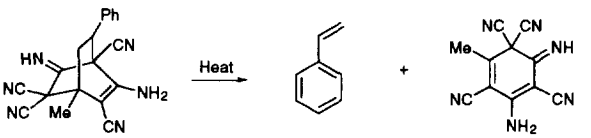


9 **10** **11** **12** **13** **14** **15** **16**

Scheme 3

reacts with **10** to yield **11**. Two consecutive intramolecular Thorpe cyclizations in **11** (*cfr.* Scheme 3, steps A and B) lead to the formation of **13**. All the spectroscopic data (IR, NMR and MS) are in agreement with 6-amino-2-imino-4-methyl-7-phenylbicyclo[2.2.2]-5-octene-1,3,3,5-tetracarbonitrile as the structure for **13**.

The presence of a 7-phenylbicyclo[2.2.2]-5-octene moiety in the molecule has been confirmed by a chemical degradation reaction. **13** must evolve by a *retro*-Diels-Alder reaction into vinylbenzene, **17**, and 4-amino-2-imino-6-methyl-3,5-cyclohexadiene-1,1,3,5-tetracarbonitrile, **18** (Scheme 4). Hence, when **13** is heated, compounds **17** and **18** are formed. Physical and spectroscopic data are in agreement with the proposed structures.



13 **17** **18**

Scheme 4

The second product obtained in the reaction between **9** and **2** was separated from the mixture by chromatography. Elemental analyses point to the empirical formula $C_{15}H_{13}N_3$. Mass spectrometry showed the molecular ion at *m/z* 235 as the base peak, confirming the empirical formula obtained from the elemental analyses. IR spectra indicated the presence of an amino group (3235, 3340 and 3412 cm^{-1}) and two cyano groups (2185 and 2219 cm^{-1}). Both ^1H and ^{13}C-NMR spectra identified a methyl group (singlets at δ 2.18 and δ 24.0 respectively), a *-CH-CH$_2$-* unit (multiplet from δ 2.36 to δ 4.06 corresponding to an ABC system in ^1H-NMR and two signals at δ 37.6 and δ 39.0 in ^{13}C-NMR which were assigned as a tertiary and secondary carbon respectively by DEPT) and a phenyl group (multiplet from δ 7.12 to δ 7.41 in ^1H-NMR and signals at δ 127.0, δ 127.5, δ 128.9 and δ 141.5 in ^{13}C-NMR). The empirical formula together with all the spectroscopic data are in agreement with 2-amino-4-methyl-6-phenyl-1,3-cyclohexadiene-1,3-dicarbonitrile as the structure for **15**. However, the isolation of a 1,3-cyclohexadiene ring is very unusual since the compounds that can become aromatic by dehydrogenation normally lose hydrogen in the basic medium even at room temperature.[6] The structure of **15** has been confirmed by X-ray analysis. In the crystal structure there are two

independent molecules (*cfr.* Fig. 1). In both cases the 1,3-cyclohexadiene ring is in the half-chair conformation (ΔC_2^{1-2} as defined in reference 7 is 5.8° for molecule I and 4.5° for molecule II). This conformation has also been found in other 1,3-cyclohexadienes.[8] The phenyl group occupies a pseudo axial position in molecule I and a pseudo equatorial position in II. The angle between the phenyl ring and the C(6)=C(1)-C(2)=C(3) mean plane is 63.2(1)° in I and 86.2(1)° in II. The bond lengths involving C(4) and C(5) (1.495-1.532 Å) are normal for sp^3 carbon atoms. The C(2)-C(3) double bond is significantly longer than the C(1)-C(6) bond because the H_2N-C=C-CN moiety is highly conjugated (push-pull system) as has been observed in a number of cases (reference 8 and references cited therein). In the crystal every molecule is

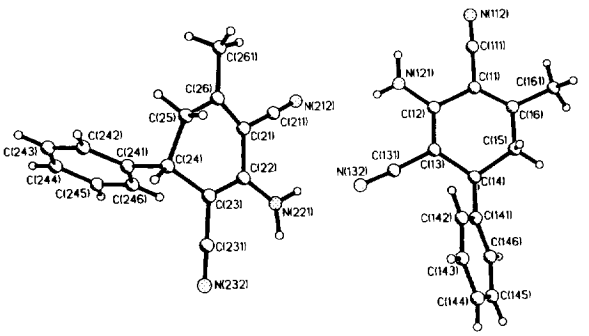


Fig. 1: Perspective view showing the two molecules of the asymmetric unit in the crystal structure of **15**.

joined to two independent neighbours by N-H....N≡C hydrogen bonding forming infinite one-dimensional zig-zag chains parallel to the *a* axis. Every molecule participates in two hydrogen bonding interactions as donor and in two more as acceptor *(cfr.* Fig. 2*)*: 1-Donor: N(121)-H(123), 0.78(3) Å; H(123)...N(212), 2.62(3) Å; N(121)...N(212), 3.353(3) Å; N(121)-H(123)...N(212), 158(2)°. 1-Acceptor: N(132)...H(223), 2.23(3) Å; H(223)-N(221), 0.84(3) Å; N(132)...N(221), 3.036(3) Å; N(132)...H(223)-N(221), 160(2)°.

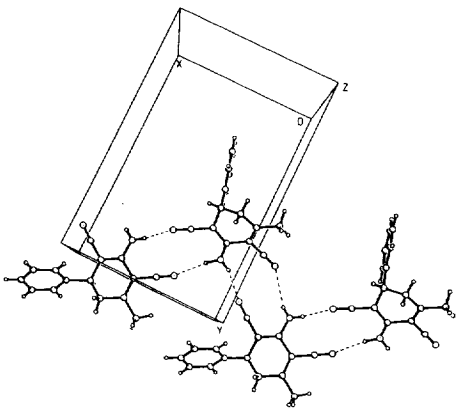


Fig. 2: Drawing showing the packing along axis *a*. Dotted lines indicate intermolecular hydrogen bonds.

2-Donor: N(121)-H(122), 0.90(3) Å; H(122)...N(232(x-1,y,z)), 2.12(3) Å; N(121)...N(232(x-1,y,z)), 3.010(3) Å; N(121)-H(122)...N(232(x-1,y,z), 173(2)°; 2-Acceptor: N(112)...H(222(x-1,y,z)), 2.19(3) Å; H(222(x-1,y,z))-N(221(x-1,y,z), 0.97(3) Å; N(112)...N(221(x-1,y,z)), 3.153(3) Å; N(112)...H(222(x-1,y,z)-N221(x-1,y,z), 170(2)°.

The compound has one asymmetric carbon (C(4)). In the crystal both enantiomers are present.

The isolation of **13** and **15** together with the 2-aminobenzene-1,3-dicarbonitrile system derived from (*E*)-4-phenyl-3-butene-2-one, **16**, prompted us to investigate if **13** and **15** were precursors of the aromatic compound **16**. To do this, **13** and sodium bicarbonate were suspended in water/ethanol and stirred at room temperature. TLC of the crude product mixture after one hour indicated that **13** had reacted to give a mixture of **15** and **16**, though five days were needed to consume all **13** and **15** . Similarly, after stirring a suspension of **15** and sodium bicarbonate in water/ethanol, TLC analysis indicated that **15** had reacted partially to give **16**. This suggests that both the bicyclo[2.2.2]-5-octene system, **13**, and the cyclohexadiene **15** evolve to the final compound under the same conditions used for the formation of the 2-aminobenzene-1,3-dicarbonitrile in the presence of only a base.

These results confirm that both the bicyclo[2.2.2]-5-octene and the cyclohexadiene systems are precursors of **16** in a new reaction pathway. The formation of **13** and its transformation into a benzene ring is depicted in Scheme 3. Michael addition of propanedinitrile to (*E*)-4-phenyl-3-butene-2-one followed by Knoevenagel condensation and Michael addition of a third molecule of propanedinitrile gives **11**. This acyclic compound is converted into the bicyclo[2.2.2]-5-octene system, **13**, by two consecutive intramolecular Thorpe cyclizations (steps A and B in Scheme 3). This compound is unstable in the basic reaction conditions and evolves to **15** by elimination of the sodium salt of 1,1,1-tricyanomethane, **14**, according to an E1cb mechanism.+ A spontaneous dehydrogenation of the cyclohexadiene system **15** yields the 2-amino-4-methyl-6-phenylbenzene-1,3-dicarbonitrile **16**. Strictly speaking, this mechanism has only been demonstrated for the reaction of one particular enone ((*E*)-4-phenyl-3-butene-2-one, **9**) in a particular basic medium (sodium bicarbonate in water and ethanol). We decided to study whether this sort of reaction pathway was taking place under the more drastic reaction conditions we use normally.[2] The crude reaction mixture of another carbonyl compound ((*E*)-3-phenylpropenal and propanedinitrile in a boiling sodium methoxide/methanol solution) was analysed by GC-MS. Under the more drastic conditions and with some starting material left, sixteen new compounds (whose structure has been assigned according to their molecular ion and fragmentation pathways) have been detected. Given the complexity of the reaction mixture, the yield in the final compounds of the different reaction pathways is not surprisingly low. This analysis has shown unequivocally the presence of vinylbenzene, which can only be explained by the *retro*-Diels-Alder reaction of the corresponding bicyclo[2.2.2]-5-octene. Furthermore, we have evidence for the more relevant evolution pathway of the bicyclo[2.2.2]-5-octene system to the 2-aminobenzene-1,3-dicarbonitrile. In the later process, the sodium salt of tricyanomethane must be formed. This compound is not stable in the basic medium conditions but we have found components in the mixture which are in agreement with addition products of dicyanocarbene (formed from tricyanomethane in the basic medium by cyanide

+ The elimination of the sodium salt of 1,1,1-tricyanomethane in the formation of 2-aminobenzene-1,3-dicarbonitriles has already been reported.[9] The sort of mechanism that Ducker and Gunter proposed would not lead in our case to the same intermediates we have isolated. As they start with a 1,3-dicarbonyl compound, two -CH-CN units are not present which could give a bicyclo[2.2.2]-5-octene system by two consecutive intramolecular Thorpe cyclizations.

elimination) to anions. These results ultimately indicate that the analogue of **13** in the case of (*E*)-3-phenylpropenal is also being formed under more drastic conditions and it is evolving to tricyanomethane and the corresponding diene system, although we have not been able either to isolate or detect them. As a result, the reaction pathway for the formation of 2-aminobenzene-1,3-dicarbonitriles described here takes place in boiling sodium methoxide/methanol as well.

The reaction pathway presented involves more steps and more difficult transformations than the reaction pathway that could be proposed from previously published works.[4,5] We can not exclude a simpler reaction pathway derived from the double Michael and Knoevenagel adduct of (*E*)-4-phenyl-3-butene-2-one and propanedinitrile (*cfr.* Scheme 2), however there is no evidence for this simpler process. In conclusion, the work presented here shows how far reaction pathways can be from the simple and elegant mechanistic rationalisations most of us propose and accept without question.

EXPERIMENTAL SECTION

(*E*)-4-Phenyl-3-butene-2-one was purchased from Fluka whereas propanedinitrile was obtained from Merck and both were used without any further purification. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). TLC was carried out using 2 mm Silica gel pre-coated plastic sheets from Macherey-Nagel. Melting points were determined on a Büchi Tottoli apparatus and are uncorrected. Nuclear Magnetic Resonance spectra were recorded on either Brucker AC-80 or Varian XL-200/F-19 spectrometers with [$^2H_6$]-DMSO as the solvent and sodium [$^2H_4$]-3-trimethylsilylpropionate as internal standard (unless otherwise noted). Ultraviolet-visible spectra were run on a Perkin-Elmer Lambda-2 instrument. Infrared spectra were recorded in KBr disk with a Bomem Michelson-100 FT-IR spectrometer. Mass spectra were recorded on either Hewlett-Packard 5995 A or Hewlett-Packard 5988 A spectrometers both operating at 70 eV. GC-MS analysis was performed with a Hewlett-Packard 5890 Series 2 gas chromatograph coupled with a Hewlett-Packard 5989 mass spectrometer. Combustion analyses were performed on a Carlo-Erba CHNS-O/EA1108 analyser. X-ray crystallographic data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer.

Treatment of (E)-4-phenyl-3-butene-2-one, propanedinitrile and sodium bicarbonate in a mixture of water and ethanol. (*E*)-4-Phenyl-3-butene-2-one (5.84 g, 0.04 mol), propanedinitrile (5.28 g, 0.08 mol), 100 ml of ethanol (EtOH) and 80 ml of a 4% aqueous sodium bicarbonate solution were stirred at room temperature for 14 hours. The white solid formed was filtered, washed with water and diethyl ether. 6-Amino-2-imino-4-methyl-7-phenylbicyclo[2.2.2]-5-octene-1,3,3,5-tetracarbonitrile, **13**, was obtained in analytical purity (0.31g, 2.4%) after drying *in vacuo* under P_2O_5: mp >300°C (Found: C, 69.92; H, 4.30; N, 25.73. $C_{19}H_{14}N_6$ requires C, 69.93; H, 4.32; N, 25.75); ν_{max}(KBr)/cm^{-1} 3421, 3343, 3261 and 3191 (NH), 2256 and 2195 (conj. CN) and 1648 (NH); δ_H(80 MHz) 1.66 (3H, s, Me), 2.13 (1H, dd, $^2J_{HH}$= 14.6 and $^3J_{HH}$= 5.7, C(8)Ha), 2.61 (1H, dd, $^2J_{HH}$= 14.6 and $^3J_{HH}$= 9.9, C(8)Hb), 3.96 (1H, dd, $^3J_{HH}$= 5.7 and $^3J_{HH}$= 9.9, C(7)H), 7.10-7.66 (7H, m, partially exchangeable with D_2O, Ph + NH_2), 12.00 and 13.07 (1H, br s, exchangeable with D_2O, C=N-H cis and trans); δ_C(50 MHz) 20.0 (Me), 37.6 (C-8), 42.6 (C-4), 43.5 and 43.7 (C-7)$^{++}$,

$^{++}$ In ^{1}H-NMR, the presence of diastereomers was suggested by broadened peaks due to overlap of the diastereoisomeric signals, whereas in the ^{13}C-NMR spectrum separate signals for C(1), C(2), C(3), C(5), C(6) and C(7) were identified for the two diastereoisomers.

46.5 and 48.5 (C-3), 56.5 and 57.5 (C-1), 72.9 and 73.2 (C-5), 111.6, 112.2, 112.9 and 115.8 (CN), 128.5-138.7 (Ph), 151.9, 153.0, 159.2 and 160.3 (C-2 and C-6); *m/z* 326 (M^+, 7%), 325 (6), 261 (13), 235 (6), 234 (5), 222 (35), 158 (8), 104 (100); λ_{max}(MeOH)/nm 206, 253 and 284 (log ε dm^3 mol^{-1} cm^{-1} 4.2, 4.0 and 4.0). The filtrate obtained in the separation of **13** was dried *in vacuo* at room temperature and the remaining oil was chromatographed through silica gel. Elution with dichloromethane furnished unreacted (*E*)-4-phenyl-3-butene-2-one (0.53 g, 9% of recovery). Further elution of the column with the same eluent gave 2-amino-6-methyl-4-phenylbenzene-1,3-dicarbonitrile **16** (0.74 g, 8%): mp 188-9 °C (Found: C, 76.90; H, 4.55; N, 18.12. $C_{15}H_{11}N_3$ requires C, 77.23; H, 4.75; N, 18.01); ν_{max}(KBr)/cm^{-1} 3464, 3340 and 3243 (NH), 2223 and 2210 (CN) and 1640 (NH); δ_H(80 MHz) 2.50 (3H, s, Me), 6.66 (2H, br s, exchangeable with D_2O, NH_2), 6.79 (1H, s, C(5)H), 7.57 (5H, br s, Ph); δ_C(20 MHz) 20.8 (Me), 92.8 and 95.7 (C-1 and C-3), 115.3 and 115.9 (CN), 119.0 (C-5), 127.9, 128.2, 129.1 and 137.5 (Ph), 147.9 and 149.4 (C-4 and C-6) and 153.2 (C-2); *m/z* 233 (M^+, 100), 232 (19), 206 (5), 205 (14), 179 (2), 178 (4). λ_{max}(MeOH)/nm 205, 228, 254 and 355 (log ε dm^3 mol^{-1} cm^{-1} 4.4, 4.5, 4.3 and 4.0). Lastly, 2-amino-4-methyl-6-phenyl-1,3-cyclohexadiene-1,3-dicarbonitrile, **15**, was obtained continuing the elution with the same eluent (0.42g, 5%): mp 134.5-135 °C (Found: C, 76.28; H, 5.45; N, 17.91. $C_{15}H_{13}N_3$ requires C, 76.57; H, 5.57; N, 17.86); ν_{max}(KBr)/cm^{-1} 3412, 3340 and 3235 (NH), 2219 and 2185 (CN) and 1650 (NH); δ_H(80 MHz, $CDCl_3$, $SiMe_4$) 2.18 (3H, s, Me), 2.36-4.06 (3H, m, -C*H*-C*H2*-), 4.91 (2H, br s, exchangeable with D_2O, NH_2), 7.12-7.41 (5H, m, Ph); δ_C(50 MHz, $CDCl_3$) 24.0 (Me), 37.6 (C-6), 39.0 (C-5), 74.6 (C-1), 104.8 (C-3), 113.9 and 118.9 (CN), 127.0, 127.5, 128.9 and 141.5 (Ph), 146.8 (C-4), 162.4 (C-2); *m/z* 235 (M^+, 80.0), 220 (23), 158 (100), 143 (18); λ_{max}(MeOH)/nm 207, 232 and 353 (log ε dm^3 mol^{-1} cm^{-1} 4.1, 4.3 and 3.5).

Isolation of vinylbenzene and 4-amino-2-imino-6-methyl-3,5-cyclohexadiene-1,1,3,5-tetracarbonitrile from the Retro-*Diels-Alder Reaction of 13.* 6-Amino-2-imino-4-methyl-7-phenylbicyclo[2.2.2]-5-octene-1,3,3,5-tetracarbonitrile, **13**, (3.0 g, 9.2 mmol) was heated to 210 °C for two hours *in vacuo* (2 torr) and vinylbenzene collected by distillation (0.36 g, 38%): bp 144-146 °C (lit.,[10] 145.2 °C). The residue in the flask was suspended in 100 ml of ethanol and heated under reflux for 1 h. The remaining solid was filtered and washed with ethanol. 4-Amino-2-imino-6-methyl-3,5-cyclohexadiene-1,1,3,5-tetracarbonitrile, **18**, was obtained in analytical purity (1.5g, 74%) after drying *in vacuo* under P_2O_5: mp > 300 °C (Found: C, 59.46; H, 2.72; N, 37.82. $C_{11}H_6N_6$ requires C, 59.64; H, 2.66; N, 37.53); ν_{max}(KBr)/cm^{-1} 3370, 3335, 3230 and 3200 (NH), 2230, 2220 and 2210 (CN) and 1660 (NH); δ_H(80 MHz) 2.52 (3H, s, Me), 6.03 (2H, br s, exchangeable with D_2O, NH_2), 8.06 (1H, br s, exchangeable with D_2O, C=NH); δ_C(50 MHz, [$^2H_6$]-DMSO + CF_3COOD) 19.8 (Me), 41.4 (C-1), 76.8 (C-3), 86.8 (C-5), 112.8, 113.4 and 117.1 (CN), 154.3 (C-6), 157.6 (C-4) and 160.3 (C-2); *m/z* 222 (M^+, 100), 195 (19), 168 (19), 157 (28), 141 (6), 130 (18), 103 (15), 92 (6), 76 (8); λ_{max}(MeOH)/nm 210, 250, 285 and 342 (log ε dm^3 mol^{-1} cm^{-1} 4.3, 4.1, 4.3 and 4.4).

Crystal data. Suitable crystals were grown by slow evaporation from a dichloromethane solution. $C_{15}H_{13}N_3$, *M*= 235.28. Monoclinic, a= 11.137(5), b=16.575(2), c= 14.190(3) Å, β=94.33(2)°, *V*=2612(1) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ=0.71069 Å), space group $P2_1/n$ (alt. $P2_1/c$, No. 14), *Z*= 8, D_x= 1.197 g cm^{-3}. Yellow, air-stable crystals. Crystal dimensions: 0.5 x 0.4 x 0.3 mm, μ(Mo-Kα)= 0.73 cm^{-1}.

Data Collection and Processing. CAD 4 diffractometer, ω/2θ mode with ω scan width= 0.80 + 0.34 tanθ, ω scan speed 1.3-5.5 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 4577 reflections measured (1≤θ≤25°, ±h, +k, +l), 4577 unique (Lp but no absorption corrections) giving 2845 with $I>2\sigma(I)$. No decay was observed.

Structure Analysis and Refinement. Direct methods (SHELXS-86 program).[11] Full-matrix least-squares refinement on F^2 for all reflections (SHELXL-93 program)[12] with all non-hydrogen atoms anisotropic. Hydrogens bound to C in calculated positions with two, overall, refined U (one for the methyl hydrogens and another for the rest of hydrogens bound to C). The weighting scheme $w=1/[\sigma^2(F_o^2) + (0.1083\ P)^2]$ where $P=[\text{Max}(F_o^2,0) + 2F_c^2]/3$. Final R and $wR2= \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ values are 0.054 and 0.155 for reflections with $I>2\sigma(I)$.

ACKNOWLEDGEMENTS

The X-ray measurements have been carried out at the *'Servei de Difracció de Raigs-X de la Universitat Autònoma de Barcelona'*. We would like to thank the DGICYT (proj. SAB89-0031) for financial support (G.G.) and the Fundació *'J. Salañer'* for a grant (A. V.-F.).

REFERENCES

1. (a) Victory, P.; Borrell, J.I.; Vidal-Ferran, A.; Seoane, C.; Soto, J.L. *Tetrahedron Lett.* **1991**, *32*, 5375. (b) Victory, P.; Borrell, J.I.; Vidal-Ferran, A. *Heterocycles* **1993**, *36*, 769.

2. Victory, P.; Borrell, J.I.; Vidal-Ferran, A.; Montenegro, E.; Jimeno, M.L. *Heterocycles* **1993**, *36*, 2273.

3. Piniella, J.F.; Alvarez-Larena, A.; Victory, P.; Borrell, J.I.; Vidal-Ferran, A.; Germain, G. *Acta Crystallogr., Sect. C* **1992**, *C48*, 208.

4. See for example: (a) Gewald, K.; Schill, W. *J. Prakt. Chem.* **1971**, *313*, 678. (b) Sepiol, J.; Milart, P. *Tetrahedron* **1985**, *41*, 5261. (c) Sharanin, Y.A.; Baskakov, Y.A.; Abramenko, Y.T.; Putsykin, Y.G.; Vasilev, A.F.; Nazarova, E.B. *Zh. Org. Khim.* **1980**, *16*, 2192.

5. Apsimon, J.W.; Hooper, J.W.; Laishes, B.A. *Can. J. Chem.* **1970**, *48*, 3064.

6. (a) Soto, J.L.; Seoane, C.; Ciller, J.A. *An. Quim. Ser. C* **1980**, 281. (b) Tyndall, D.V.; Al Nakib, T.; Meegan, M.J. *Tetrahedron Lett.* **1988**, *29*, 2703. (c) Al-Arab, M.M. *J. Heterocycl. Chem.* **1989**, *26*, 1665.

7. Duax, W.L.; Weeks, C.M.; Roher, D.C. *Top. Stereochem.* **1976**, *9*, 271.

8. Lankin, D.C.; Griffin, G.W.; Bernal, I.; Korp, J.; Watkins, S.F.; DeLord, T.J.; Bhacca, N.S. *Tetrahedron* **1984**, *20*, 2829.

9. Ducker, J.W.; Gunter, M.J. *Aust. J. Chem.* **1975**, *28*, 581.

10. Weast, R.C. *CRC Handbook of Chemistry and Physics*, 63rd edition; CRC Press: Boca Raton (Florida), 1983; p. C-521.

11. Sheldrick, G.M. SHELXS 86. In *Crystallographic Computing*, Sheldrick, G.M.; Krüger, C.; Goddard, R. Eds.; Oxford University Press: Oxford, 1985, vol. 3; p. 175-189.

12. Sheldrick, G.M. SHELXL 93, Program for the Refinement of Crystal Structures from Diffraction Data. University of Göttingen, Germany, 1993.

(*Received in UK* 26 *September* 1994; *revised* 18 *October* 1994; *accepted* 21 *October* 1994)