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Retro-Diels-Alder Fragmentation of 2,5,6-Triphenyl-3,4-didehydropyridine Generated by Flash Vacuum Pyrolysis at 900°C

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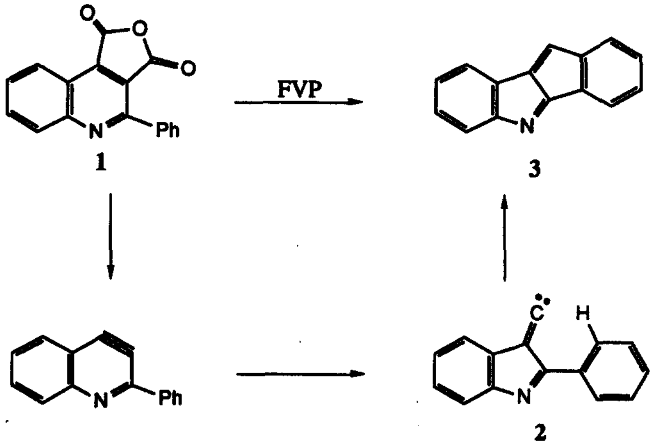
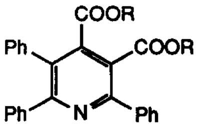
Summary: 2,5,6-Triphenyl-3,4-didehydropyridine, generated by FVP of the corresponding 3,4-dicarboxylic anhydride (**6**) at 900°C/0.02 mm, undergoes mainly retro-Diels-Alder cleavage to 1,4-diphenylbutadiyne and benzonitrile.

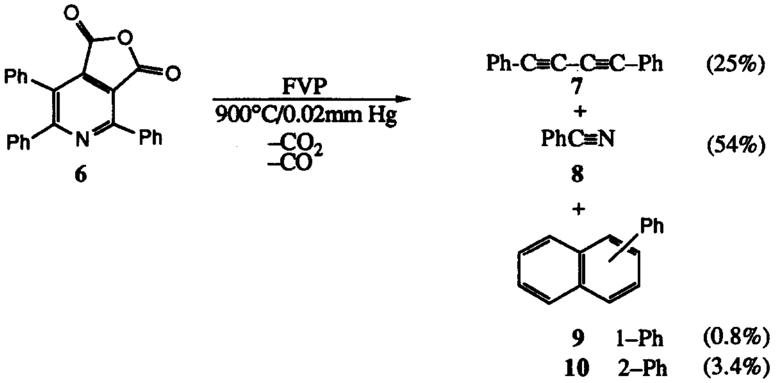
Synthetic use of the ring contraction of arynes to exocyclic carbenes[1] can be extended to heteroarynes formed on flash vacuum pyrolysis (FVP) of heteroaromatic anhydrides. 2-Phenylquinoline-3,4-dicarboxylic anhydride (**1**) behaved on FVP like the corresponding naphthalene anhydride[1] and formed indeno[1,2-b]indole (**3**) by intramolecular insertion in the carbene (**2**).[2]



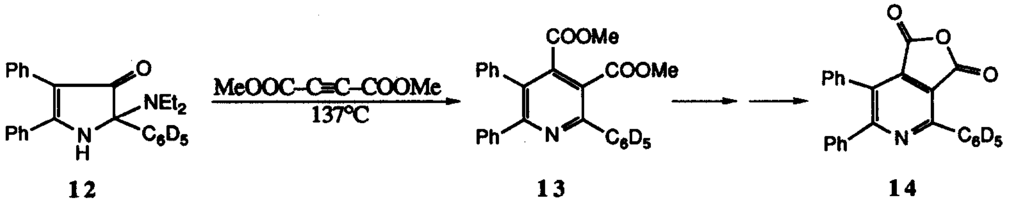
Tetraphenylphthalic anhydride also underwent ring contraction to 1,2,3-triphenylbenzopentalene on FVP[3] but the pyrolytic behaviour of the structurally similar triphenylpyridine anhydride (**6**) was quite different. The known diester (**4**) [4] was hydrolysed with LiOH/dimethoxyethane/H_2O and the diacid (**5**) [5] was heated with acetic anhydride to give the anhydride (**6**) [6] Pyrolysis of the anhydride (**6**) at 900°C/0.02mm Hg[7] gave 1,4-diphenylbutadiyne (**7**; 25%) and benzonitrile (**8**; 54%) with the minor products 1-phenyl- (**9**) and 2-phenylnaphthalene (**10**) (0.8 and 3.4%, respectively).



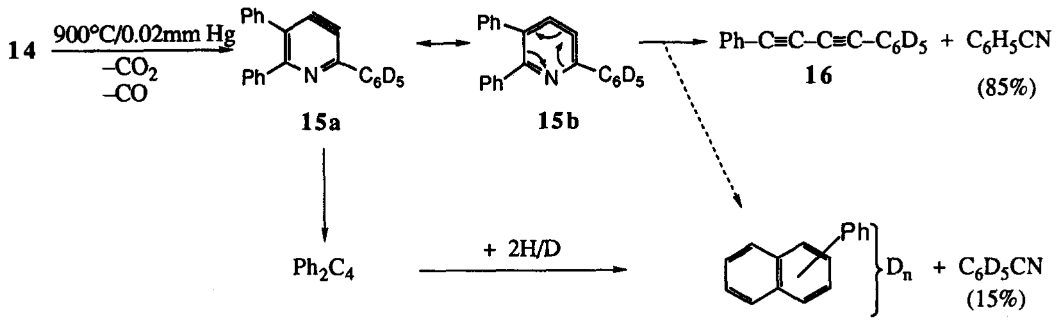
4 : R=CH_3
5 : R=H



It is evident that ring contraction to an exocyclic carbene has been replaced by ring cleavage of the presumed intermediate triphenyl 3,4-pyridyne. Such a cleavage is ambiguous, however; the benzonitrile might be derived from either Ph-C2-N or Ph-C6-N. We have resolved this ambiguity by pyrolysis of the labelled anhydride (**14**) bearing a 2–C_6D_5 group. Pentadeuterobromobenzene[8] was converted to C_6D_6CN with NaCN in dimethylformamide.[9] Treatment with Et_2NMgBr[10] gave C_6D_5–C(=NH)NEt_2 (**11**) [11], which was added to diphenylcyclopropenone to give the crude pyrrolone (**12**). Heating (**12**) with dimethyl acetylenedicarboxylate[4] gave the pyridine diester (**13**) [12] which was further transformed to the anhydride (**14**).[13]



Pyrolysis of the deuterated anhydride (**14**) at 900°C/0.02mm Hg gave a pyrolysate which was analysed mainly by GC-MS.[14] The diyne was found to be solely the D_5 species (**16**), but the benzonitrile was mainly C_6H_5CN (85%) with some C_6D_5CN (15%). The major pathway of fragmentation of anhydride (**14**) may now be shown as proceeding through the 3,4-pyridyne (**15a** ⟷ **15b**) and the retro-Diels-Alder cleavage shown on structure (**15b**). This does not account for the minor formation of C_6D_5CN. The phenylnaphthalene fraction (**17**) and (**18**) showed formation of a range of deuterated species, which we have not attempted to interpret. A further trace component showed GC-MS behaviour consistent with a *ca* 1:1 mixture of undeuterated and pentadeuterated phenylbutadiyne (**19**). Hydrocarbons (**17**), (**18**) and (**19**) are possible secondary transformation products of the diyne (**16**), but FVP of diphenylbutadiyne (**7**) at 900°C/0.02mm Hg gave no sign of their formation and starting material was recovered. The minor pathway of ring cleavage, which leads to C_6D_5CN from labelled anhydride (**14**), will lead also to a different species of composition Ph_2C_4 which could be involved in the formation of hydrocarbons (**17**), (**18**) and (**19**) by addition of hydrogen or deuterium.



17 1-Ph: *m/z* 201-209

18 2-Ph: *m/z* 200-209

19 $\left\{\begin{array}{l} \text{Ph–C≡C–C≡C–H} \\ C_6D_5\text{–C≡C–C≡C–H} \end{array}\right.$

Pyrolytic ring opening and ring cleavage have been reported for pyridine-2,3-dicarboxylic anhydride[15] and pyridine-3-diazonium-4-carboxylate,[16] but these reactions were less clean than the retro-Diels-Alder cleavage of the present heavily phenylated species (**15**).

Acknowledgement

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References and Notes

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5. Diacid (**5**): 95% yield, colourless crystals from benzene - light petroleum, m.p. 129-131°C (with resolidification at 132-4°C to the yellow anhydride m.p. 215°C) (Found: C, 75.7; H, 4.2; N, 3.8. $C_{25}H_{17}NO_4$ requires C, 75.9; H, 4.3; N, 3.5%). ν_{max} (mull) 3600-2400 (OH) and 1732 (C=O) cm^{-1}.

6. Anhydride (**6**): 82% yield, yellow platelets from benzene - light petroleum, m.p. 216-217°C (Found: C, 79.7; H, 3.7; N, 3.4. $C_{25}H_{15}NO_3$ requires C, 79.6; H, 4.0; N, 3.7%). ν_{max} (mull) 1853, 1833, 1779 cm^{-1}. ^1H n.m.r. (300 MHz, $CDCl_3$): δ 7.22-7.44, m, 10H (5-Ph and 6-Ph); 7.54-7.59, m, 3H and 8.08-8.15, m, 2H 2-Ph). Mass spectrum: *m/z* 377(M^+, 80%), 348(78), 305(100), 202(72).

7. FVP was carried out with a silica tube (hot zone 300 by 25mm i.d.). The anhydride (65.7 mg) was sublimed at 180-200°C during 1h into the tube heated at 900°C/0.02mm Hg. Products were detected by GC-MS and yields estimated by capillary GC of the pyrolysate and of standard samples (BP21 column, 80° 2 min, 80-200° at 10°/min).

8. C_6D_5Br (2.0 g) was 98% D_5 material from Cambridge Isotope Laboratories.

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11. Amidine (**11**): Mass spectrum: *m/z* 181(M$^+$, 10%), 179(88), 109(100).

12. D_5 diester (**13**): 69% yield from crude (**12**) m.p. 229-230°C (lit.[4] 222-223·C). ν_{max} (mull) 1739, 1727 (2 x COOMe) cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 3.57, 3.68 (2 x OMe); 7.1 - 7.4, 10H (5-Ph and 6-Ph). Mass spectrum: *m/z* 428(M$^+$, 80%), 427(100), 310(79).

13. D_5 anhydride (**14**): 90% yield from the diester; m.p. 214-216°C. ν_{max} (mull) 1852, 1819, 1780 cm^{-1}. Mass spectrum: *m/z* 382(M$^+$, 72%), 353(56), 310(100), 207(57), 202(20).

14. GC-MS: Capillary GC (BP20, 110°C 2 min, 110-230°C at 5°/min) coupled to a V.G. Trio-1 quadrupole spectrometer. Deuterated pyrolysate: Benzonitrile, r.t. 2.9 min, *m/z* 108(18%) and 103(100). Phenylbutadiyne (trace), 7.0 min, *m/z* 131(95%), 126(100). 1-Phenylnaphthalene, 25.7 min; 2-phenylnapthalene, 30.6 min; for MS see structures **17** and **18**. Diphenylbutadiyne, 27.2 min, *m/z* 207(100).

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