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PHOTOCHEMICAL REACTIONS INVOLVING PYRROLES - PART I

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Abstract - The photochemical behaviour of pyrrole derivatives was described showing that the photochemical methodologies in this field can offer some interesting synthetic procedures. Furthermore, pyrrole derivatives has been used in photochemical reactions for the synthesis some interesting products.

CONTENTS

1. INTRODUCTION

Some years ago the first book on the photochemical behaviour of heterocyclic compounds appeared.[1] In that book the photochemistry of pyrrole was described in two pages. It seems to show a really unusual photochemical behaviour that avoids being rationalised. From that time a lot of experimental works has been described, and author consider it useful for scientists to attempt a systematic organization of available data.

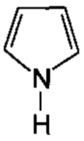
2. PHOTOLYSIS IN VAPOUR PHASE

Uv spectrum of pyrrole (**1**) in vapour phase showed absorptions at 211.0, 217.0, and 237.5 nm (ε 8020, 3250, and < 150 M^{-1} cm^{-1}, respectively). The absorption at 237.5 nm was identified as relative to a π,π* transition and no decomposition of the starting material was observed.[2] Successively, pyrrole vapours were irradiated at 214 nm at room temperature showing that some decomposition products were obtained: so propyne, allene, ethylene, acetylene, and propene were observed in the reaction mixture together with HCN.[3] Primary processes were identified as:

Py* = CH_3CCH + HCN

Py* = CH_2CCH_2 + HCN

It should be noted that authors identified only decomposition products, while they did not find isomerisation products, as in vapour phase photochemistry of furans and thiophenes. Furthermore, vapour phase photolysis of 2,5- and 2,4-dimethylpyrroles (**2** and **3**) at 214 and 229 nm showed only hydrogen, methane, and ethane, while no product derived from ring opening was observed.[4]



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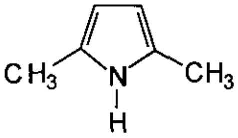

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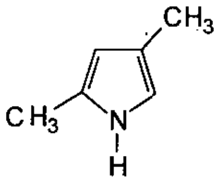

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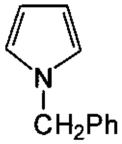
3. REACTIONS ON *N*-SUBSTITUENTS

The photochemistry of pyrrole derivatives showed its differences from that of furan and thiophene derivatives with substituents on N-1. When *N*-benzylpyrrole (**4**) was irradiated without solvent or in methanol at 254 nm, a mixture of 2- and 3-benzylpyrrole (**5**) and (**6**) was obtained.[5] No interconversion from **5** to **6** was observed.



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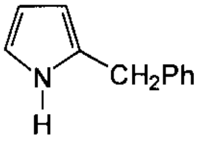

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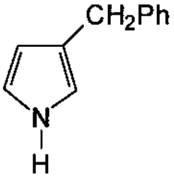

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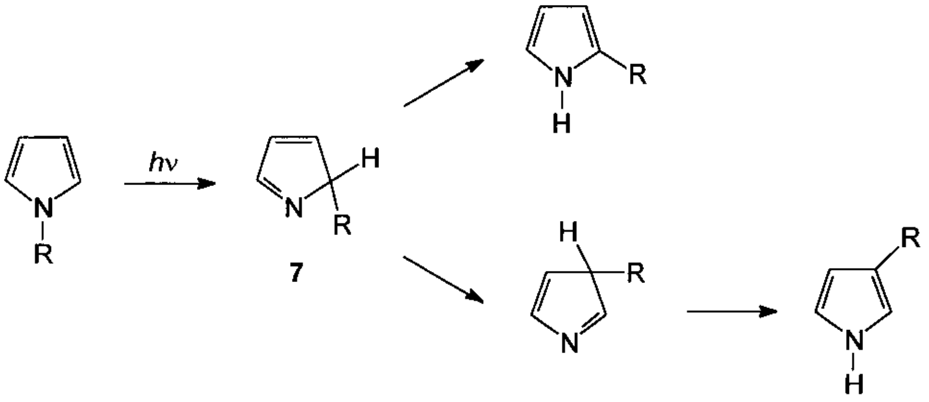
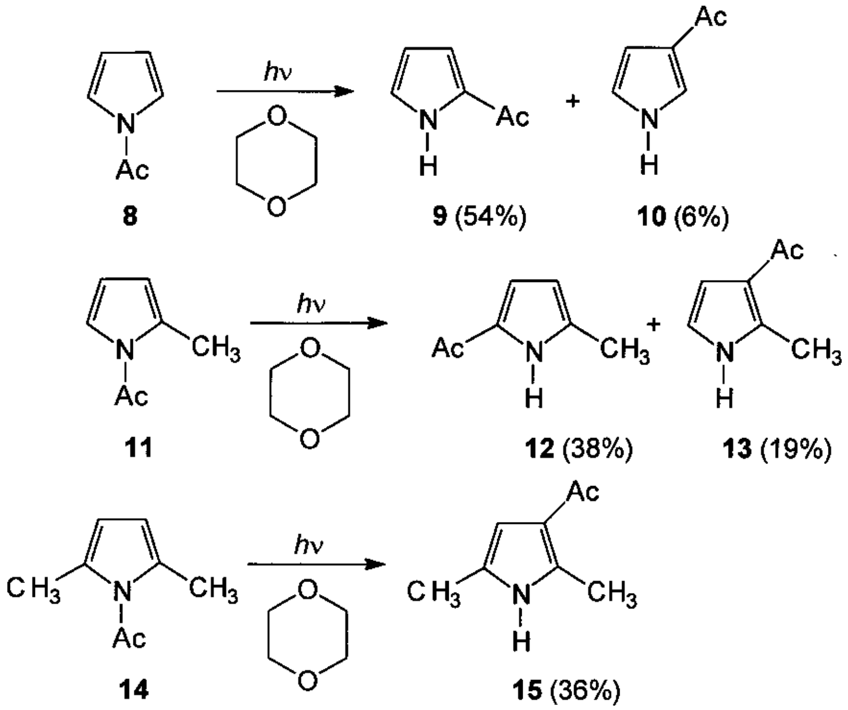
When (+)-*N*-(1-phenylethyl)pyrrole was used as a substrate, the same trend was observed, only 32% configuration retention was observed when the reaction was performed in methanolic solution. Then, optical activity was lost during photoisomerisation. All the data were in agreement with two mechanism hypotheses. The isomerisation can occur *via* direct 1,2 and 1,3 migration or *via* the formation of a common intermediate (**7**) (Scheme 1).

Scheme 1

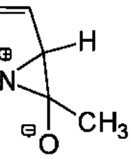


Similar behaviour was observed when *N*-acetylpyrroles were used as the starting material.[6,7] The irradiation of (**8**) in dioxane at 254 nm gave the same mixture observed with alkyl derivatives (Scheme 2).

Scheme 2



The yields of the 3-isomer increased to reach a maximum when 2,5-dialkyl derivative (**14**) was tested. The formation of the 2-isomer was suggested to involve the formation of the intermediate (**16**).[8]



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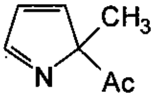


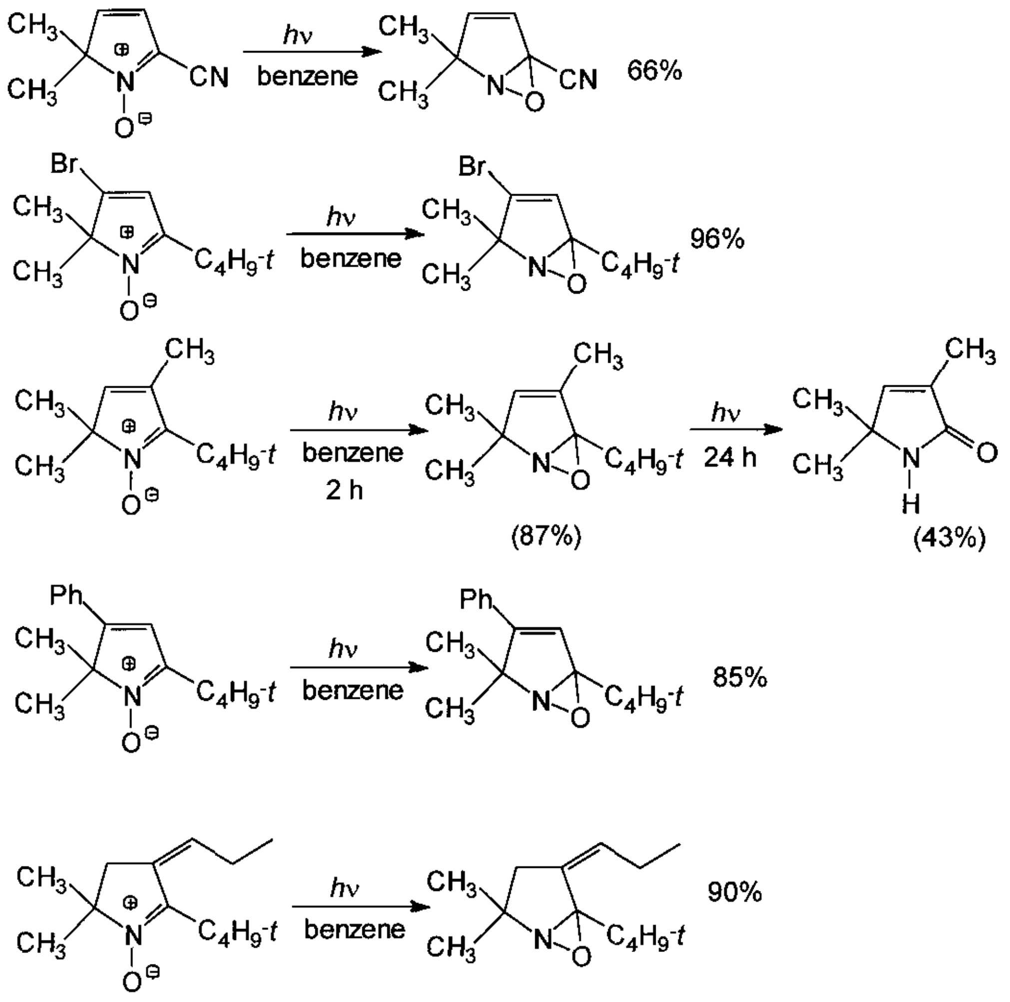
17

The 3-isomer (**13**) can be obtained by direct migration but the fact that (**17**) was not isolated in the reaction of (**11**) may suggest that (**13**) was obtained from (**17**) *via* thermal isomerization.

Reaction products involving 1,2 migration of type (**16**) were obtained using as starting materials *N*-oxides (Scheme 3).[9,10] The oxaziridine thus obtained can be converted into the corresponding amides through a photochemical isomerisation followed by elimination of the substituent at C-2.

The hypothesis reported in Scheme 2 does not involves the formation of free radicals in the reaction

Scheme 3

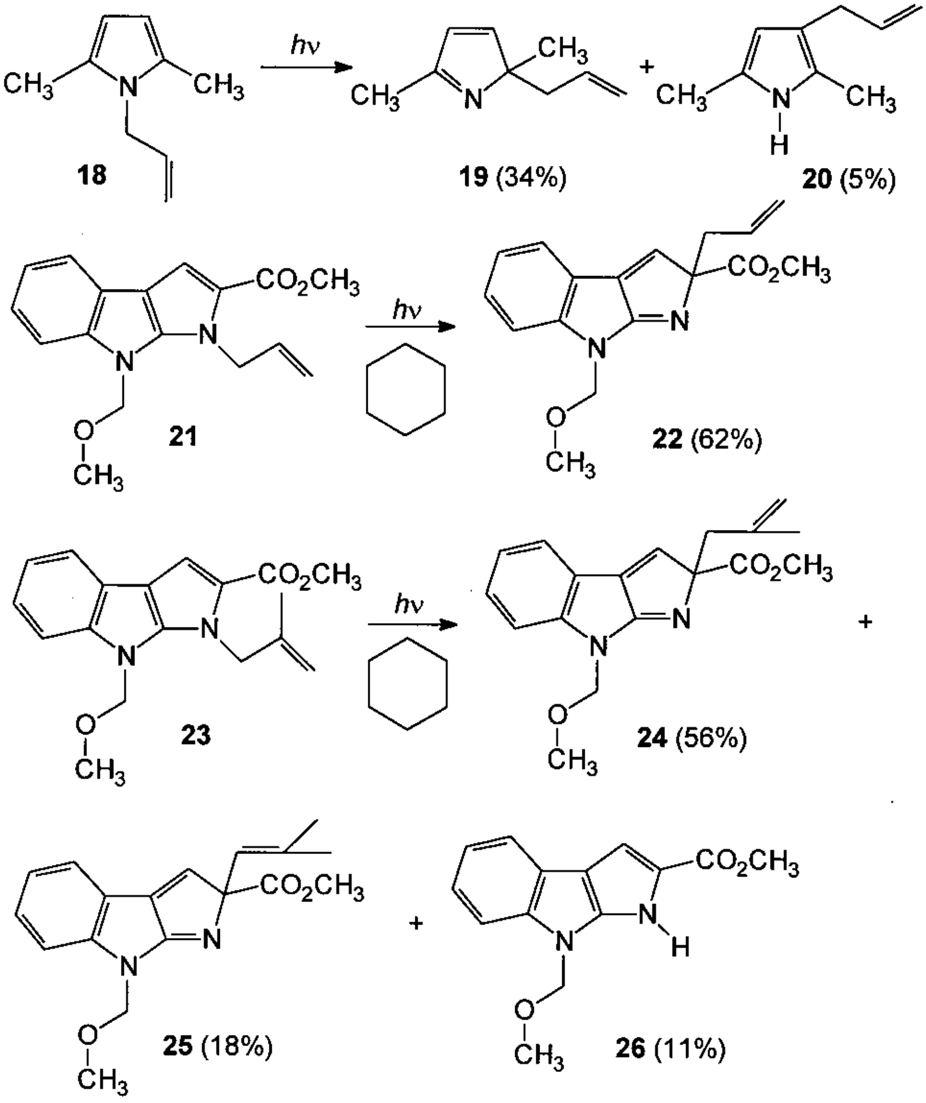


mixture. Flash photolysis experiments on *N*-phenylpyrrole is not in agreement with this statement.[11] The authors reported the presence of a transient with absorption at λ 360 nm and τ 0.5 ms. In *i*-PrOH a second transient was observed with absorption maximum at 520 nm (τ 0.6 ms), while after several flashes a band at 290 nm was observed. The transient at 520 nm was identified as the triplet excited state of *N*-phenylpyrrole while the absorption at 360 nm was due to the triplet-triplet transition of biphenyl. This compound could be formed by coupling of the phenyl radical. Finally the absorption at 290 nm was ascribed to 2-phenylpyrrole formed during the flash. Then, in this case, the involvement of free radicals into the photoisomerization of *N*-substituted pyrrole seems to be proved.

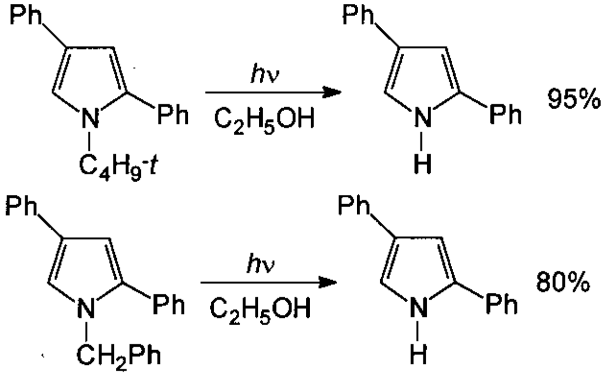
Photoisomerisation of *N*-allyl pyrroles was first described by Patterson (Scheme 4).[12] In the case of 2,5-diakylpyrroles, the 2-isomer was isolated in excellent yields, while this isomer was not isolable by using *N*-acetyl derivatives. This reaction was tested also by using condensed pyrroles (Scheme 4).[13,14]

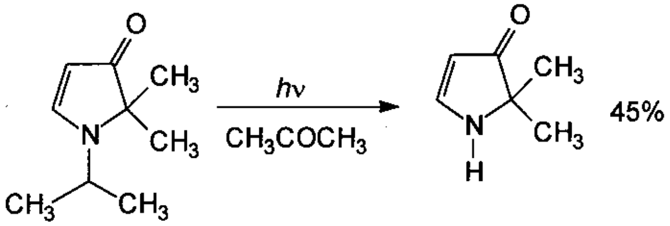
During the photoisomerisation of *N*-allyl derivative (**18**) ca. 10% of 2,5-dimethylpyrrole was also

Scheme 4



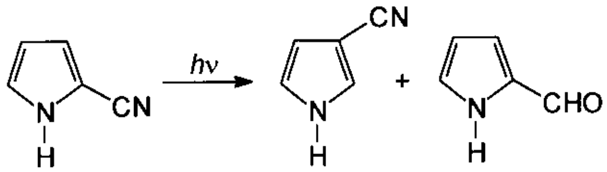
recovered. Elimination of the *N*-alkyl substituents was observed in **23** that gave **26** in 11% yields. Elimination reactions were observed by Padwa using 2,4-diphenylpyrroles. In this case, *N*-*t*-butyl and *N*-benzyl derivatives gave elimination products in very high yields.[15] In the case of the *t*-butyl derivative the formation of the stable *t*-butyl radical to give isobutene is involved. In fact, the *N*-cyclohexyl derivative did not react under the same reaction conditions. *N*-Isopropyl derivatives were converted into a 3-hydroxypyrrole derivative when they were irradiated in acetone at 300 nm for a long time (120 h).[16]





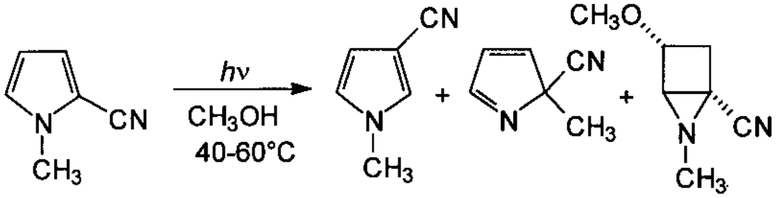
4. PHOTOREARRANGEMENTS

In 1970 Hiraoka reported that 2-cyanopyrrole (**27**), irradiated in methanol with a low pressure mercury arc for 20 h, gave a mixture of 3-cyanopyrrole (**28**) and pyrrole-2-carbaldehyde (**29**).[17]



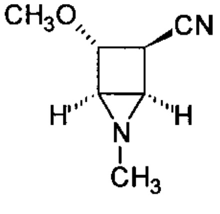
27 **28** (55%) **29** (5%)

The photoisomerizations are well known reactions in the photochemistry of furans, thiophenes and of some other heterocycles.[1,18] In the photochemistry of pyrroles only 2-cyanopyrroles seem to give this type of reaction. Theoretical calculations on pyrrole are in agreement with experimental results. In fact, they showed that the decomposition reactions to give acetylene were more likely than the photoisomerizations. Furthermore, they showed that strong electron donor or acceptor substituents can modify this behaviour.[19] 1-Methyl-2-cyanopyrrole (**30**) also gave this reaction.[20] In this case the author isolated the product of isomerisation (**31**), the product of the shift in C-2 of the *N*-methyl group (**32**), and a third product that can be assumed to be derived from the addition of methanol to dewar pyrrole.



30 **31** **32** **33**

The use of a specific temperature seems to be in agreement with the presence of a thermal activated step in the reaction. No reaction occurred when the reaction was performed at - 68 °C.[21] More recently, the nature of compound (**33**) was reevaluated and the structure (**34**) was proposed.[21]



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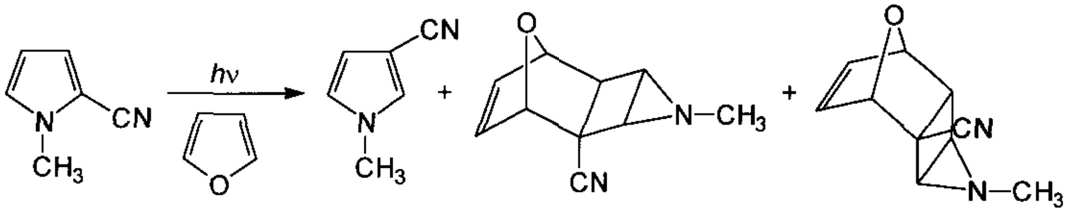
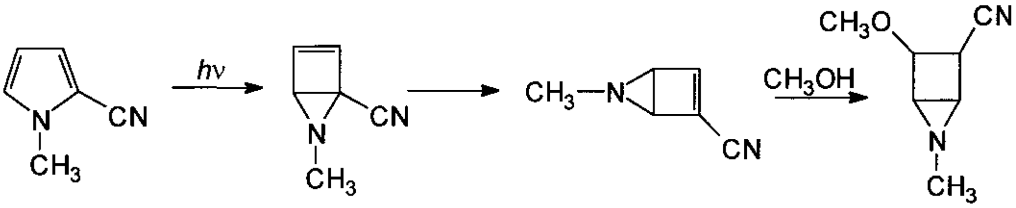
This structure was confirmed also by performing the reaction in the presence of furan. In this case 4+2 photoadducts (**35**) and (**36**) were isolated in 1:1 ratio.



30 **31** **35** **36**

All these data seem to be in agreement with a mechanism depicted in Scheme 5, where the thermal activated step is the 1,2-sigmatropic shift between **37** and **38**.

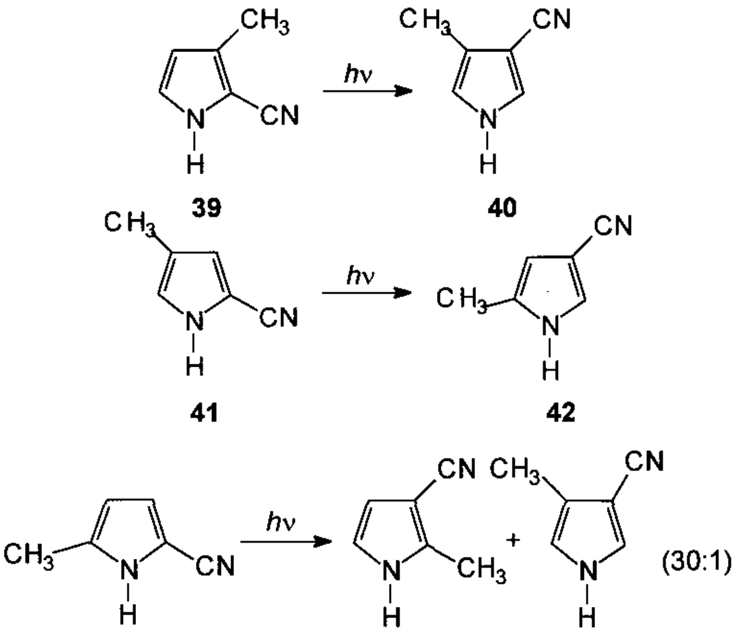
Scheme 5



30 **37** **38** **34**

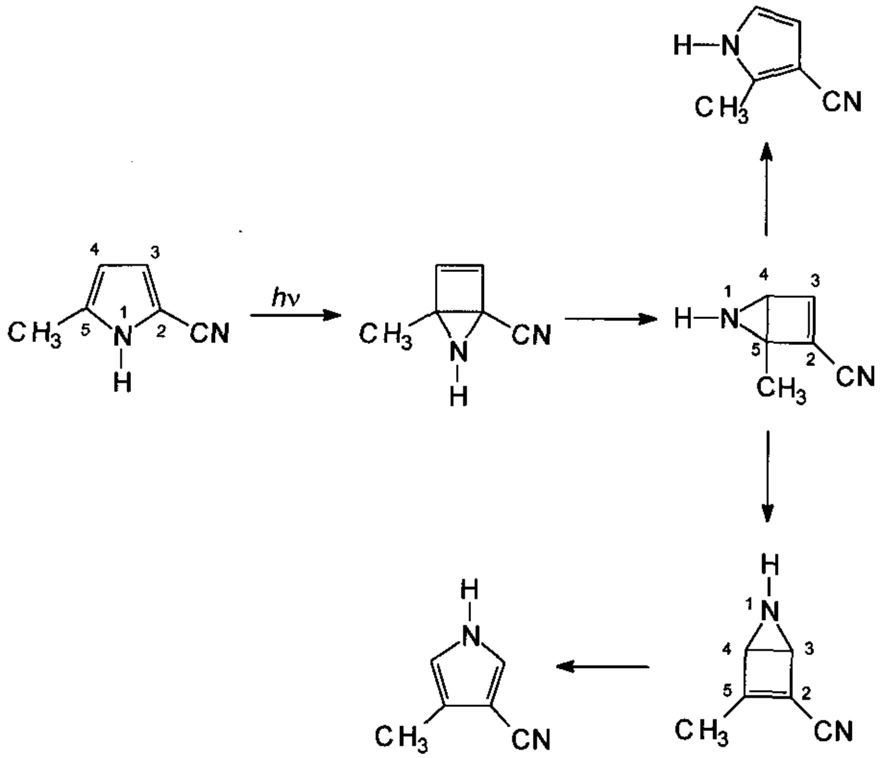
Subsequently, using methyl substituted 2-cyanopyrroles, the results reported in Scheme 6 were obtained.[22]

Scheme 6



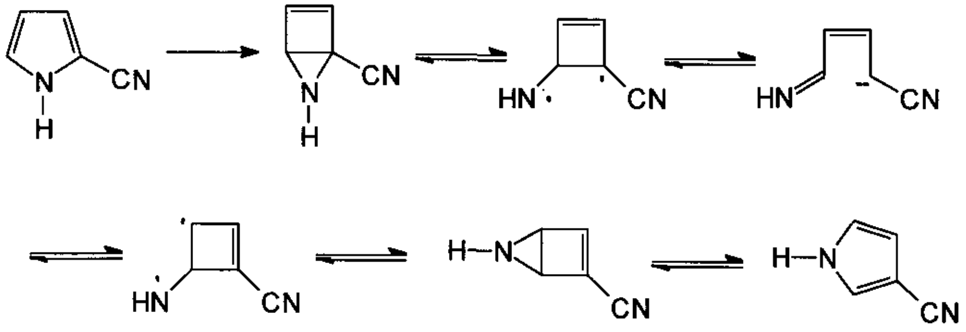
43 **44** **40**

While the obtainement of compound (**40**), (**42**), and (**44**) is in agreement with the mechanism depicted in Scheme 5, the formation of **40** in the last reaction needs a further 1,3-sigmatropic shift.

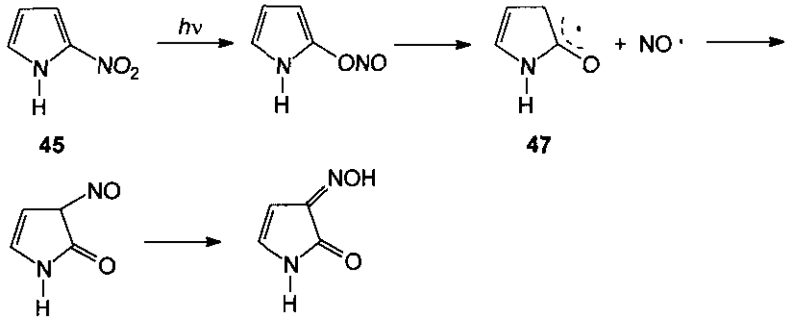


Recently, the 1,3-sigmatropic shift on 2-cyanopyrrole was studied by using the SINDO1 semiempirical method.[23] This study showed that the reaction occurred *via* a π, π* transition and that some biradical intermediates are probably involved in the reaction as reported in Scheme 7.

Scheme 7

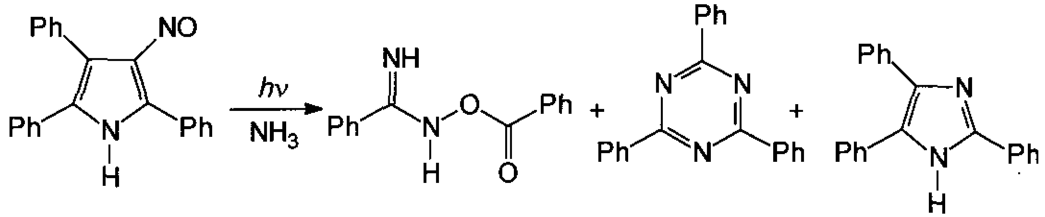


A photorearrangement was observed also in 2-nitropyrrole (**45**).[24,25] Irradiation of **45** in acetone with a medium pressure mercury arc gave **46** in 15% yields. The same trend was observed with 2-nitrofuran.[18] ESR spectrum did not show any hydrogen abstraption reaction. The reaction can be explained by a initial rearrangement of the nitro group followed by the formation of radicals (i.e. **47**) and recombination in C-3 to give **46**.

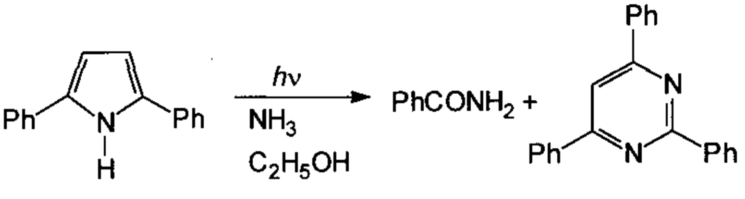


45 **47** **46**

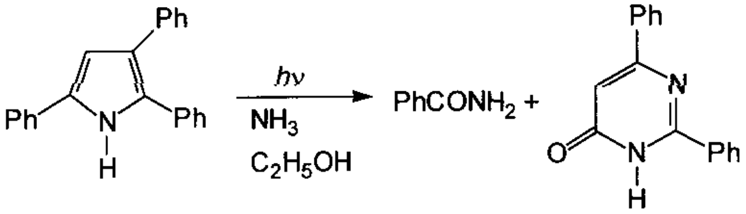
Photorearrangements were observed also in bi-, tri- and tetraphenylpyrroles. When 3-nitroso-2,4,5-



48 **49** **50** **51**



52 **53**



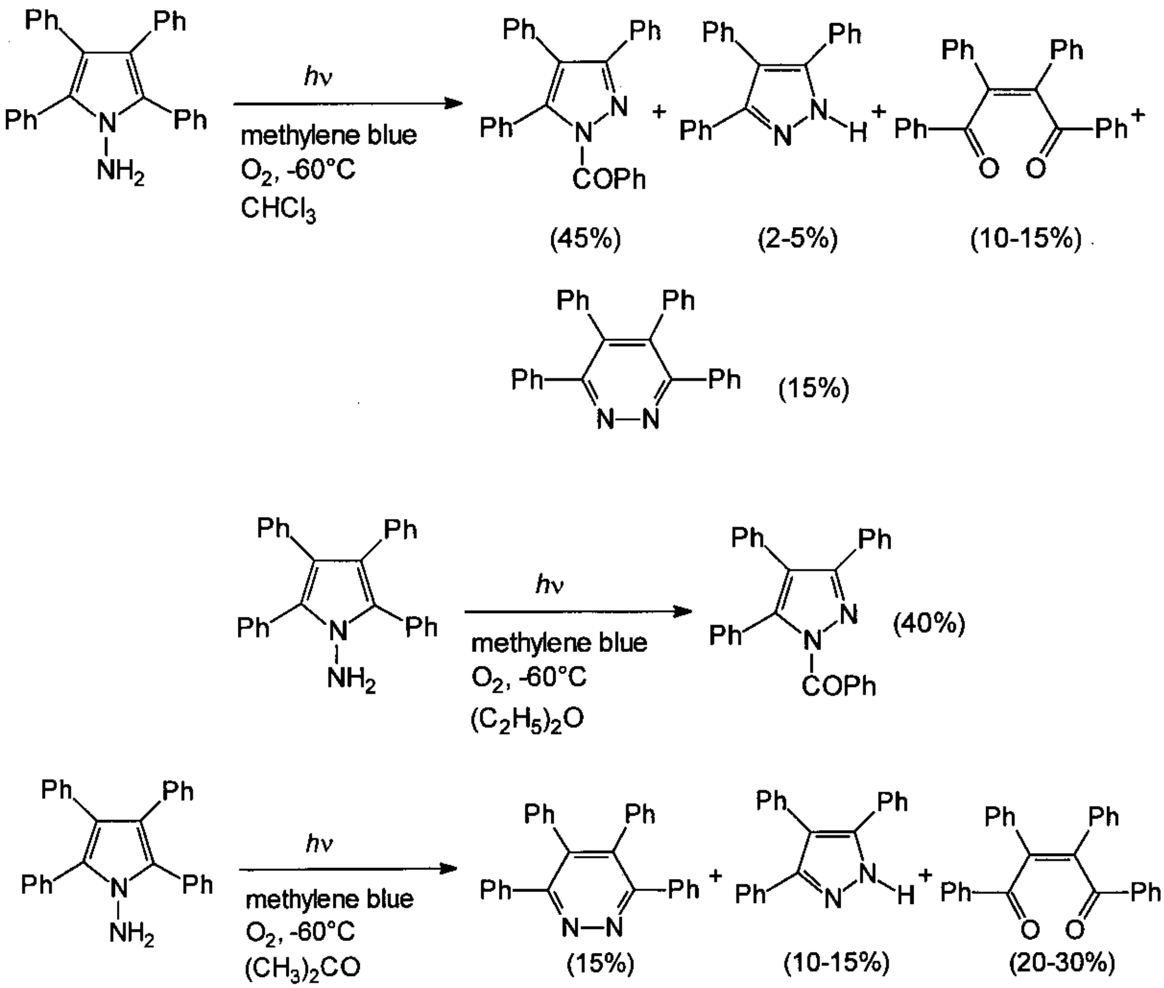
54 **55**

triphenylpyrrole was irradiated in ammonia, benzamidine benzoate was observed but also the new heterocycles (**50**) and (**51**).[26] 2,5-Diphenylpyrrole and 2,3,5-triphenylpyrrole, when irradiated in the presence of ammonia, gave the corresponding pirimidine derivatives.[27]

Irradiation of *N*-ammino-2,3,4,5-tetraphenylpyrrole in several solvents gave 2,3,4,5-tetraphenylpyrrole.[28] However, when the reaction is performed in oxidative medium in the presence of methylene blue and oxygen at - 60 °C, a mixture of pyrazole and pyridazine derivatives together with dibenzoylstilbene was obtained (Scheme 8).

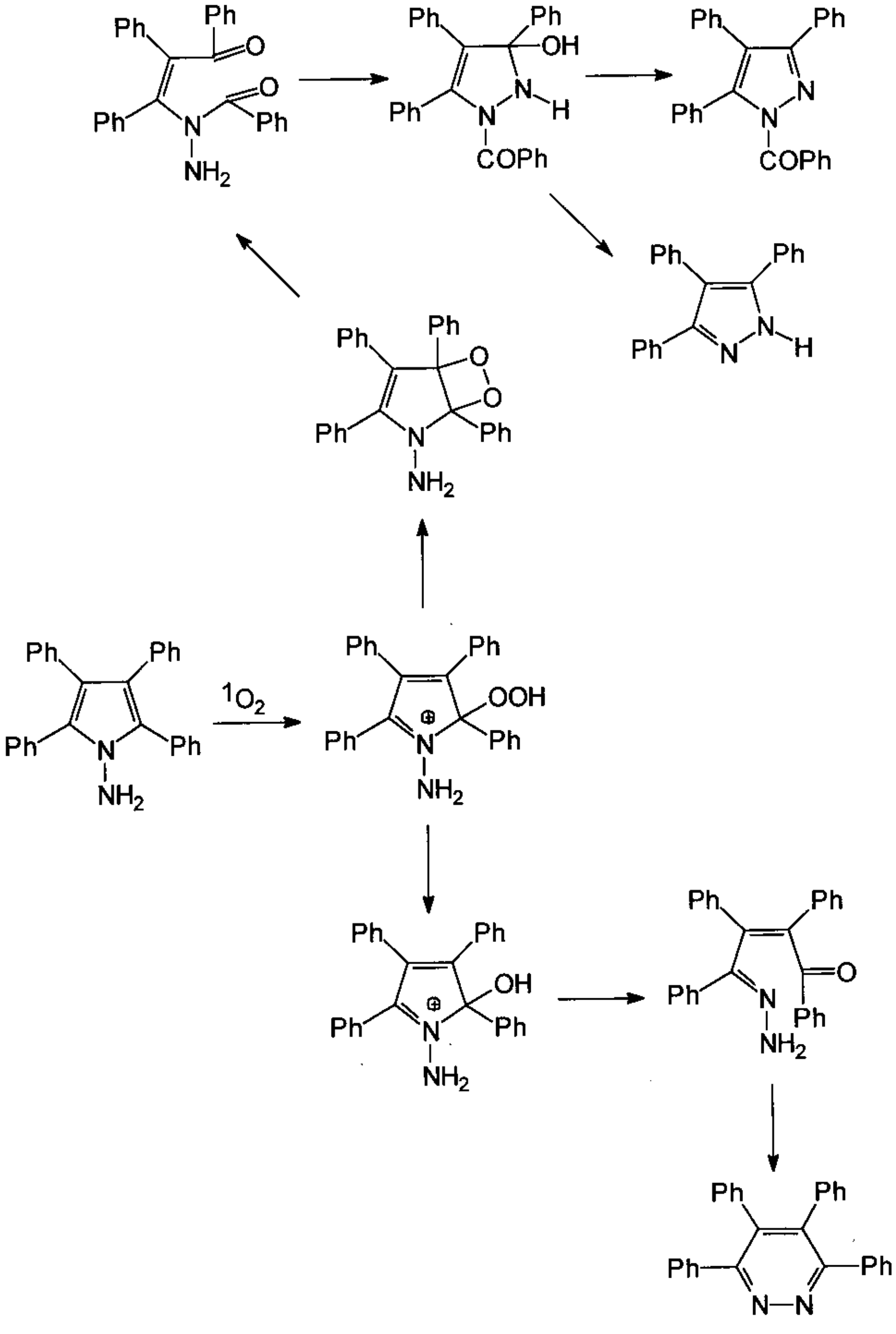
The mechanism of this reaction can be explained considering the formation of a hydroperoxide (Scheme

Scheme 8

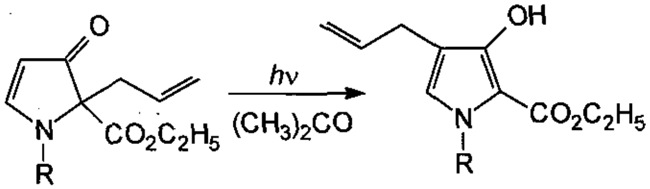


9). Compound (**56**) was irradiated at λ > 280 nm but only a slow decomposition of the starting material was observed.[29] Using acetone as sensitizer the pyrrole (**57**) was obtained through an energy transfer

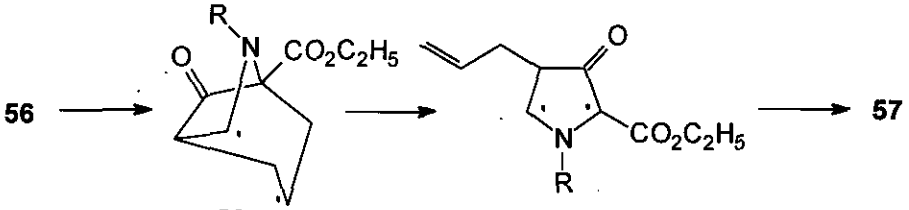
Scheme 9



process. When positions at C-4 and C-5 were substituted no reaction was observed. The first step could be a 2+2 cycloaddition reaction to give a biradical (**58**) that did not give ring closure but a transposition reaction to **59** where the radical is stabilized by the carboester group.

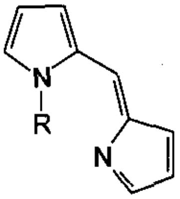


56 **57**



58 **59**

Finally, the pyrrole (**60**) did not give any reaction but only *Z,E* isomerization when irradiated in hexane or carbon disulfide at 0 - 10 °C.[30]



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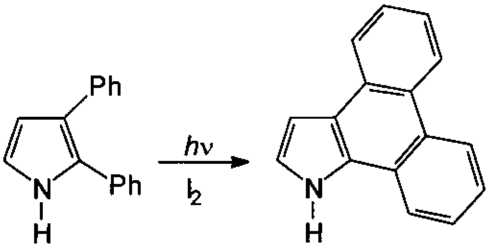
5. PHOTOSUBSTITUTIONS

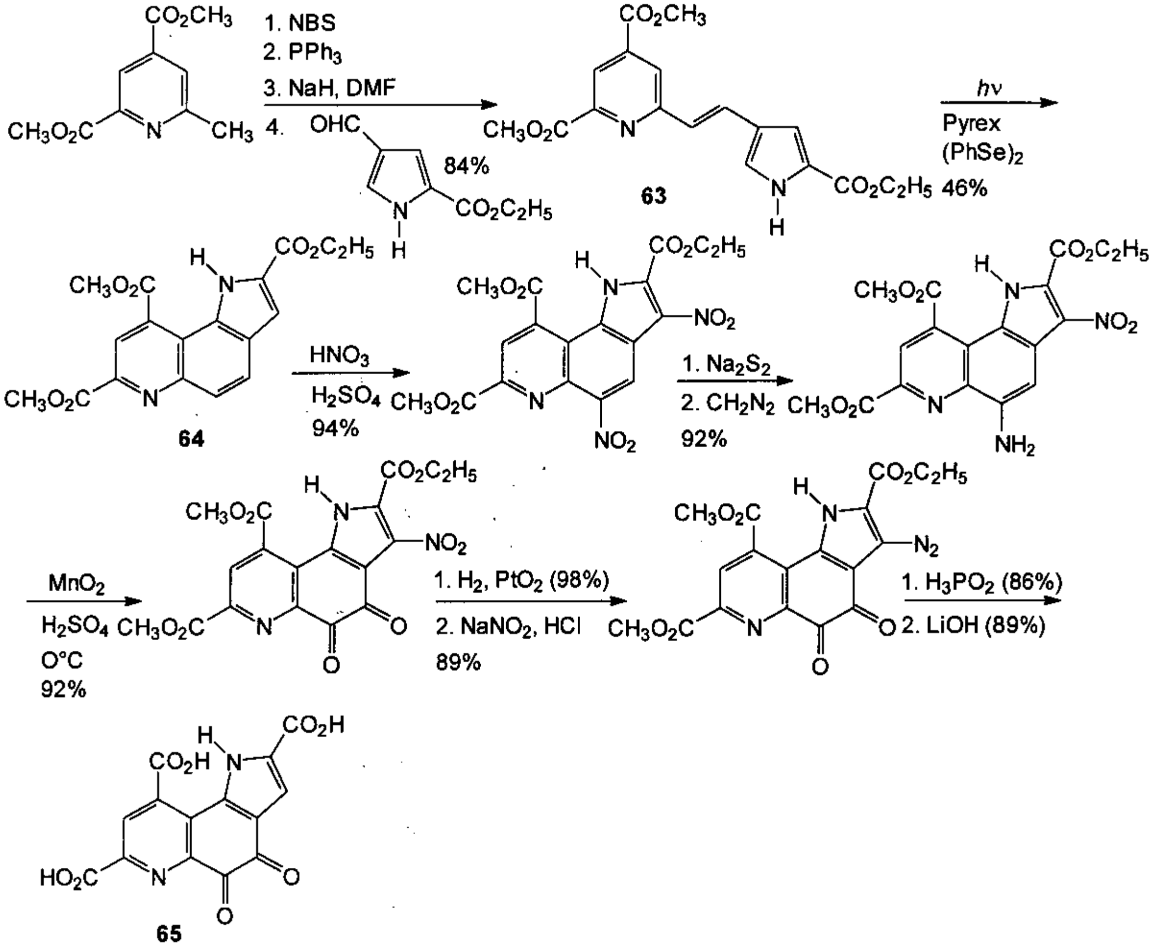
5.1 INTRAMOLECULAR ARYLATIONS

The photocyclization of 1,2-diarylethylenes is a well known reaction and several reviews appeared in literature on this field.[31-33] This type of reaction has been used also on pyrrole derivatives. 2,3-Diphenylpyrrole (**61**) gave the indole derivative (**62**) when irradiated in cyclohexane in the presence of iodine.[34]



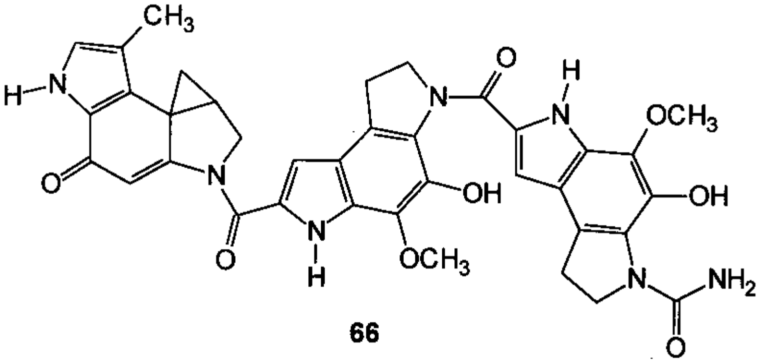
61 **62**

Scheme 10



In the compound (**61**) not only the ethylenic part of the pyrrole moiety but also pyrryl ethylenes were used as starting materials. In a project devoted to the synthesis of coenzime methoxatin (**65**) the key-step for the skeleton synthesis was the cyclization of a 3-pyrrylethylene derivative (Scheme 10).[35,36]

In this case, the cyclization of **63** required the presence of both diphenyldiselenide and very long irradiation time (3 - 4 weeks) to give **64**. In the synthesis of units B and C of antitumor agent CC-1065 (**66**) and ofthe related substances PDE-I (**67**) and PDE-II (**68**) that were able to inhibit cyclic adenosine-3',5'-monophosphate phosphodiesterase and showed a low toxicity, the photocyclization of pyrrylethylenes has been investigated with care.



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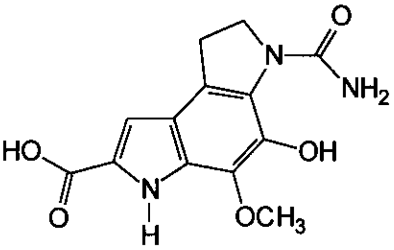

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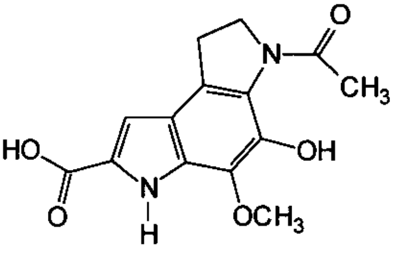

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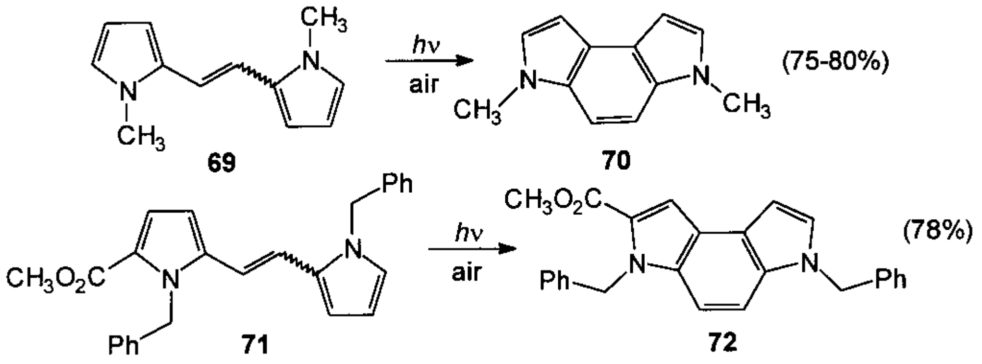
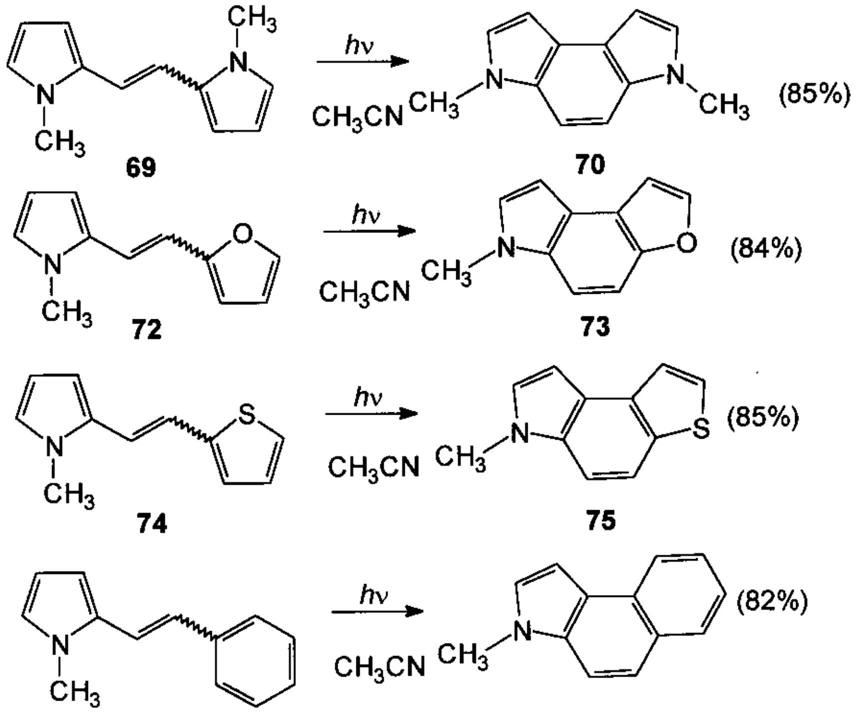
1,2-Dipyrryl derivatives (**69** and **71**) can be cyclized when irradiated in a Pyrex tube in the presence of air. The reaction can be performed also in the presence of a thiophene, a furan or a simple aromatic ring in the molecule.[37] However, this reaction is not useful for preparative purpose. In the presence of air the extensive oxidation of the indolic product was observed.

When the reaction was performed in the presence of 5% Pd/C and with a nitrocompound to avoid reduction of the carbon carbon double bond, the reaction seems to be a very useful and general synthetic procedure (Scheme 11).[38]

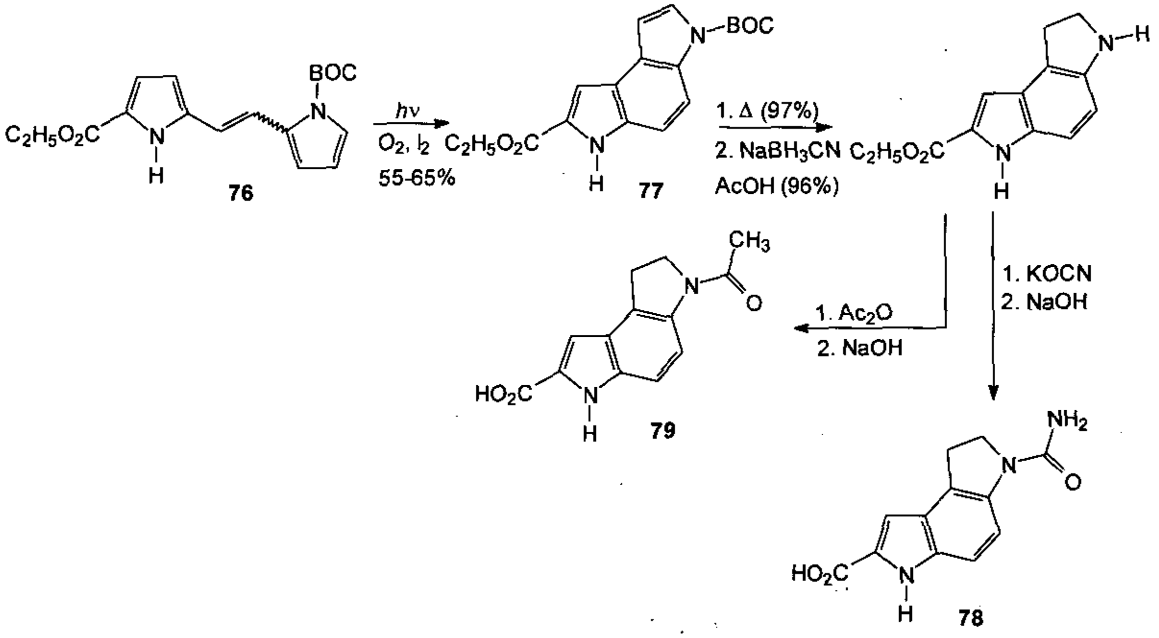


Scheme 11



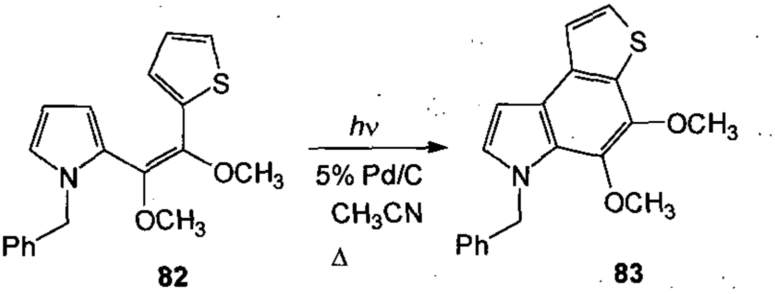
Unfortunately, this reaction did not work with *N*-BOC derivative (**76**). This reaction worked in moderate yield in the presence of air and the cyclization product (**77**) was used in the synthesis of dehydroxy PDE-I and PDE-II (**78** and **79**), respectively (Scheme 12).[39]

Scheme 12



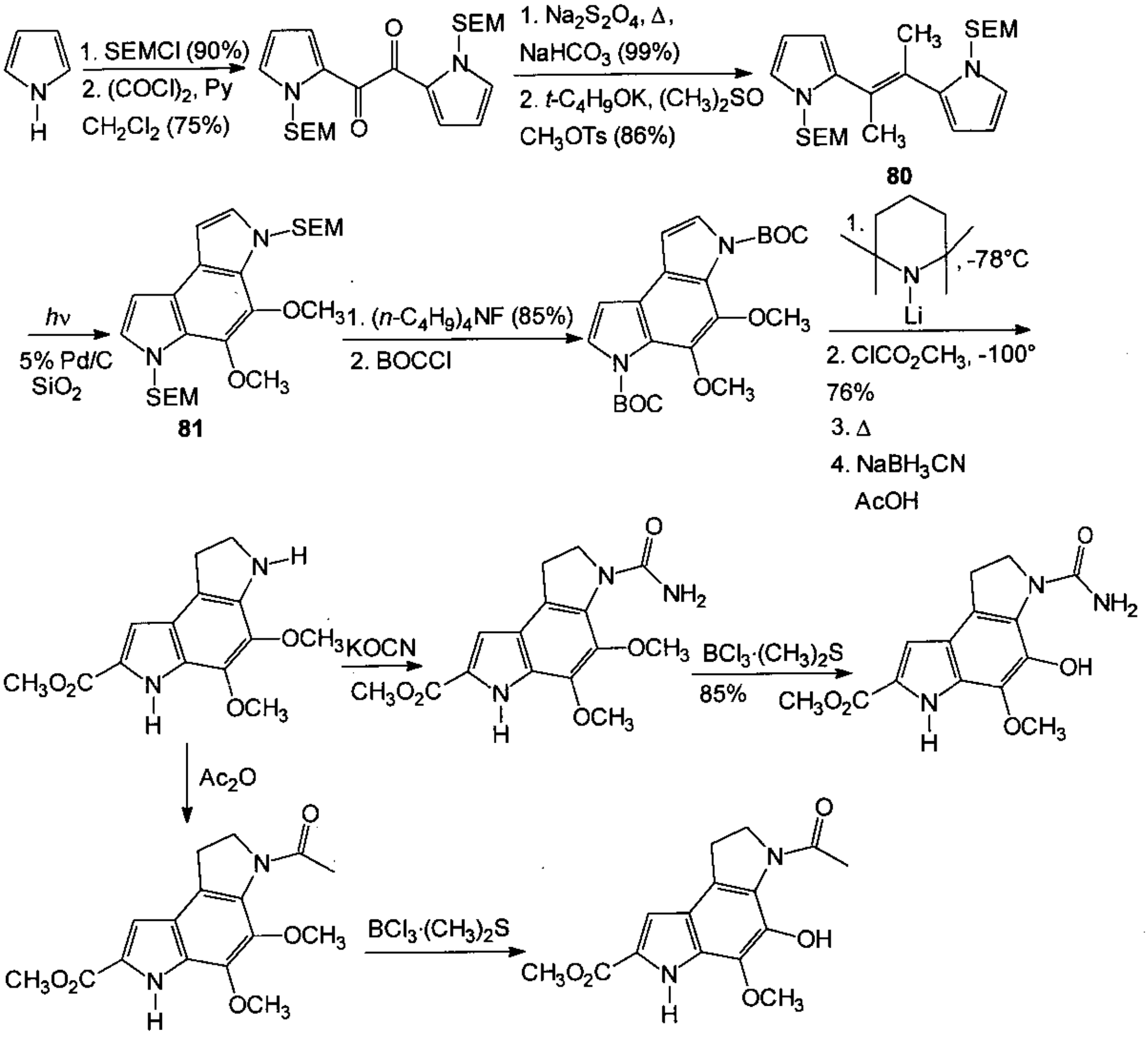
In Scheme 13 the synthesis of PDE-I and PDE-II using the described photochemical approach is depicted. In this case the photochemical reaction was performed on a dimethoxy derivative (**80**). Using this substrate the above described procedure using 5% Pd/C seems to work very well.[40]

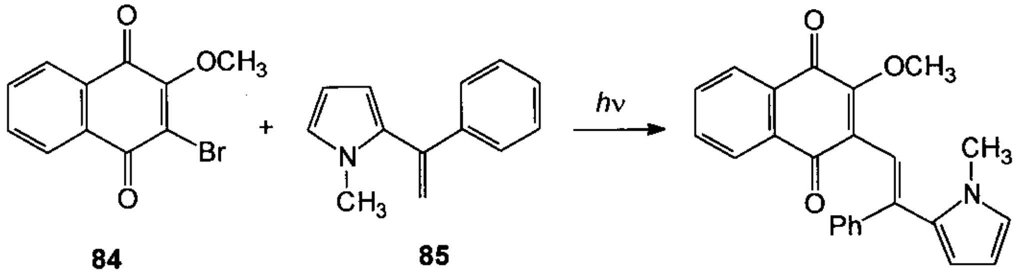
The same synthetic scheme was used to synthesize thiophene analogs of PDE-I and PDE-II. In this case the photochemical reaction on **82** by using Pd on carbon methodology gave **83** in 64% yield.[41]

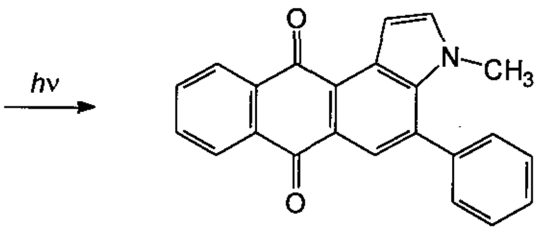


The reaction of the haloquinone (**84**) with the pyrryl derivative (**85**) gave the ethylenic coupling product that, in the reaction mixture, underwent a cyclization reaction to give **86**.[42-44]

Scheme 13


1. SEMCl (90%)
2. (COCl)$_2$, Py
CH$_2$Cl$_2$ (75%)
SEM
1. Na$_2$S$_2$O$_4$, Δ,
NaHCO$_3$ (99%)
2. t-C$_4$H$_9$OK, (CH$_3$)$_2$SO
CH$_3$OTs (86%)
CH$_3$
80
hν
5% Pd/C
SiO$_2$
OCH$_3$
81
1. (n-C$_4$H$_9$)$_4$NF (85%)
2. BOCCl
BOC
1. Li, -78°C
2. ClCO$_2$CH$_3$, -100°
76%
3. Δ
4. NaBH$_3$CN
AcOH
CH$_3$O$_2$C
KOCN
NH$_2$
BCl$_3$·(CH$_3$)$_2$S
85%
OH
Ac$_2$O
BCl$_3$·(CH$_3$)$_2$S


OCH$_3$
Br
84
+
CH$_3$
85
hν
Ph

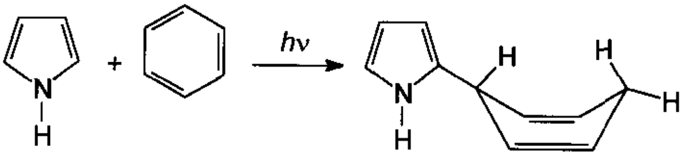


86

Nanosecond laser excitation showed that quinones and pyrroles can interact to give the corresponding pyrryl radical cation. This step could be the basis of the coupling reaction.[45]

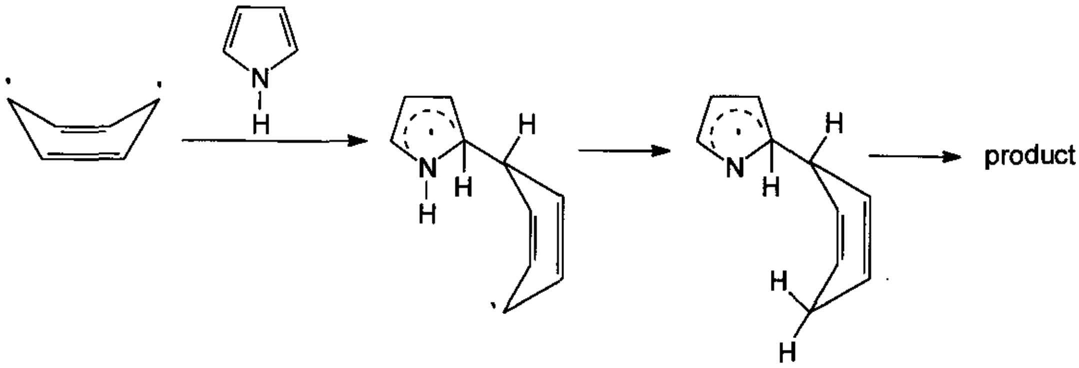
5.2 INTERMOLECULAR ARYLATIONS

The reactions described before clearly showed that the pyrrole ring can interact with an aromatic ring under photochemical conditions. The direct photochemical reaction of pyrrole with benzene gave the coupling product (**87**).[46,47]



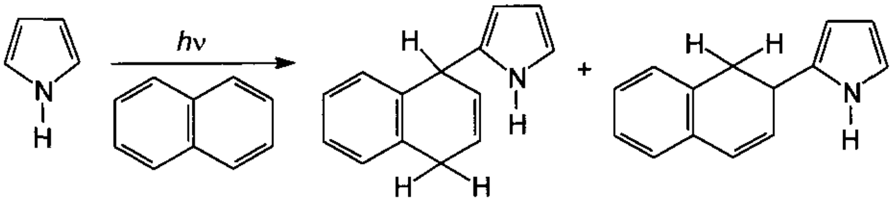
87

In this reaction there is not direct irradiation of pyrrole. The reaction seems to involve the excitation of benzene or the irradiation of a 1:1 complex between pyrrole and benzene,[48] as described in the following



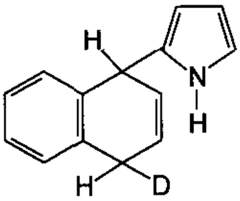
Scheme.[46]

Another key-step in this mechanism is the intramolecular shift of *N*-hydrogen on cyclohexadiene radical intermediate. In agreement with this hypothesis is the fact that *N*-methylpyrrole does not react under the same reaction conditions. Interaction between pyrrole and aromatic compounds was found also with naphthalene. In this case, upon irradiation at λ > 300 nm, two reaction products (**88** and **89**) were obtained.[49,50]



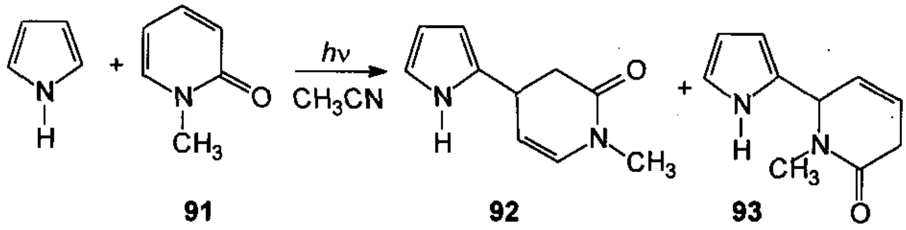
88 (64%) **89** (25%)

The best solvents for this reaction were *n*-hexane or benzene while it did not work well in acetonitrile and methanol. The reaction occurred *via* the lowest excited singlet state of naphthalene: in fact, both benzophenone and acetophenone were not able to sensitize the reaction while pyrrole was able to quench naphthalene fluorescence. Finally, by using *N*-D-pyrrole, the product (**90**) was isolated in agreement with the reaction mechanism previously described for benzene coupling. The data were in agreement with a mechanism involving the previous formation of an exciplex or a radical ion pair between pyrrole and naphthalene that underwent a proton transfer followed by the formation of carbon - carbon bond. The formation of an exciplex between 2,5-dimethylpyrrole and naphthalene was observed at room temperature and at 15 K in non polar solvents.[51] It showed an emission band at 390-400 nm with $\tau = 85$ ns.



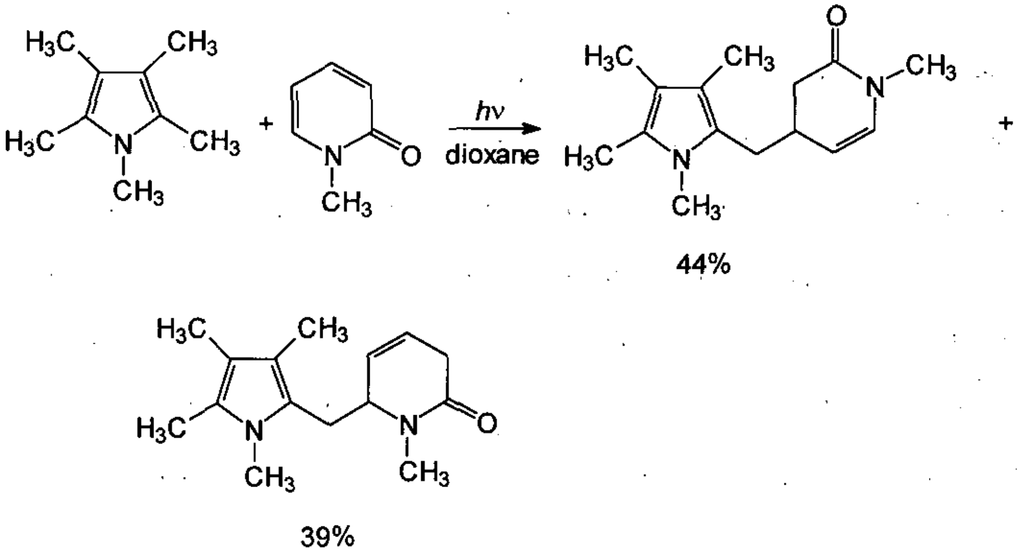
90

The photochemical coupling between pyrrole and pyridine derivatives was also described. The reaction of pyrrole with *N*-methyl-2-pyridone (**91**) gave a mixture of two products (**92**) and (**93**) in 19 and 23% yields, respectively.[52]



91 **92** **93**

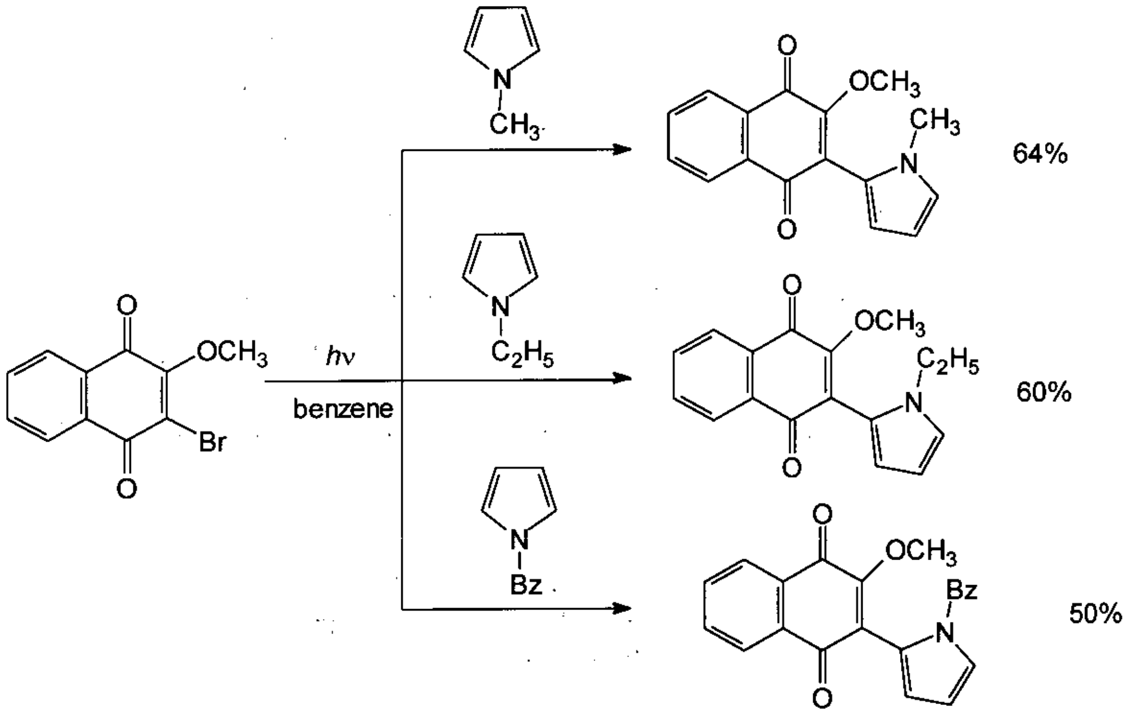
The same results were observed using 2,5-dimethylpyrrole where the coupling occurred in β positions. On the contrary, *N*-methylpyrrole did not give any reaction in agreement with the previous reported data. Using 1,2,5-trimethylpyrrole or 1,2,3,4,5-pentamethylpyrrole as a substrate, photochemical coupling products were obtained but in this case these substrates showed participation of a methyl group.[53] A SET mechanism was also proposed.



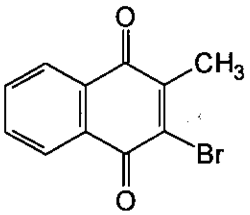
In the case of photocatalyzed porphyrin synthesis, an energy transfer process between two pyrryl species accounted for the catalytic effects of light. However no chemical reaction was observed.[54]

Pyrroles were used as aromatic partners in arylation reactions with halogeno derivatives. The quinone (**84**) reacts with pyrrole derivatives giving the corresponding pyrryl derivatives (Scheme 14).[55]

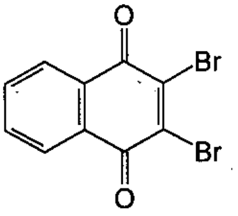
Scheme 14



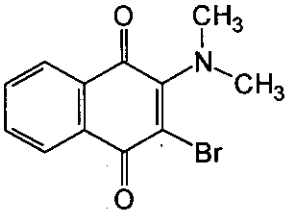
The reaction occurred also with other quinones, such as **94** or **95**, while it did not work with **96** bearing an electron donating group.



94



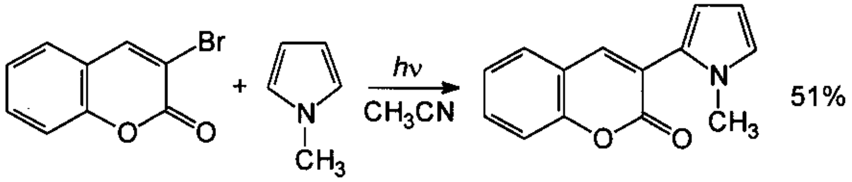
95



96

The reaction occurs *via* the formation of a charge transfer complex at the ground state. For example, **84** gives a complex with *N*-methylpyrrole that shows an absorption maximum at 449 nm.

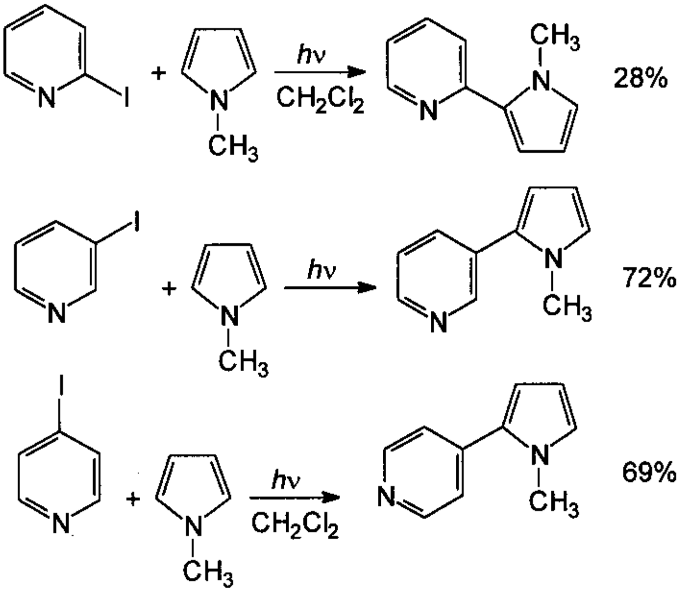
Several examples are available on the photochemical arylation on halogenoheterocyclic compounds. The lactones (**97**) reacted with *N*-methylpyrrole to give the coupling product (**98**), while pyrrole did not give the same reaction.[56] The same results were obtained using iodo substituted coumarins.[57]



97 **98**

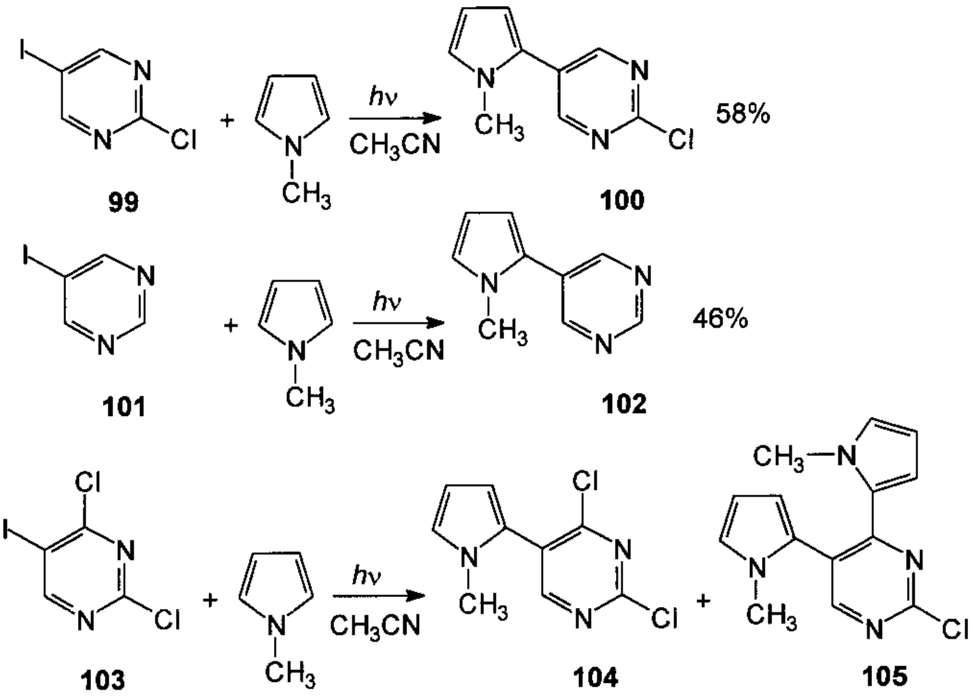
Halopyridine derivatives gave arylation products when irradiated in the presence of pyrryl derivatives. Nevertheless, 2-iodopyridine gave low yields of the coupling product when *N*-methylpyrrole was used as substrate, while 3-iodopyridine gave very high yields of the coupling product (Scheme 15).[58-60]

Scheme 15

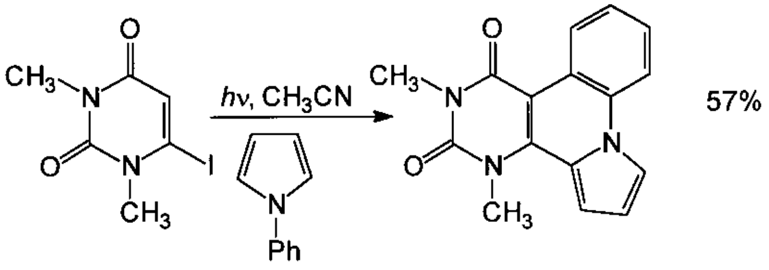


The same results were obtained with quinoline derivatives.[61] Pyrimidine derivatives gave also coupling products.[62] In this case, chloro-iodo derivatives were used as a substrate showing that usually chlorine atom is not involved in the reaction. Neverthess, 2,4-dichloro-5-iodopyrimidine gave traces of other products where **105** was identified (Scheme 16).

Scheme 16

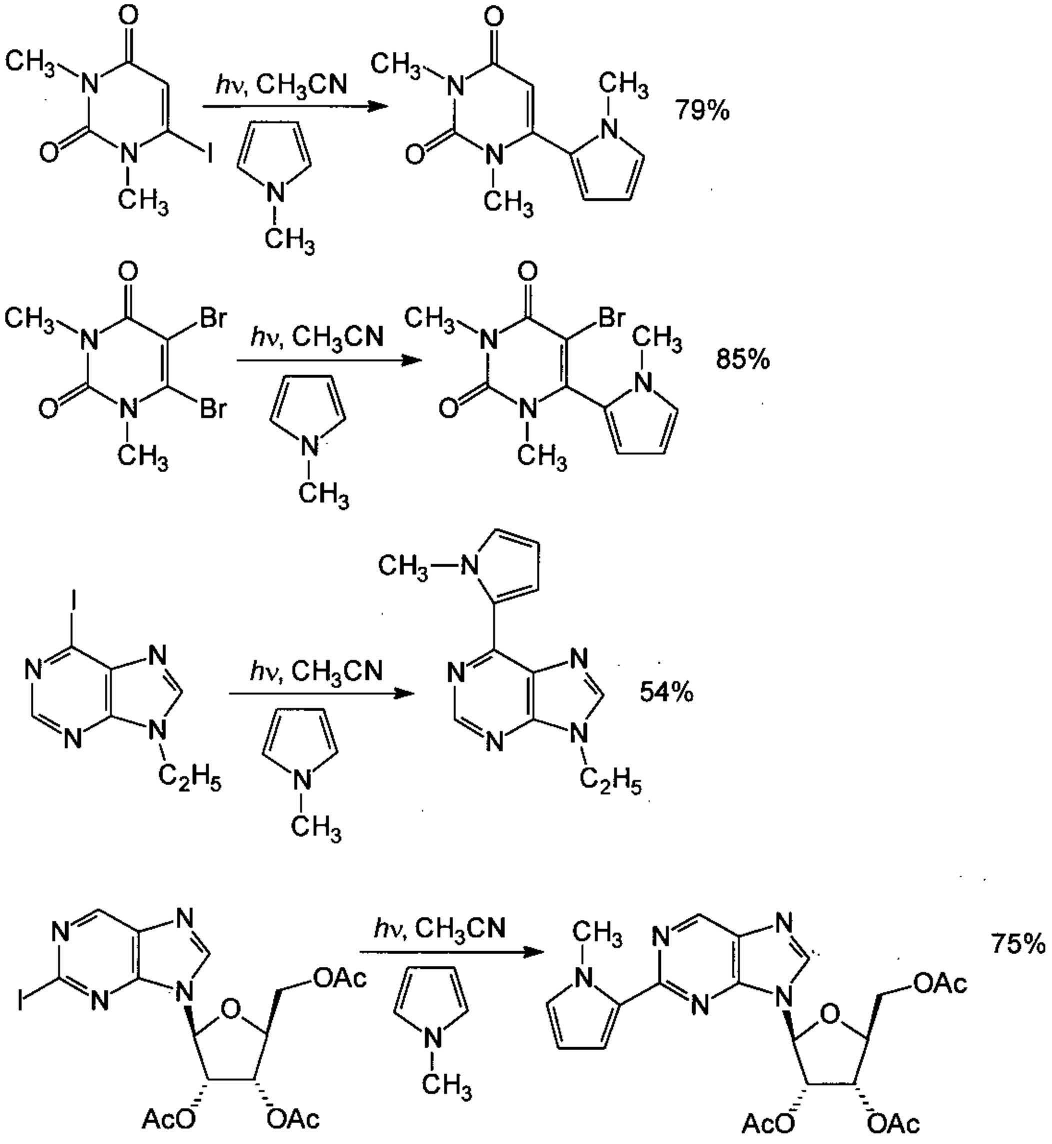


The same trend was observed using halogenouracil derivatives or halogenopurines as substrates, as reported in Scheme 17.[63-65] In the case of halogenouracil derivatives, when *N*-phenylpyrrole was used as the reagent, double arylation reaction was observed to give condensed products.[63]

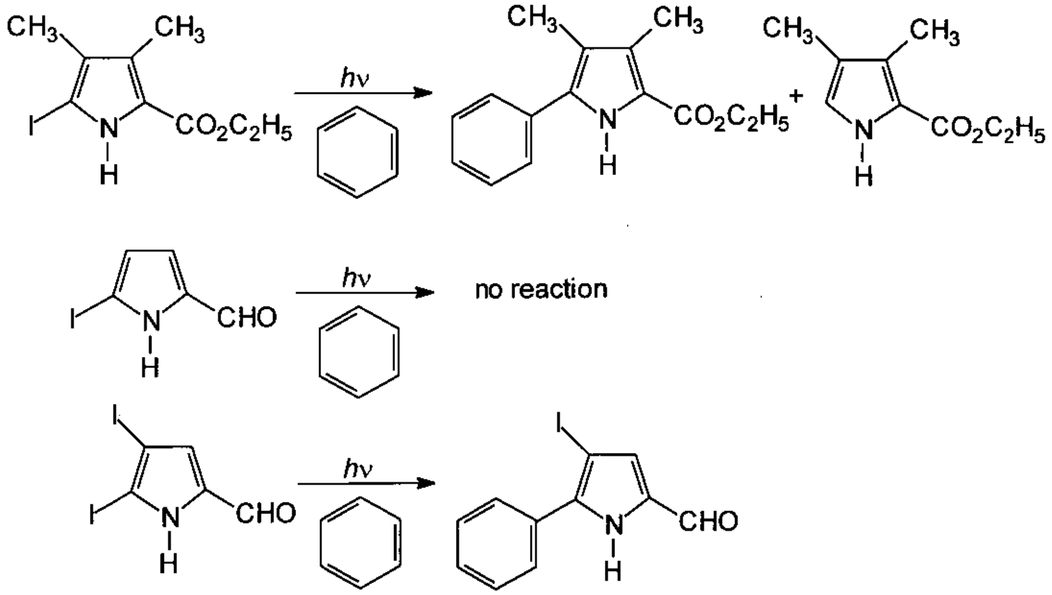


Above we have reported that pyrrole derivatives were used as reagent in the presence of halogenoaryles. In literature we did not find any report on arylation reactions of halogenopyrroles. Only very few data are

Scheme17



available: when ethyl 5-iodio-3,4-dimethyl-pyrrole-2-carboxylate was irradiated in benzene the coupling product was obtained in 50% yield in the presence of the same yield of dehalogenation product. On the contrary, 5-iodio-pyrrole-2-carbaldehyde did not give this reaction at all, while the corresponding 4,5-diiodio derivatives gave the corresponding coupling product in five position.[66]



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