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# ON THE TRANSFORMATION OF TETRAPHENYLCYCLOPENTADIENONE TO PENTAPHENYLPYRROLE IN BOILING NITROBENZENE

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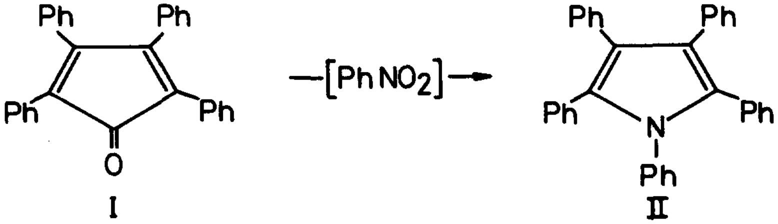
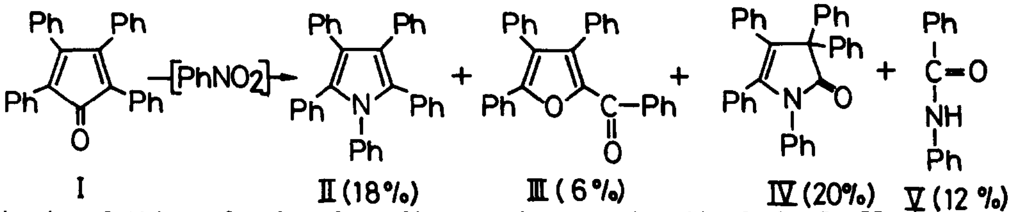
One of the fascinating problems in organic reaction mechanisms is the formation of pentaphenylpyrrole (II) from tetraphenylcyclopentadienone (I; tetracyclone) on boiling with nitrobenzene. This observation, originally made by Dilthey[1] is still the method of choice for II[2]:



Our examination of this reaction has led to characterization, from the complex reaction mixture, three additional compounds, namely the furan III[3], the lactam IV[4] and benzanilide V*:



On basis of this and related studies we have rationalized the I $\rightarrow$ II change and

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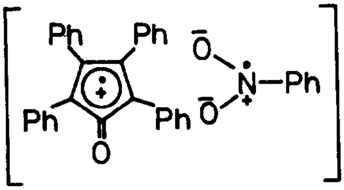
* I(3.84g) in $PhNO_2$(25 ml) was refluxed for 15 hr. Solvents were removed by vacuum distillation followed by steam distillation and the residue chromatographed over silicic acid. Elution with hexane-benzene (1:1) and benzene gave II(0.81 g, mp 283-284°), III (0.24 g, mp 166-167°), IV(0.93 g, mp 158-159°) and with ethyl acetate V(0.24 g, mp 162-163°). The reaction when carried out under nitrogen or extended periods gave no improved yields and in solvents such as water, dioxan and pyridine I was recovered unchanged.

Structural assignments were initially made on basis of IR, analysis and subsequently by direct comparison with authentic samples.

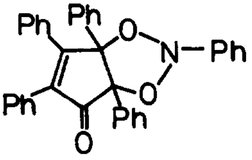
in this process have added to the intriguing transformations that are characteristic of systems derived from tetracyclone.[5]

Slightly enhanced yields of II and IV can be obtained by replacement of nitrobenzene with nitrosobenzene in boiling xylene. Significantly, under these conditions the furan III and benzanilide are not formed. Of great mechanistic importance is the formation of carbondioxide in the I → II change, irrespective of whether nitrobenzene or nitrosobenzene is employed, a fact that was reported by Dilthey[1] and confirmed by us; further the carbondioxide formation is associated with pyrrole formation, since wherever compounds related to the lactam are exclusively formed, only carbonmonoxide is liberated. Detectable amounts of nitrosobenzene are formed in the I → II change with nitrobenzene.

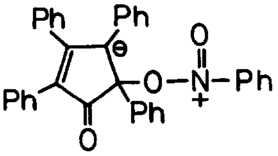
We feel that the path leading to II involves three distinct stages, namely, oxygen transfer from nitrobenzene to tetracyclone, adduct formation involving the nitrosobenzene so produced with I and finally the loss of elements of carbondioxide from the adduct. Oxygen transfer from nitrobenzene is indeed extremely rare[6] and in the present case must be attributed to the readiness with which tetracyclone can be oxidized by procedures that involve initial acceptance of nucleophiles.[5] With I, such a transfer can take place either by means of the charge-transfer complex VI or through the product of cycloaddition VII or the dipolar ion VIII:



VI

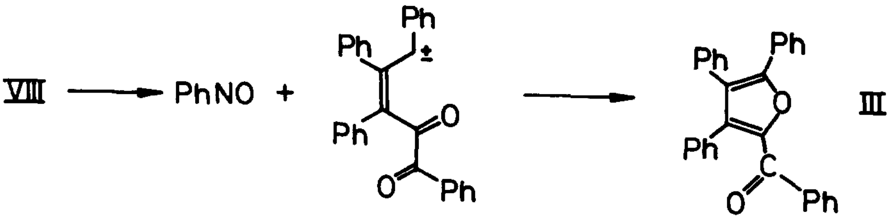


VII

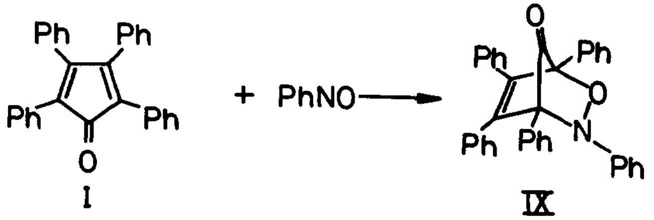


VIII

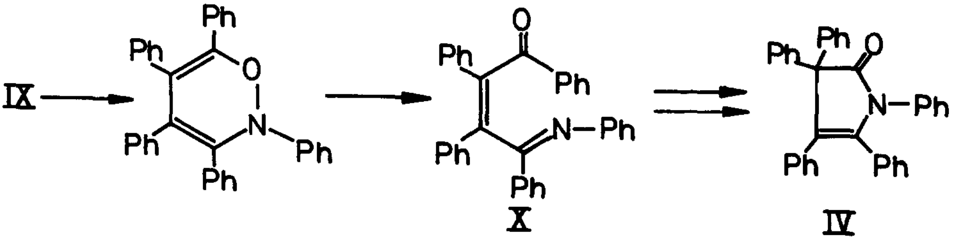
UV and ESR probes have not given any evidence for VI. Principles of conservation of orbital symmetry dictate that addition of nitrobenzene to olefins to form adducts such as VII is a thermally allowed process, although such an addition has not been reported and our own efforts in this direction have not yet succeeded.[7] Blank experiments have shown that the epoxide which in principle could arise from VIII does not yield the furan. We rationalize the formation of III as follows:



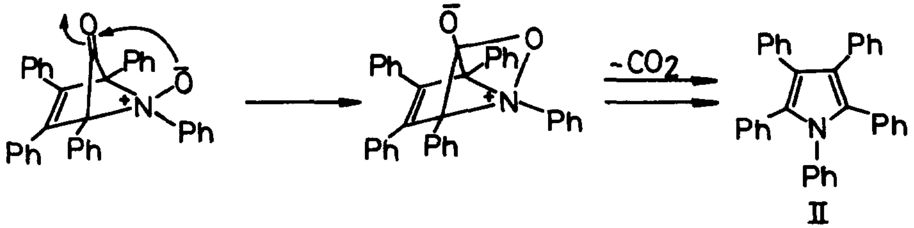
Pentaphenylpyrrole II and the lactam IV can arise from the key intermediate IX, resulting from a (4 + 2) addition of I and nitrosobenzene:



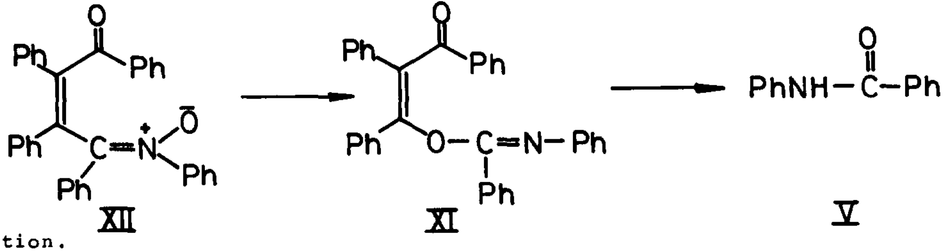
The IX → IV change is rationalized on basis of a sequence involving (4+1) cyclo reversion, ($\pi 4s + \sigma 2s$) addition and a benzilic acid type rearrangement:[8]



The apparently unusual loss of carbondioxide from IX leading to pentaphenylpyrrole can quite easily be explained in terms of pathways envisaged for related cases.[9,10,11] Alternately and more simply the formation of II can be explained on basis of a novel (4 + 1) addition involving I and nitrosobenzene followed by loss of elements of carbondioxide:[12]



We have no satisfactory explanation for the formation of the relatively significant amounts of benzanilide and all efforts to identify as possible precursors, species such as X and II were not fruitful. The possibility that benzanilide arises from intermediate XI *via* XII resulting from interaction of tetracyclone and nitrobenzene by a (4 + 2) process is currently receiving attention.



ACKNOWLEDGEMENT

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12. We are grateful to the referee for suggesting this possibility.