

PHOTOCHEMICAL REACTIONS INVOLVING PYRROLES - PART II

Maurizio D'Auria

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100

Potenza, Italy

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

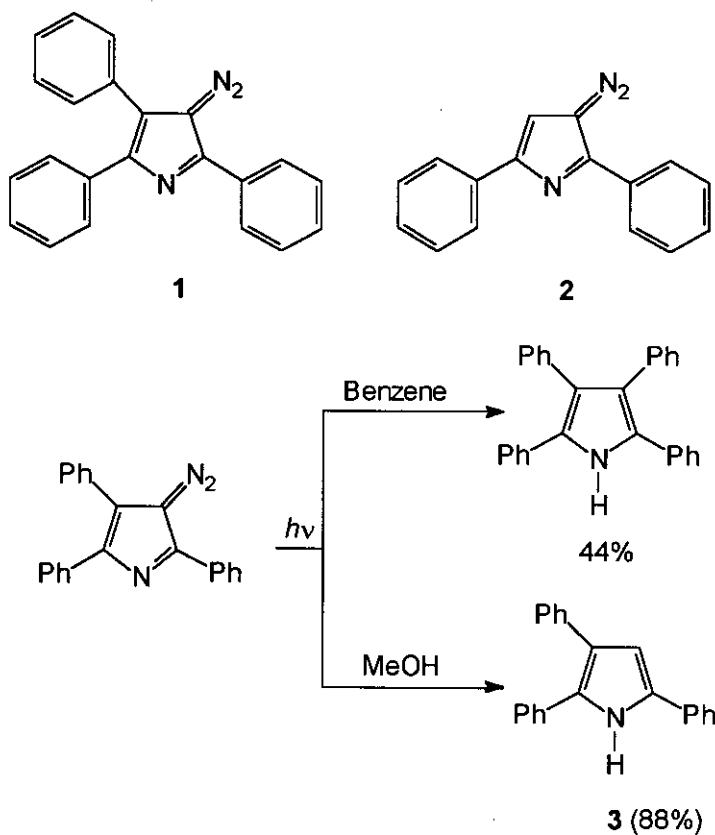
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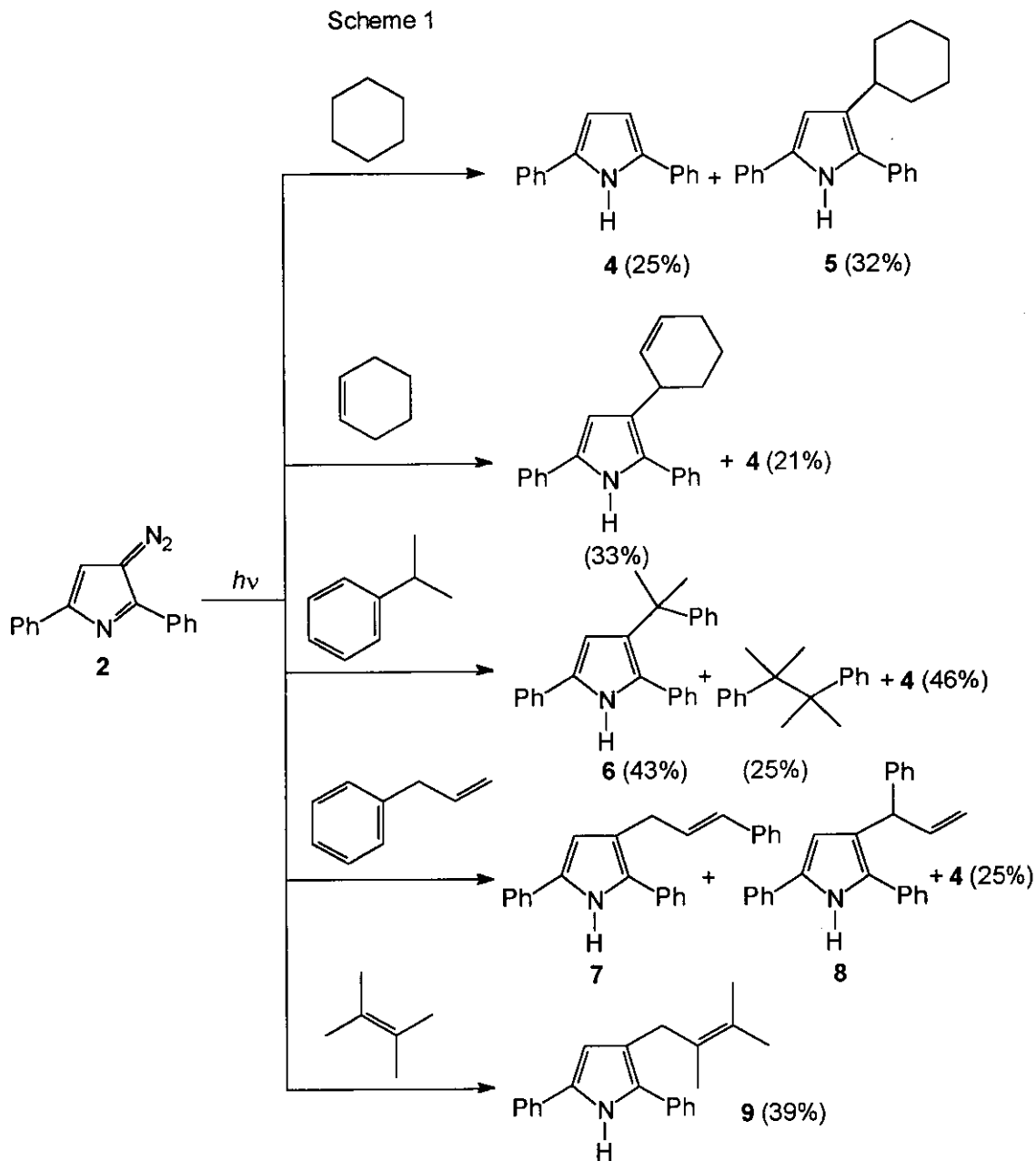
1. PHOTOSUBSTITUTIONS

1.1 PHOTOCHEMICAL REACTIONS OF DIAZOPYRROLE DERIVATIVES

The photounstability of diazopyrrole derivatives was described several years ago. 3-Diazo-2,4,5-triphenylpyrrole (**1**) and 3-diazo-2,5-diphenylpyrrole (**2**) were described as very unstable in the presence of light.^{1,2}

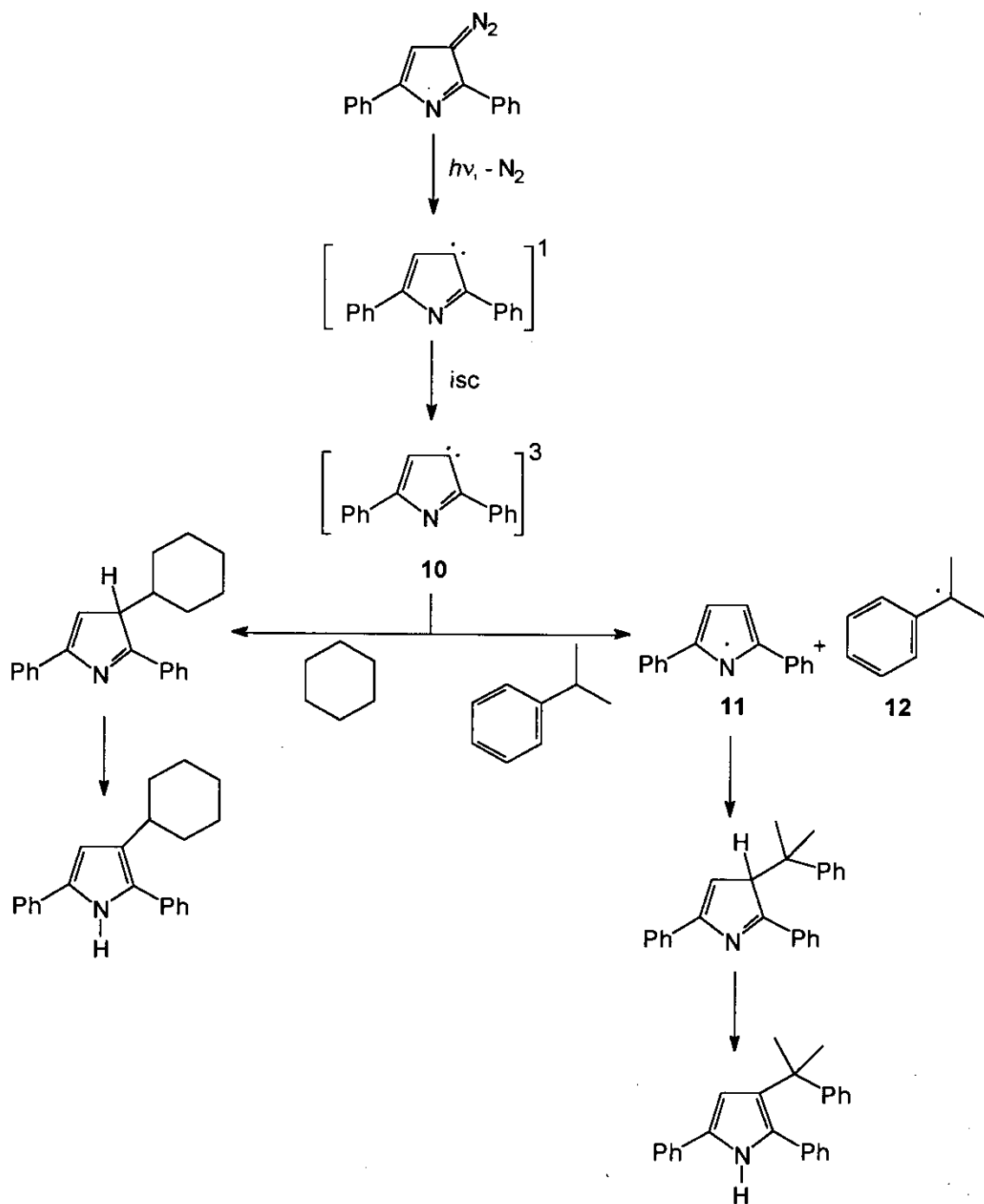


Nevertheless, in 1968 some authors described that the irradiation of **1** at 360 nm in Pyrex under nitrogen and in the presence of benzene gave tetraphenylpyrrole. Furthermore, the irradiation in methanol gave 2,3,5-triphenylpyrrole (**3**).³ The photochemical behaviour of **2** was the object of an intense study. The irradiation of **2** in cyclohexane gave a mixture of two products, 2,5-diphenylpyrrole (**4**) and the cyclohexyl substituted compound (**5**) (Scheme 1).⁴



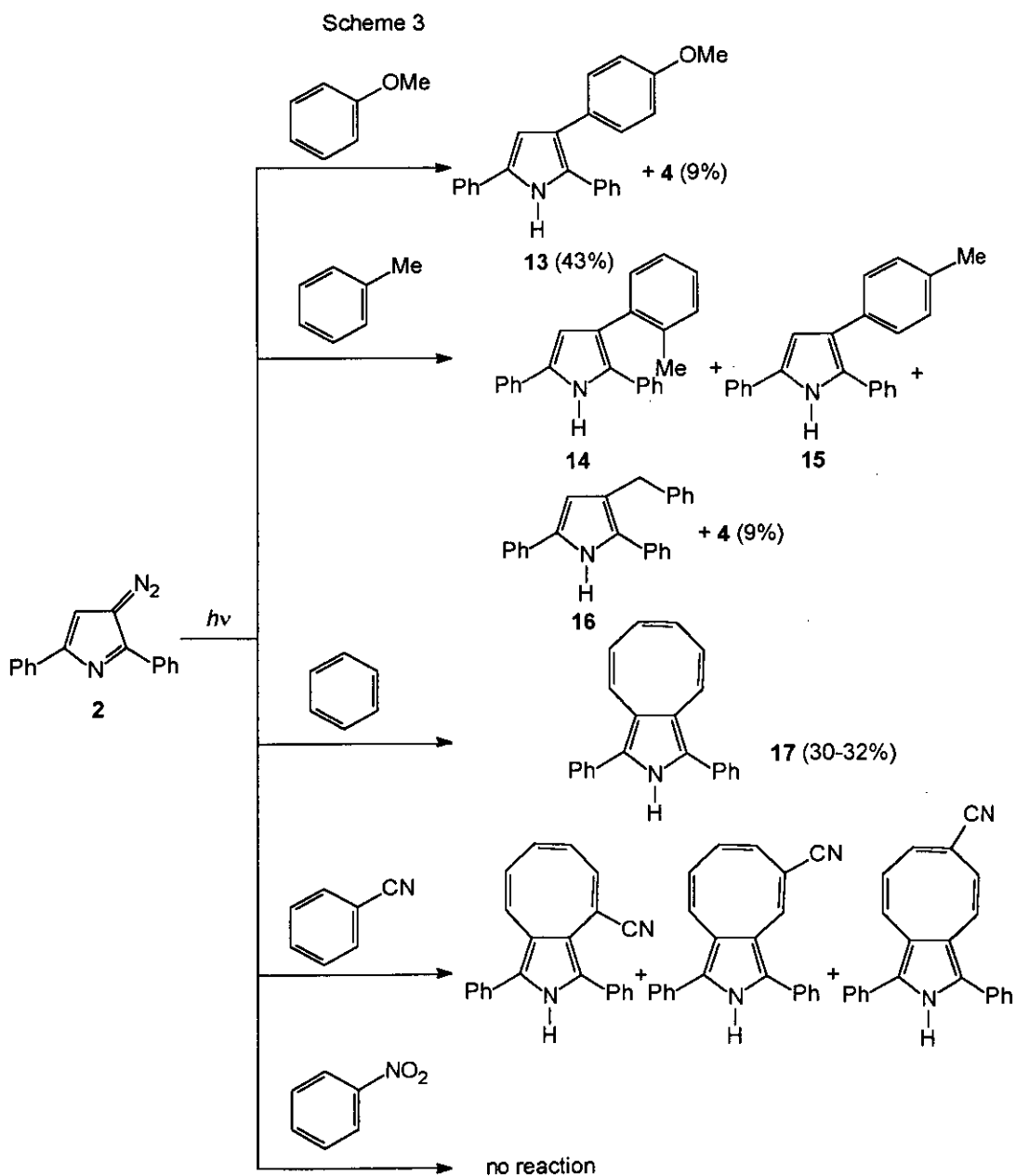
The same trend was observed when the reaction was performed in the presence of cyclohexene. Also the irradiation in the presence of cumene gave the substitution product (**6**) (Scheme 1). 1-Phenylpropene gave a mixture of regioisomeric products with an overall yields of 33%. Finally, 2,3-dimethyl-2-butene gave the substitution product (**9**) in 39% yield. The formation of these products can be explained on the basis of the mechanism reported in Scheme 2. The formation of 2,5-diphenylpyrrole can

Scheme 2

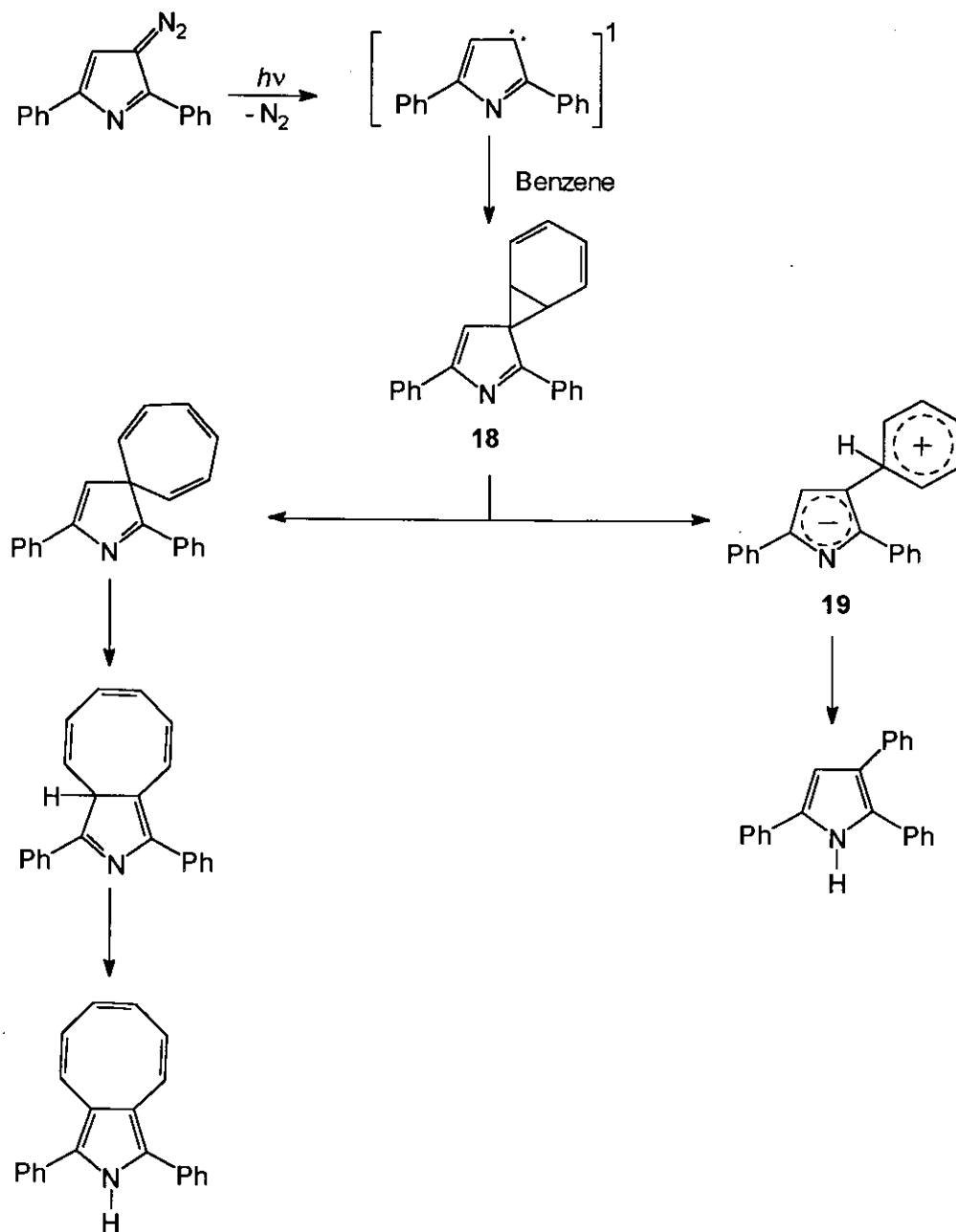


be explained as a product of a hydrogen abstraction from triplet (**10**). The formation of **5** can be explained assuming the presence of an insertion reaction between **10** and cyclohexane followed by a 1,3-sigmatropic

shift of hydrogen. On the contrary, in the presence of a compound able to give stable radical, such as cumene or 2,3-dimethyl-2-butene, hydrogen abstraction to give **11** and **12** can occur. Subsequent recombination of radical fragments and 1,3-sigmatropic shift of hydrogen can account of the formation of the products. The photochemical behaviour observed when the reaction was performed in the presence of aromatic compounds showed some differences (Scheme 3).^{4,5}



Scheme 4



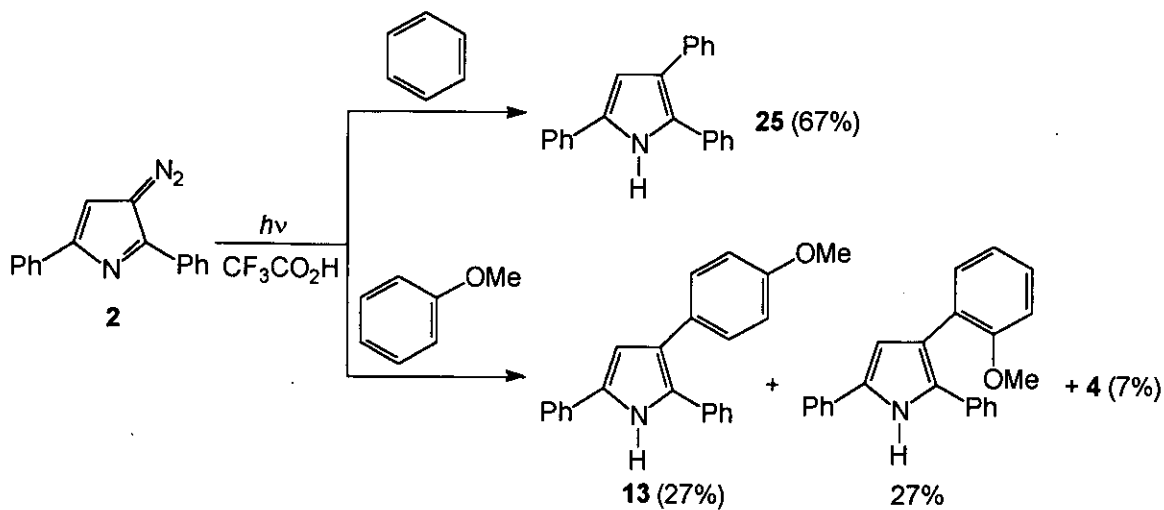
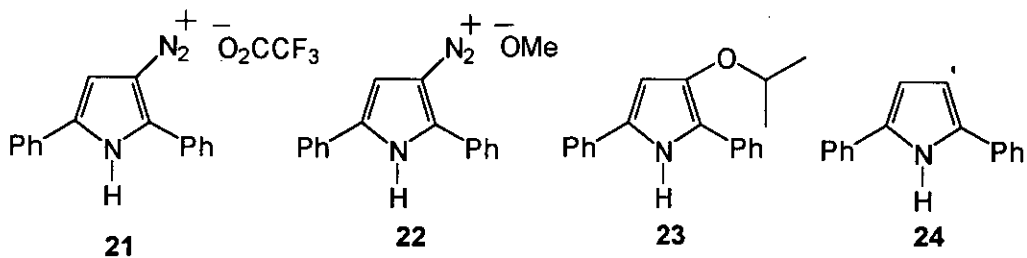
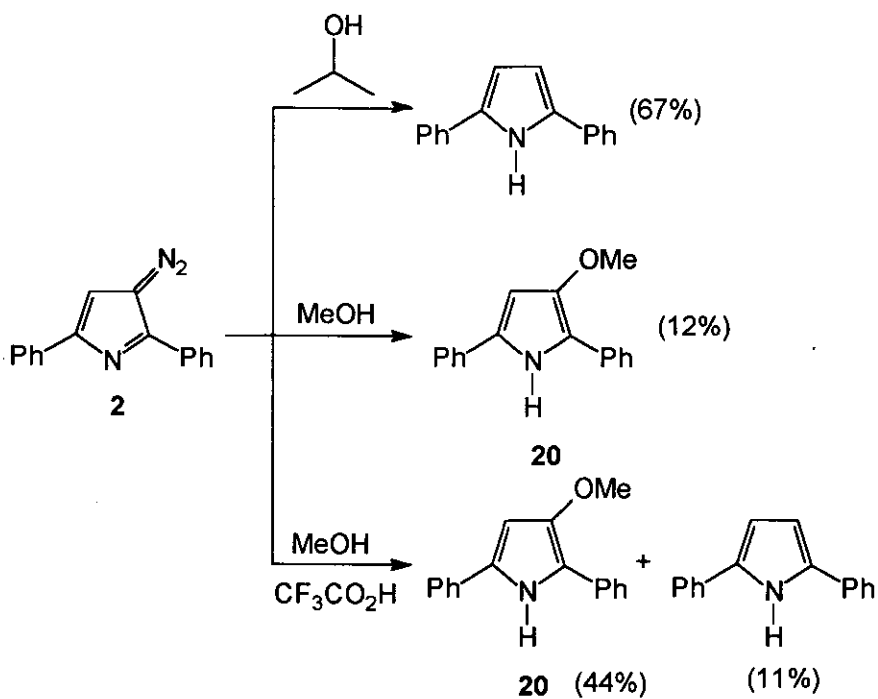
The product of the irradiation of 2 with anisole was apparently a substitution product similar to those described in Scheme 1. Nevertheless, only the *para* substituted compound (13) was obtained. Using toluene, together the usual product (16) also some other substitution products on the aromatic ring were

observed with an overall yield of 34%. In this case the authors observed the formation of a 1:1 mixture of *ortho* and *para* substituted derivatives (14) and (15), while no trace of the *meta* isomer was recovered. This behaviour is not in agreement with a mechanism involving a triplet. Furthermore, when 2 reacted with benzene, a ring enlargement product (17) was isolated in the reaction mixture. The statement that triplet state is not involved in these reactions was demonstrated sensitizing the triplet state with thioxanthone. In this case the reaction with benzene gave 2,3,5-triphenylpyrrole in 45% yields. The photochemical behaviour of 2 with aromatic compounds can be explained on the basis of the hypothesis reported in Scheme 4.

In this Scheme the observed reactivity was understood assuming that singlet (10) can give the addition product (18). The subsequent ring enlargement and transposition can give 17. On the contrary, the opening of the cyclopropyl ring can give 19, a precursor of products of the type of 13.

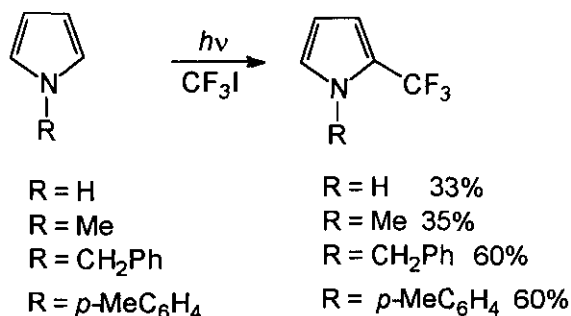
In a research devoted to broaden the synthetic utility of the above described reaction the photochemical behaviour of 2 in the presence of other solvents was studied. Thus, the irradiation of 2 in isopropanol gave 2,5-diphenylpyrrole in 67% yield, while the irradiation in methanol yielded 20 in 12% yield only. Nevertheless, when the reaction was attempted in the presence of trifluoroacetic acid, 20 was obtained in 44% yields.⁴

The need of an acid medium in this reaction allows the authors to admit the formation of 21 and 22 as intermediates. The reaction of 2 in the presence of trifluoroacetic acid in isopropanol showed the formation of an other product, 23, in 24% yield. The same result was obtained using 21 as starting material, showing that this compound is probably involved in this type of reaction. Finally, the reaction of 2 in the presence of trifluoroacetic acid was studied using aromatic compounds as reaction partners. In this case, only coupling products were obtained.⁴ All these reactions seems to be in agreement with the mechanism involving the formation of a radical intermediate (24) that, then, was trapped by the electron rich substrates.

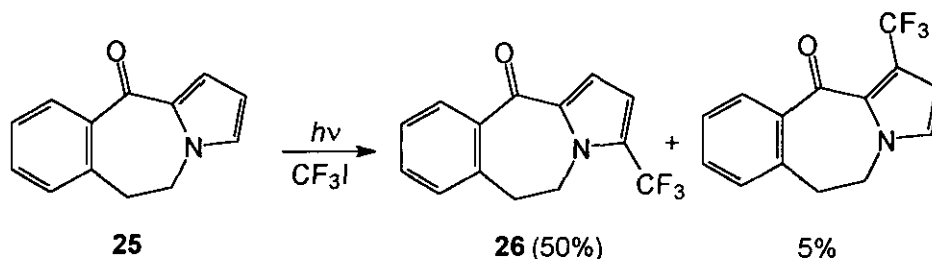


1.2 TRIFLUOROMETHYLATION

Several studies were carried out on trifluoromethylation reaction of pyrroles. Trifluoromethyl derivatives can be considered interesting targets because both trifluoromethyl moiety can be converted into the corresponding ester and the presence of this functional group increases the lipophilic properties of the molecules and then can increase the biological activities of the same molecules. Pyrrole and *N*-methylpyrrole reacted with trifluoromethyl iodide in a sealed tube under vacuum when irradiated with a low pressure mercury arc for two days.⁶



On the other hand, *N*-benzyl and *N*-*p*-tolylpyrrole reacted with CF₃I in acetonitrile in the presence of pyridine for 30 h giving good yields of the corresponding trifluoromethyl derivatives.⁷ The same reaction can be performed on **25** giving **26**, with the presence of a small amount of regioisomeric product.⁷

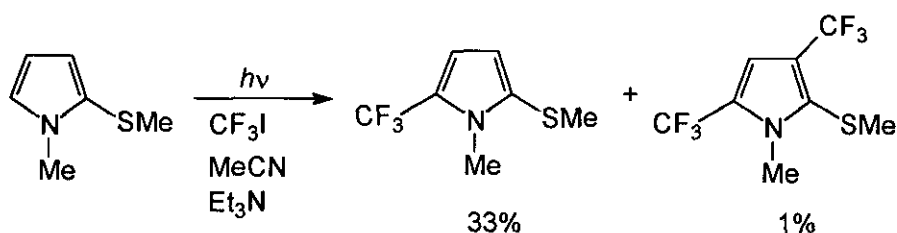


More recently a study of the reaction of *N*-methylpyrrole with trifluoromethyl iodide in acetonitrile in the presence of a base showed that, by using 1.2 equivalents of CF₃I, the trifluoromethyl derivatives was

obtained in 37% yield while, by using 2.5 equivalents of the reagent, the yields of the product decreased at 32% showing the formation of 2,5-ditrifluoromethyl-*N*-methylpyrrole in *ca.* 7% yield.⁸

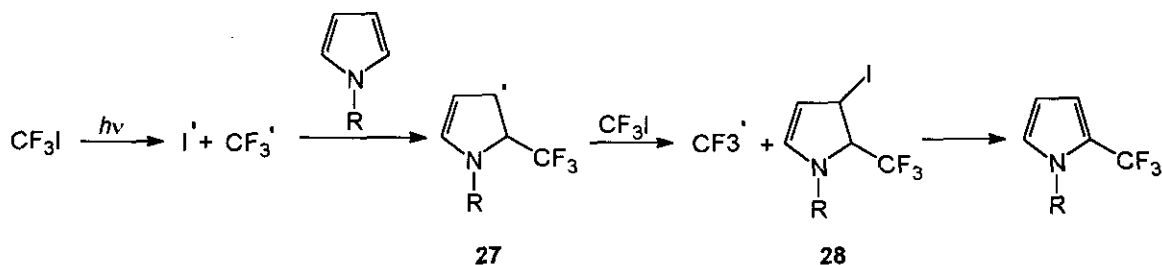
When 2-methylthio-*N*-methylpyrrole was used as substrate in the presence of 2.5 equivalents of the reagent, the corresponding 5-substituted isomer was obtained in the presence of only 1% of a disubstituted isomer.⁸

The methylthio group can be removed by hydrogenolysis *via* Raney Ni.



The mechanism of trifluoromethylation was assumed to be characterized by the homolytic cleavage of C-I bond to give CF_3 radical that reacted with pyrrole to give the radical **27**. This radical reacted with another molecule of trifluoromethyl iodide giving **28** that gave the product by loss of HI (Scheme 5).

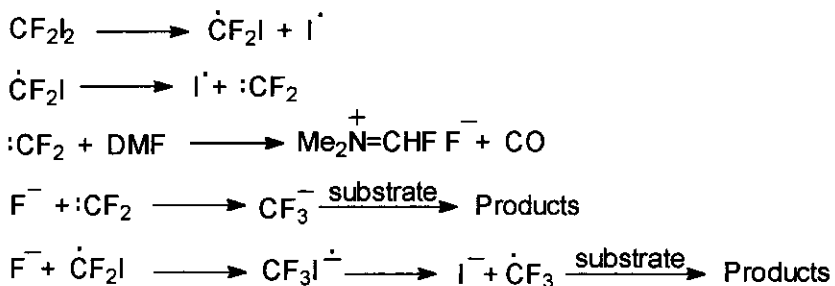
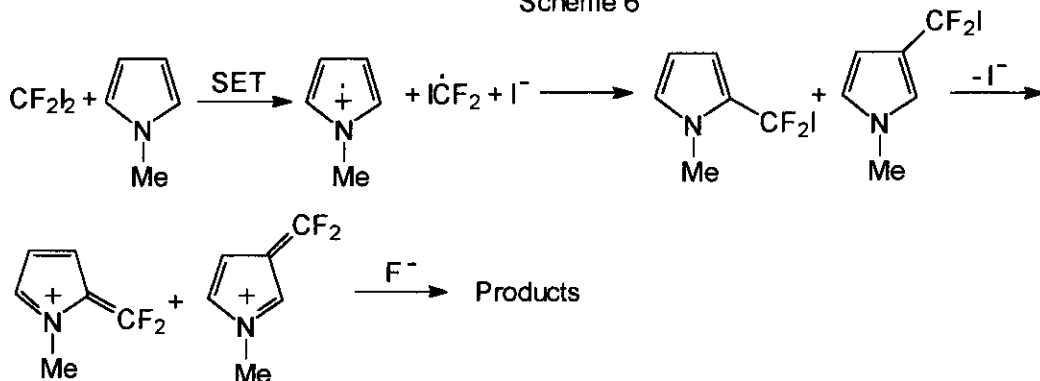
Scheme 5



Trifluoromethyl iodide is an expensive reagent. An attempt to use trifluoromethyl bromide gave only 6.5% yield of 2-trifluoromethyl-*N*-methylpyrrole when *N*-methylpyrrole was used as substrate.⁹ Also difluorodiodiomethane was used as trifluoromethylating agent.¹⁰ The irradiation of *N*-methylpyrrole with this reagent in DMF for 8 h gave the 2-trifluoromethyl derivative in 46% yield in the presence of only 3% of 3-isomer. The mechanism of this reaction can be explained on the basis of the reaction sequence

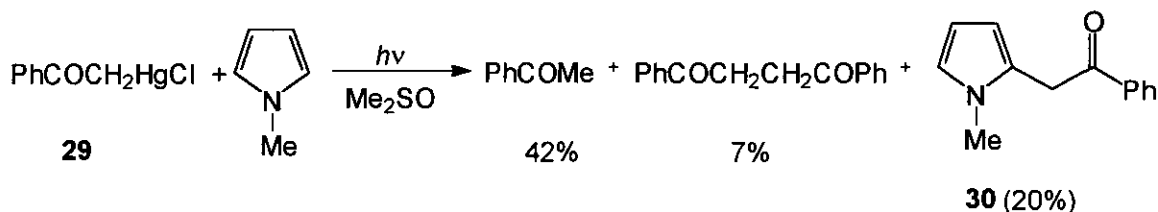
depicted in Scheme 6. The key step is the reaction of $:CF_2$ with DMF that is able to make available the fluoride ion. In fact, the presence of the fluoride ion is required in all the sequences able to give the product.

Scheme 6

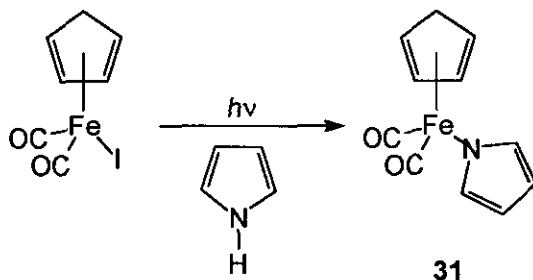


1.3 ORGANOMETALLIC REAGENTS

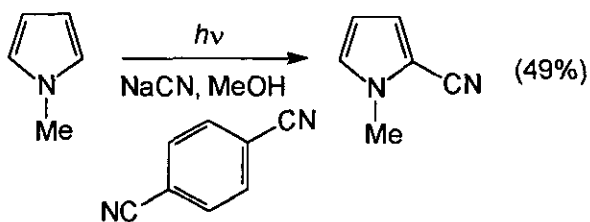
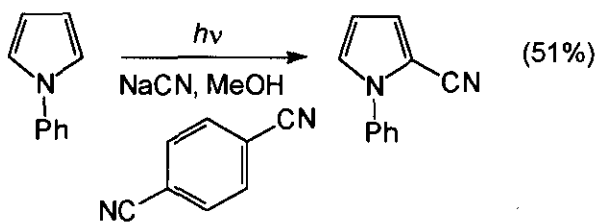
Photosubstitution reactions have been attempted also with organometallic reagents. Unfortunately, this approach does not seem to give interesting results. In fact, the reaction of **29** with *N*-methylpyrrole gave **30** but only in 20% yield.¹¹



Furthermore, the reaction of $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ with pyrrole gave the $\eta^1\text{-N}$ -pyrrolyl complex (**31**). This product can be decarbonylated in refluxing benzene giving the corresponding azaferrocene in good yields.¹²



Photosubstitutions can be obtained using electron transfer processes. *N*-Phenylpyrrole and *N*-methylpyrrole can be transformed into the corresponding 2-cyano derivatives in the presence of 1,4-dicyanobenzene.¹³

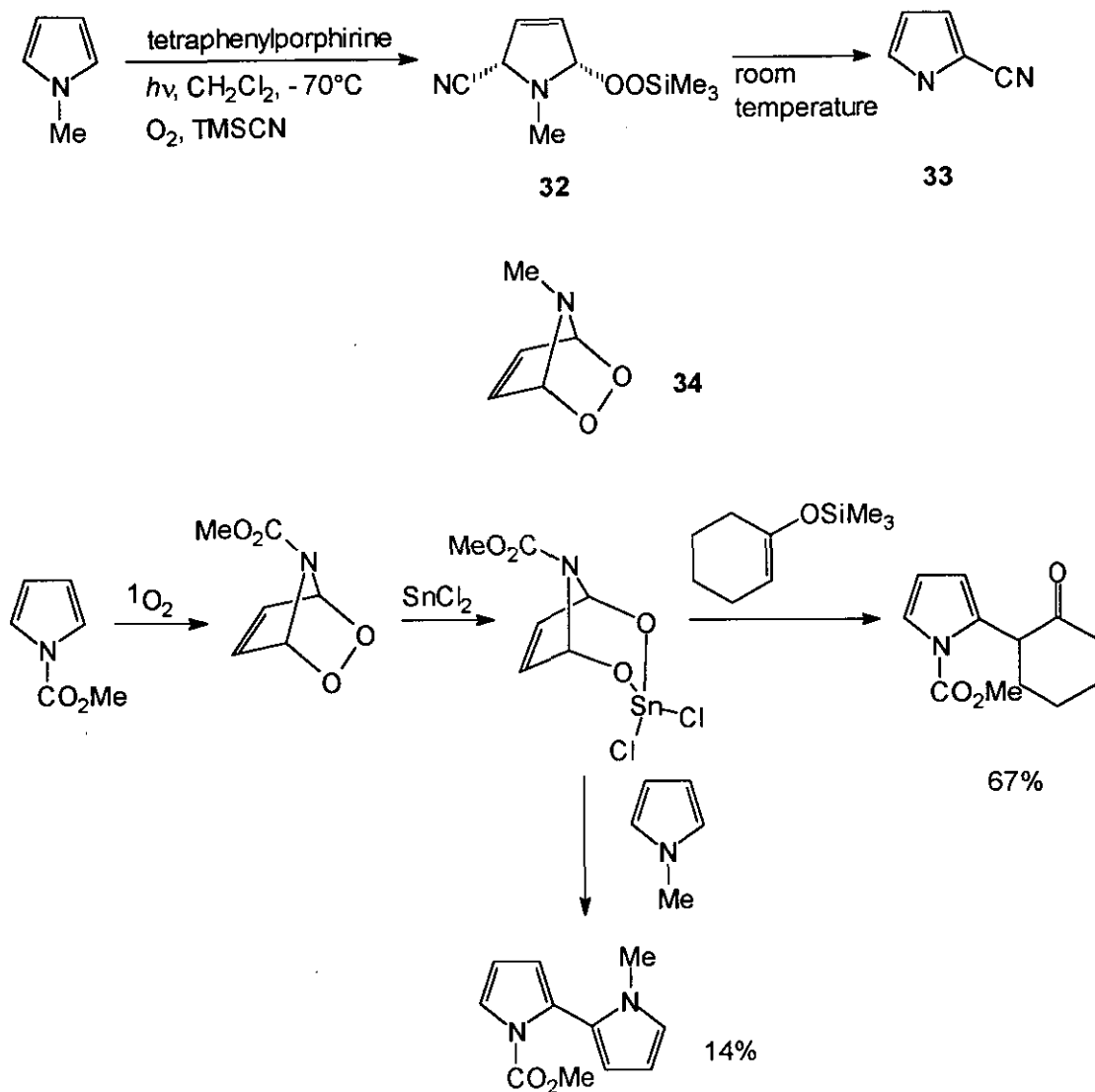


Interestingly, the irradiation of *N*-methylpyrrole in the presence of acetylacetone gave the corresponding 3-acetyl derivative.¹⁴ We think that some efforts should be made in order to clarify this reaction.

1.4 PHOTOSUBSTITUTIONS IN OXIDATIVE MEDIUM

Some other substitution reactions have been performed in oxidative medium. Then, *N*-methylpyrrole can

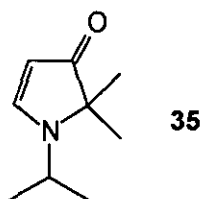
be treated at -70°C with singlet oxygen and then with trimethylsilylcyanide to give **32** in quantitative yields. Compound (**32**) at room temperature was converted into **33** in 90% yield.¹⁵ Nmr study of this reaction allowed to identify **34** as intermediate in the formation of **32**.



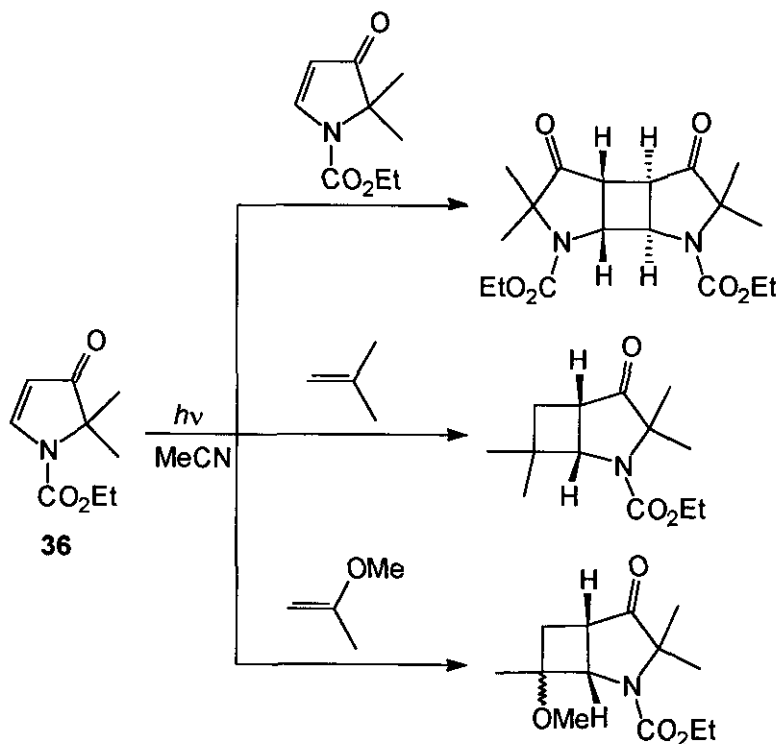
The same behaviour was observed using *N*-carboxymethylpyrrole as substrate in a reaction with singlet oxygen in the presence of both SnCl_2 and a suitable nucleophile such as an enol silyl ether or *N*-methylpyrrole. This way, 2-substituted products were obtained.¹⁶

2. ADDITIONS

Cycloaddition reactions are very common using furan as substrate. With pyrroles we have few examples of this type of reactivity. Cycloaddition reactions have been attempted mainly on dihydropyrroles. Nevertheless, the pyrrole derivative (35), irradiated at λ 366 nm did not give any interesting reaction. It was tested without the presence of reagents or in the presence of both 2,3-dimethyl-2-butene and 2-methylpropene. In all the experiments only decomposition products were observed.¹⁷ This lack of reactivity was attributed to the presence of a self-quenching mechanism due to an efficient back electron transfer reaction.



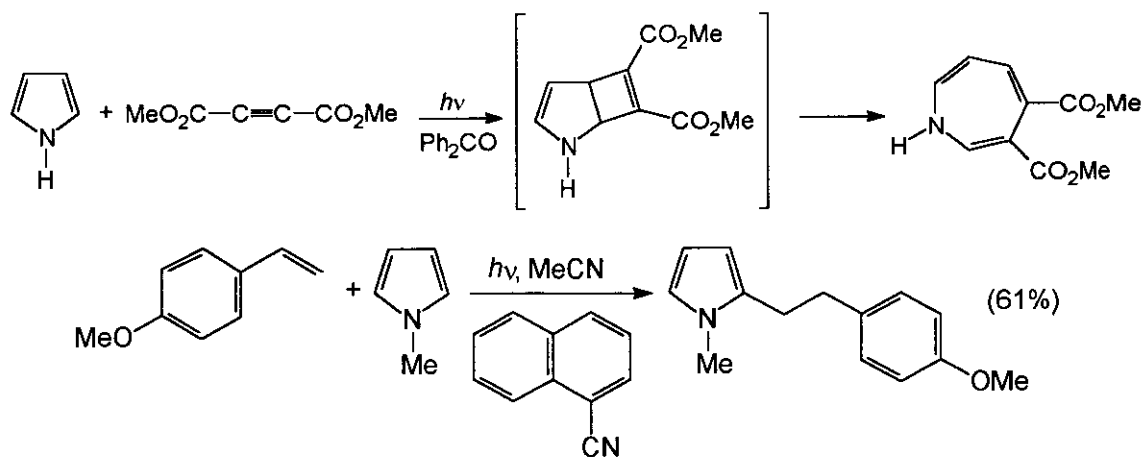
Scheme 7



On the contrary, pyrrole derivative (**36**), characterized by the presence of an electron withdrawing group at the nitrogen, gave, if irradiated at λ 350 nm in acetonitrile, the corresponding [2+2] cycloadducts (Scheme 7).¹⁸ The effect of the substituents can be explained considering that, in the presence of an EWG, the substrate becomes less electron-donating one.

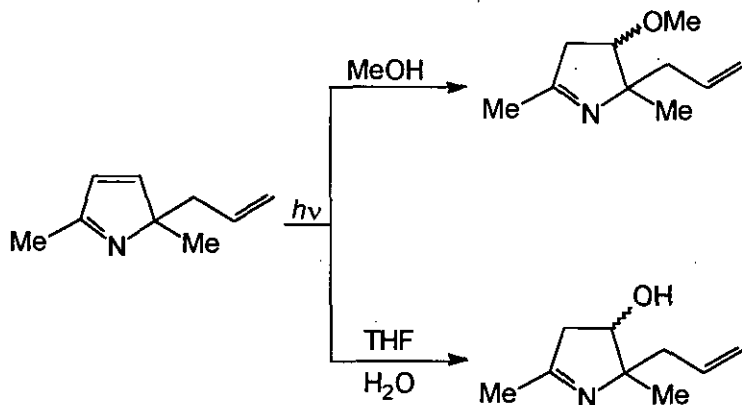
Pyrrole can react with dimethyl acetylenedicarboxylate (DMAD) in the presence of benzophenone as a sensitizer to give with low yields the corresponding 1*H*-3,4-dicarbomethoxyazepine. The reaction probably occurs *via* the formation as intermediate of the cycloaddition products which, then, underwent a ring enlargement reaction.¹⁹

Furthermore, *N*-methylpyrrole, irradiated in the presence of *p*-methoxystyrene in acetonitrile and in the presence of 2-cyanonaphthalene, gave the corresponding addition product. Styrene was unable to give the same reaction.²⁰ Pyrrole reacted also with stilbene without the presence of 2-cyanonaphthalene to give a 4:1 mixture of the addition products in 2 and 3 positions, respectively. *N*-Methylpyrrole did not react under the same conditions, while addition products (2.5:1 isomeric ratio) were isolated when the reaction was carried out in acidic medium. Probably, the addition involves singlet-excited *trans*-stilbene and a polarized exciplex.^{21,22}

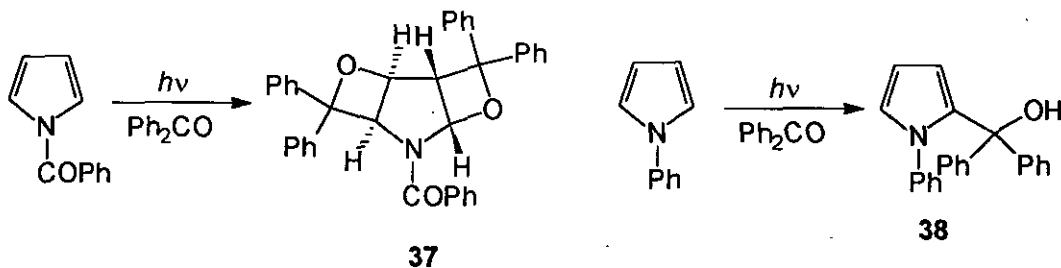


Also 2*H*-pyrroles gave addition reactions. If irradiated in methanol, addition of methanol on the carbon in 3 and 4 positions was observed. In the same way, the irradiation in THF-water 1:1 gave the addition of

water in the same positions.²³ The reaction seems to be insensitive to the presence of oxygen and; then, the authors supposed that the reaction occurred *via* the singlet excited state.

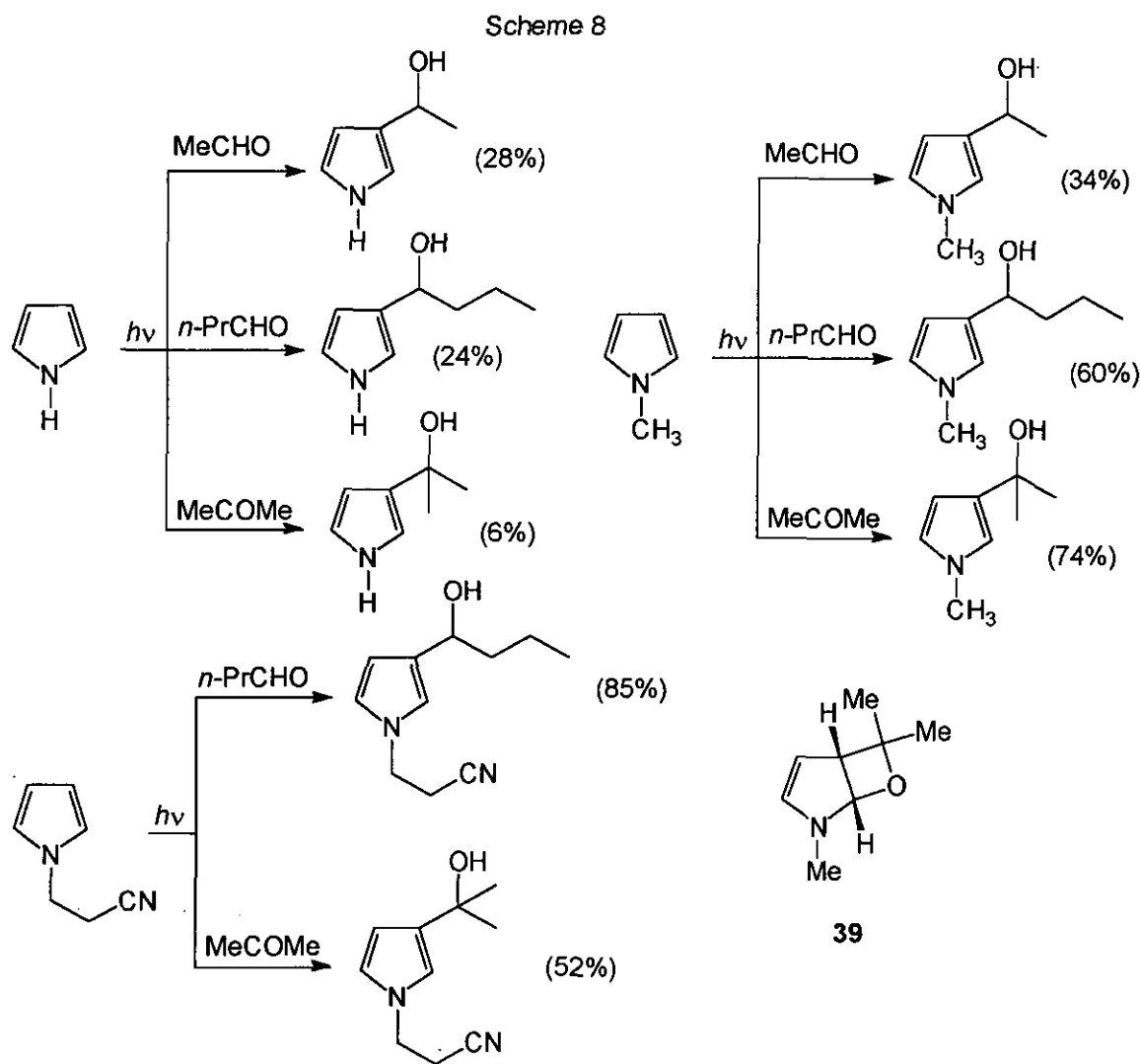


Nevertheless, the most important cycloaddition reaction in pyrrole chemistry is the addition of a carbonyl group. The Paternò-Buchi reaction is a very well known reaction.

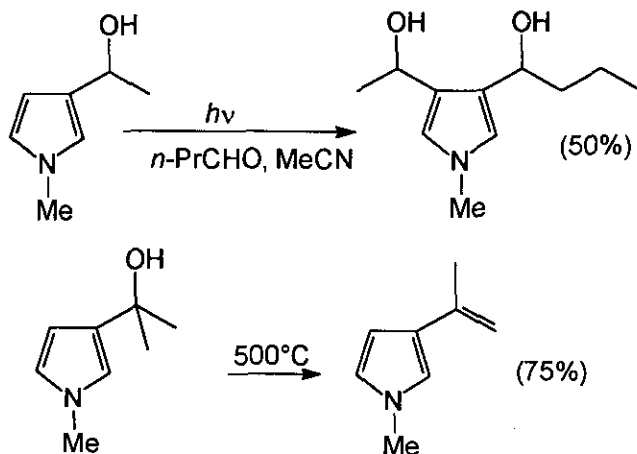


In particular its application in furan chemistry attracted much attention during the last years. *N*-Benzoylpyrrole gave the compound (37) when irradiated in benzene in the presence of benzophenone.²⁴ The authors reported that the benzoyl group was the only substituent able to give this reaction. Successively, they reported that also *N*-phenylpyrrole gave the reaction affording the carbinol (38)²⁵

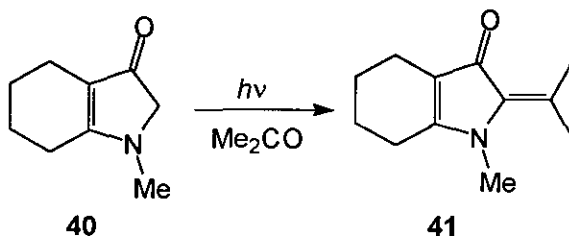
Authors reported that other substituents did not give interesting results. However, some years later, also pyrrole and *N*-methylpyrrole were described to give the corresponding alcohols if irradiated in the presence of carbonyl compounds (Scheme 8).^{26,27}



It was interesting to note that a completely different regiochemical behaviour was observed. Nmr evidences are in agreement with the previous formation of the oxithane (39) as intermediate in these reactions. This evidence was obtained irradiating *N*-methylpyrrole in acetone at 0°C. All the products of these reactions underwent the same reaction if irradiated with an other carbonyl compound. Furthermore, treatment at 500°C of the products gave the corresponding alkenes in high yields.



Finally, also the pyrrole derivative (40) gave a reaction with ketones. In this case, the product was 41.

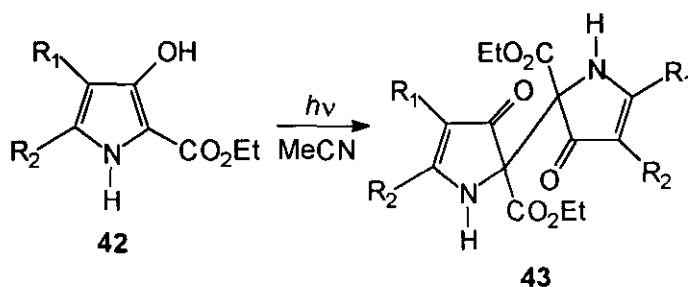


Compound (41) represented the product of an ideal aldolic condensation between 40 and the ketones. However, in this case, an electron transfer mechanism giving $40^{\cdot+}$ and $\text{R}_2\text{CO}^{\cdot-}$ was supposed. Subsequently hydrogen abstraction and radical coupling gave a carbinol that underwent an elimination reaction to give 41.²⁸

3. DIMERIZATION

The irradiation of pyrrole derivatives (42) in acetonitrile gave a dimerization product (43).^{29,30} The reaction did not occur on *N*-methyl derivatives. This behaviour can be understood on the basis of an electron transfer mechanism. The resulting radical cation can evolve by means of a loss of *N*-hydrogen, to

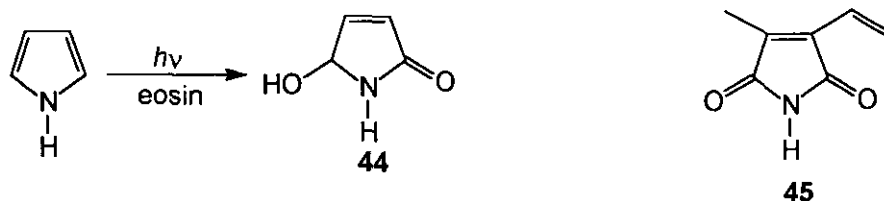
give the corresponding radical. Methyl derivatives can not give this type of reaction, thus explaining the observed unreactivity of *N*-methyl derivatives. Subsequently, the resulting radical can dimerize to give the product.



4. OXIDATION

4.1 OXIDATION OF ALKYL SUBSTITUTED COMPOUNDS

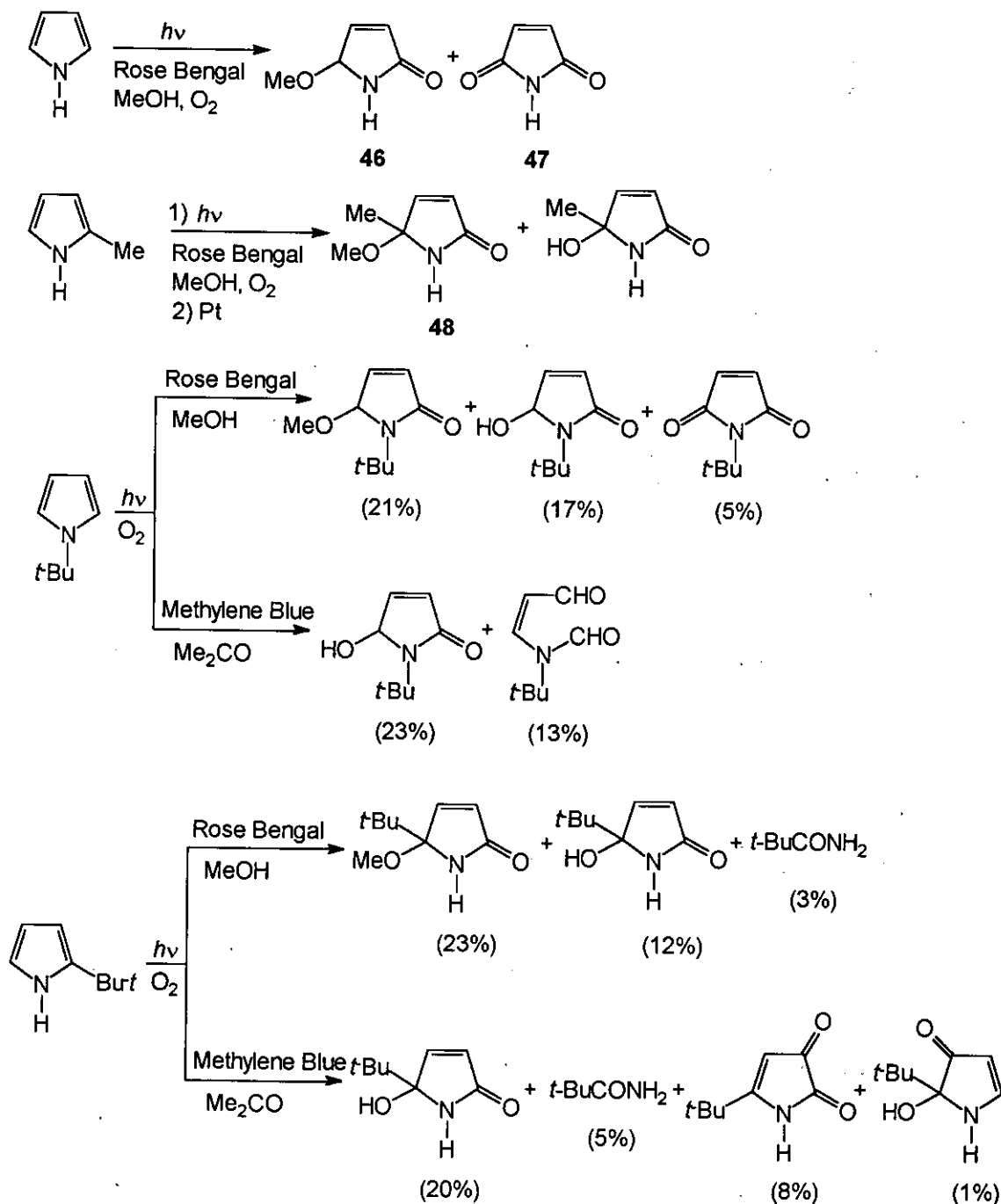
While photoreduction of pyrrole derivatives does not work,³¹ the photooxidation is a well known reaction and was studied at the beginning of organic chemistry and photochemistry. Photochemical oxidation of pyrrole to give the corresponding imide was described by Ciamician and other scientists.^{32,33} Successively, it was found that pyrrole in water, acetone or methanol in the presence of eosin or methylene blue gave an unidentified product in 58% yield.³⁴ In 1962 de Mayo reported that, by using a very diluted solution of pyrrole (0.1%), eosin sensitized pyrrole oxidation to give 44 in 32% yield.³⁵



This type of reaction could be carried out also by using a polymer supported Rose Bengal. In this case, *N*-methylpyrrole was oxidized in 36% yield.³⁶ Photochemical oxidation of pyrrole derivatives showed to be

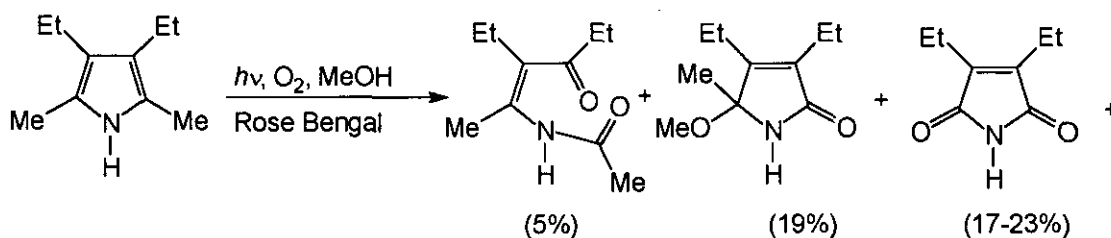
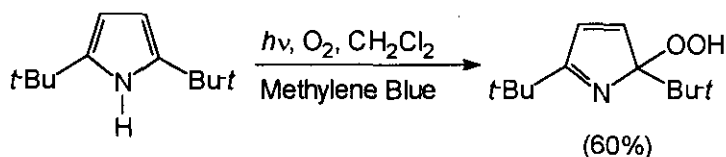
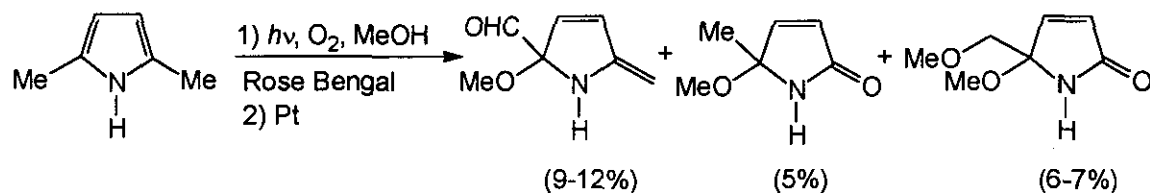
very important in biological systems. For example, photochemical therapy is used in the treatment of hyperbilirubinemia in newborn infants. This treatment is due to the oxidation of bilirubin in the presence of oxygen to give 45.^{37,38}

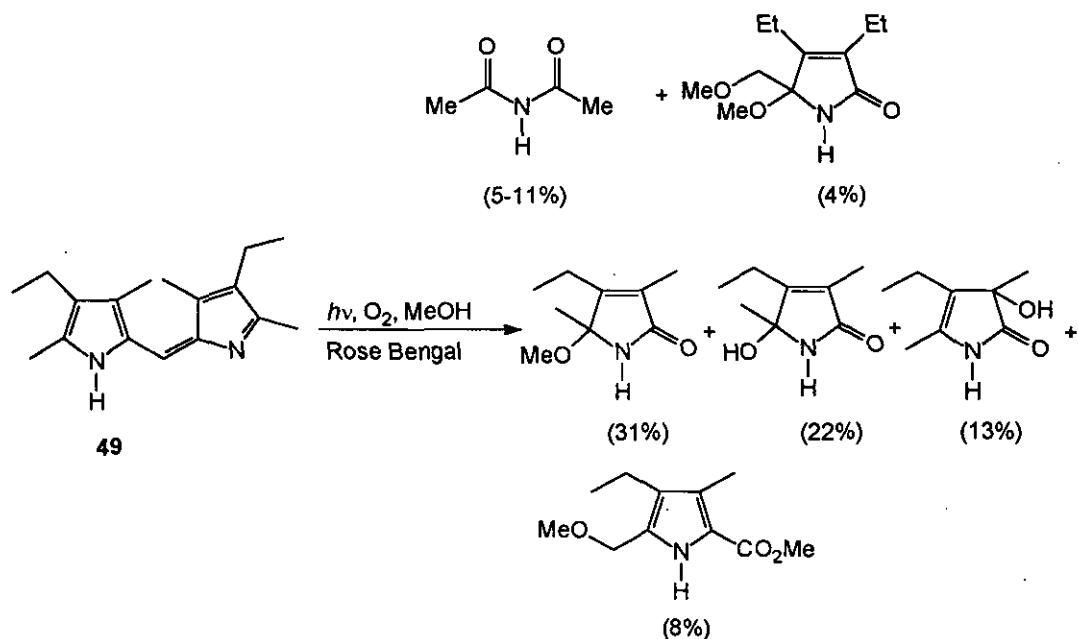
Scheme 9



The photochemical oxidation of pyrrole in methanol using Rose Bengal as sensitizer gave **46** in 13% yield in the presence of a small quantity of **47**. Compound (**47**), similar to **45**, probably was formed in the reaction mixture but then destructed photochemically (Scheme 9).³⁹

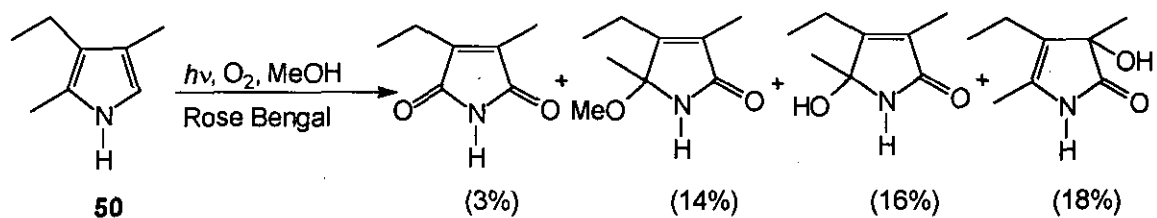
In the same way, 2-methylpyrrole gave **48** in 20% yield.^{40,41} *N*-*t*-Butylpyrrole and 2-*t*-butylpyrrole gave the same type of products when irradiated in methanol.⁴² On the contrary, when the same substrates were irradiated in acetone, the reactions gave products deriving from 1,2 attack on pyrrole. 3-Methylpyrrole and 3-*t*-butylpyrrole gave a complex mixture of products deriving from both 1,4 and 1,2 attack of oxygen on pyrrole ring.^{42,43} 2,4-Dimethylpyrrole gave products similar to those reported for 2-methylpyrrole.⁴¹ Similar results were obtained with β -disubstituted pyrroles.³⁹ On the contrary, 2,5-dimethylpyrrole, that can not give the usual products, reacted only in low yields giving non conventional oxidation products,⁴⁰ while 2,5-di-*t*-butylpyrrole, when irradiated in methylene chloride, gave the hydroperoxide in good yields.⁴⁴





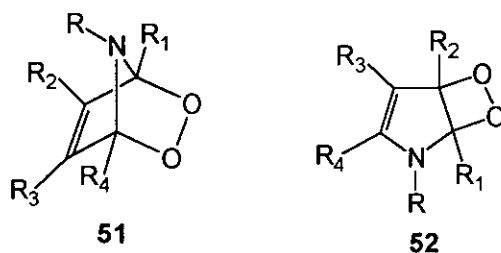
The same behaviour was observed by using other highly substituted pyrroles, that were unable to give oxidation products without C-C bond cleavage. Thus, 2,5-dimethyl-3,4-diethylpyrrole gave a complex reaction mixture when ring opening products were isolated, and also compound (49) gave products deriving from C-C bond cleavage.^{45,46}

Trisubstituted pyrroles reacted following the reactivity pattern just described before.⁴⁴⁻⁴⁸ Thus, compound (50) gave the following mixture of oxidation products,⁴⁷ while 2,3,5-tri-*t*-butylpyrrole, irradiated in methylene chloride, gave the corresponding hydroperoxide in high yields.⁴⁴

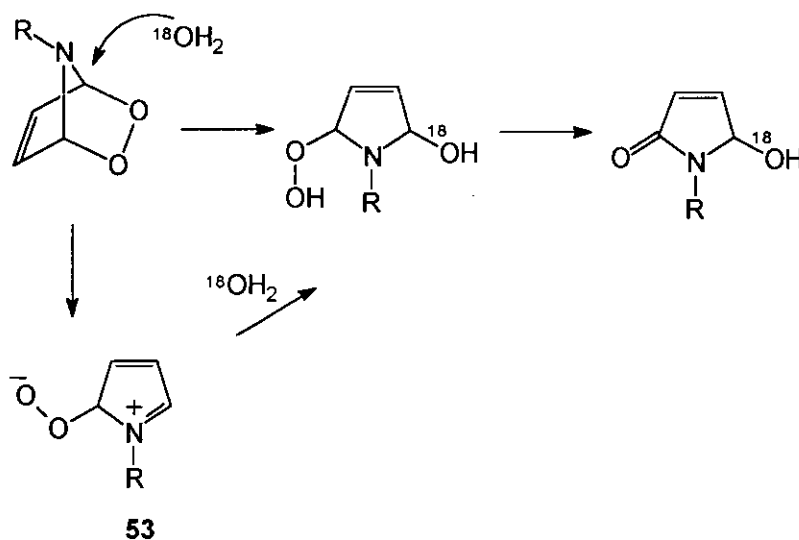


All the described reactions can be explained assuming the formation of the endo-peroxide (51), where products deriving from 1,2 attack can be formed *via* isomerization to 52. Nmr data seems to be in

agreement with this hypothesis because only **51** were identified.^{42,49} Compound (**51**) can be attacked by a nucleophile such as water, or can be transformed into the zwitterion (**53**) that undergoes the attack of water (Scheme 10). Experiments with $^{18}\text{OH}_2$ were in agreement with these hypotheses. Nevertheless, no nmr evidence of **53** was found.

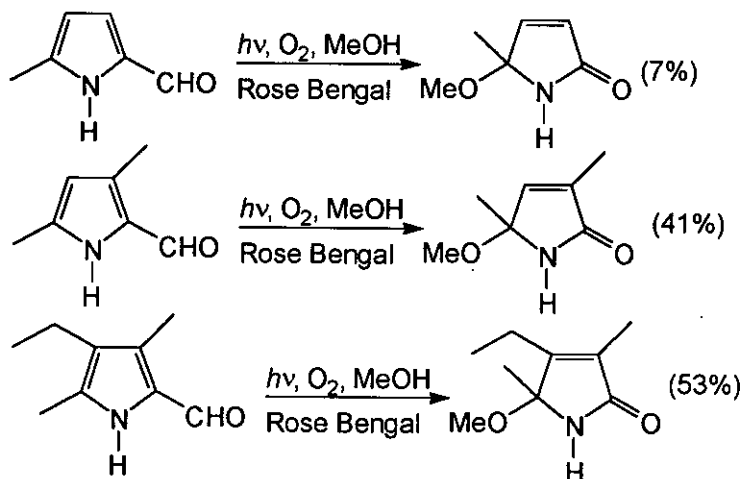
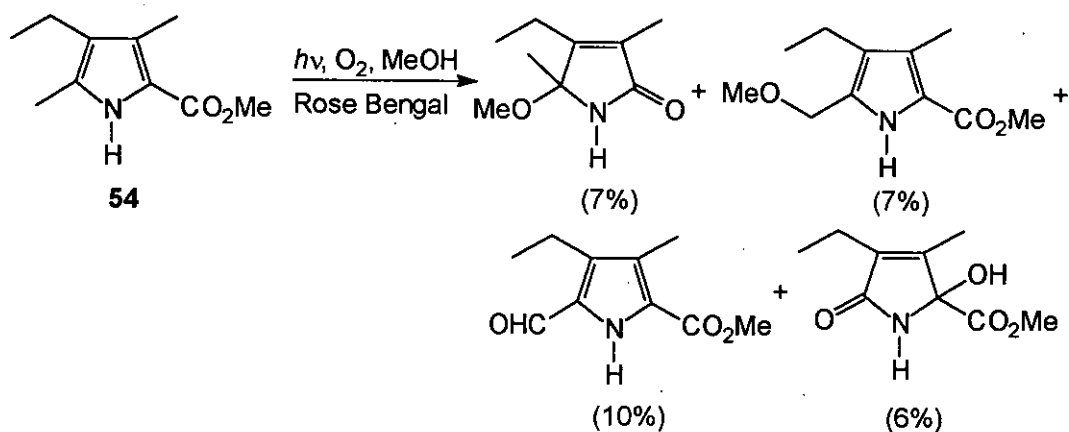


Scheme 10

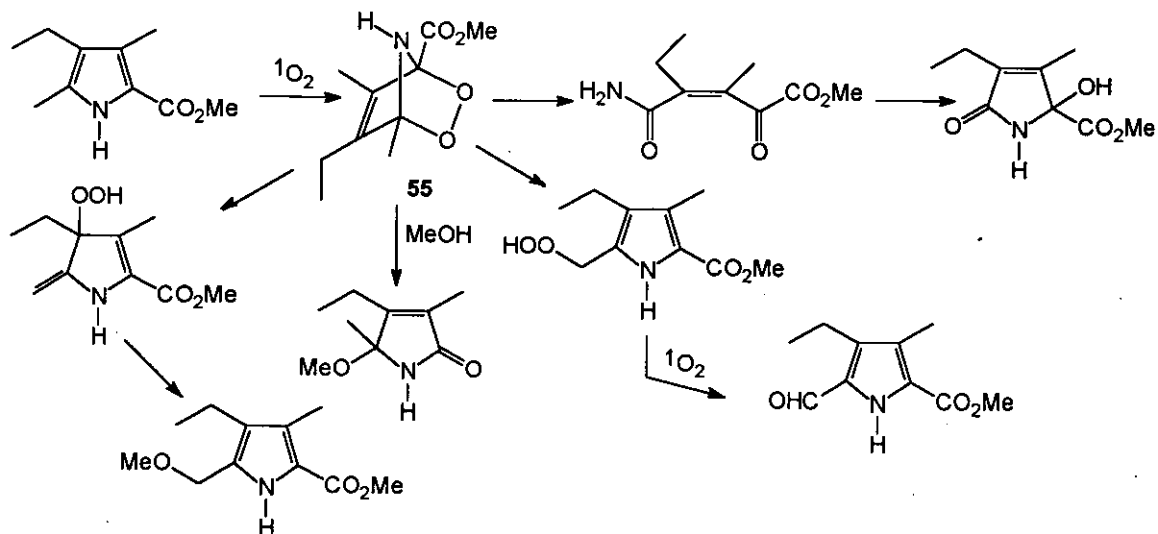


Both the carboxylic acid derivative of pyrrole and the aldehyde were resistant to the oxidation. This behaviour was not true when these molecules are alkyl substituents. The ester (**54**) gave a complex mixture of products in low yields, while the reactivity of the aldehyde was more simple and, then, synthetically more useful (Scheme 11).^{50,51} It is interesting to note that the reactivity of the ester can be

Scheme 11



Scheme 12



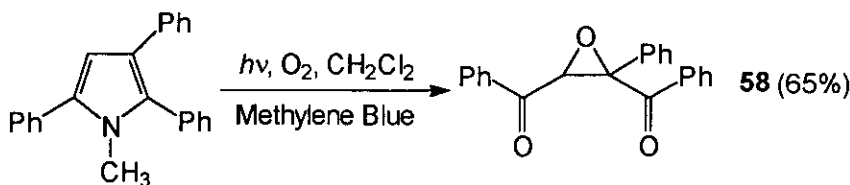
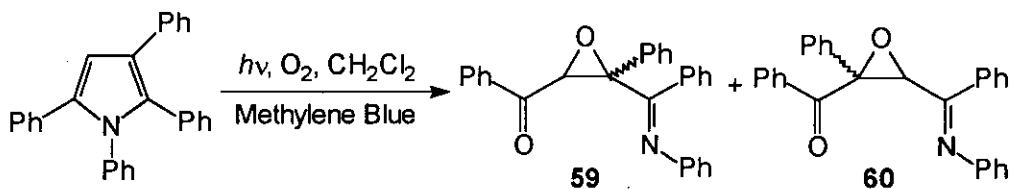
explained on the basis of the previous formation of the endo-peroxide (55) that give all the products as described in Scheme 12.⁵⁰

4.2 OXIDATION OF ARYL SUBSTITUTED COMPOUNDS

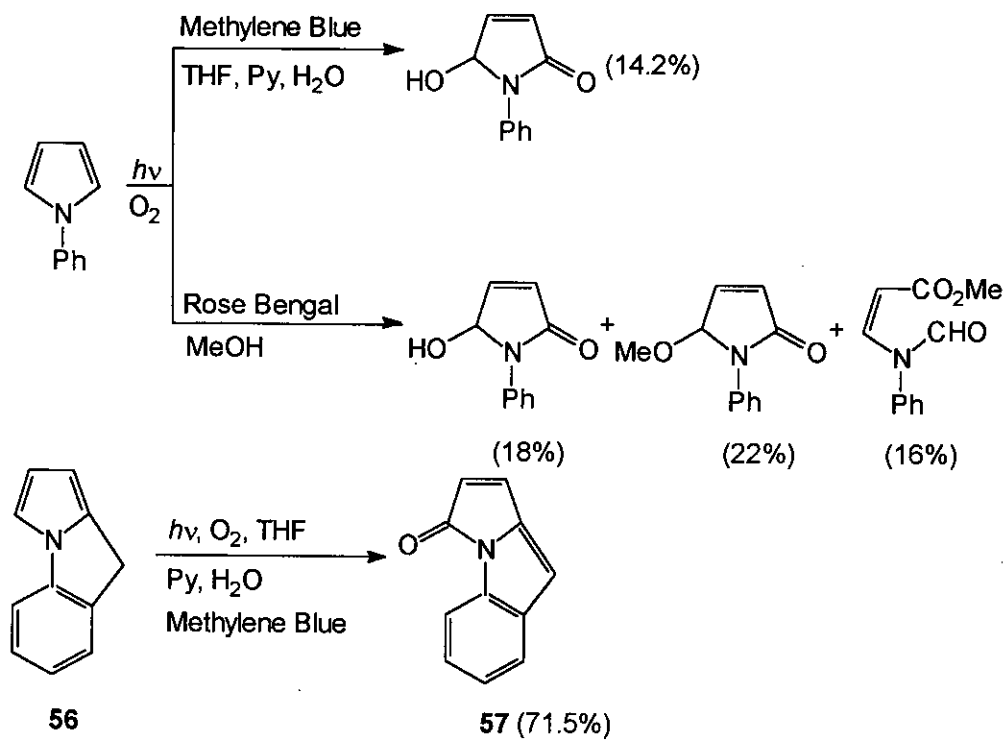
Phenyl derivatives gave results that differs from those obtained with the alkyl analogues for some aspects.

The irradiation of *N*-phenylpyrrole gave products in agreement with the above reported results.^{52,53} Thus, compound (56) gave the lactame (57) in very high yields (Scheme 13).⁵²

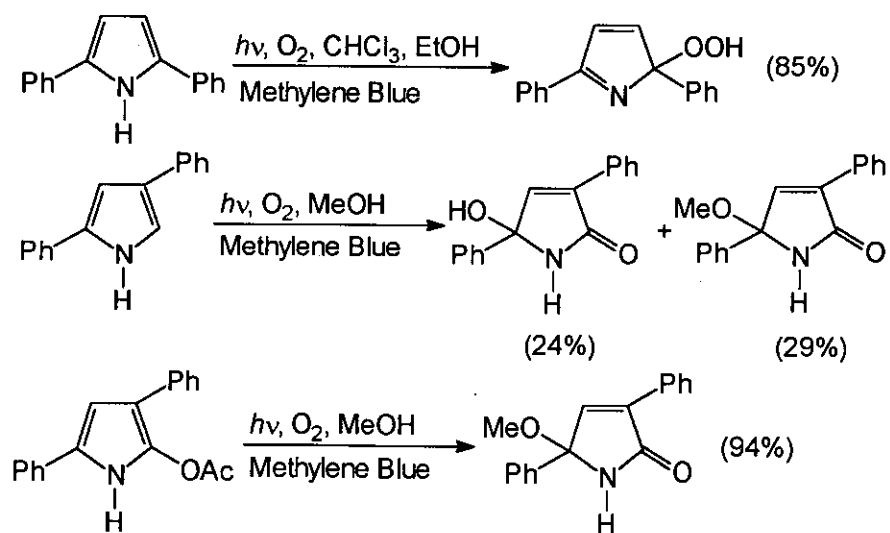
Also in this case nmr evidences are available on the formation of the endoperoxide. The ring opening product observed in methanol probably derived from the 2,3-endo-peroxide. This endoperoxide can be obtained from 1,4-endo-peroxide through isomerization. 2,5-Diphenylpyrrole gave the corresponding hydroperoxide in 85% yields.⁵⁴ 2,4-Diphenylpyrrole, on the contrary, can give the corresponding lactams in low yields.⁵⁴ Nevertheless, 2,4-diphenyl-5-acetoxypyrrole gave the lactams in very high yields (Scheme 14).⁵⁴



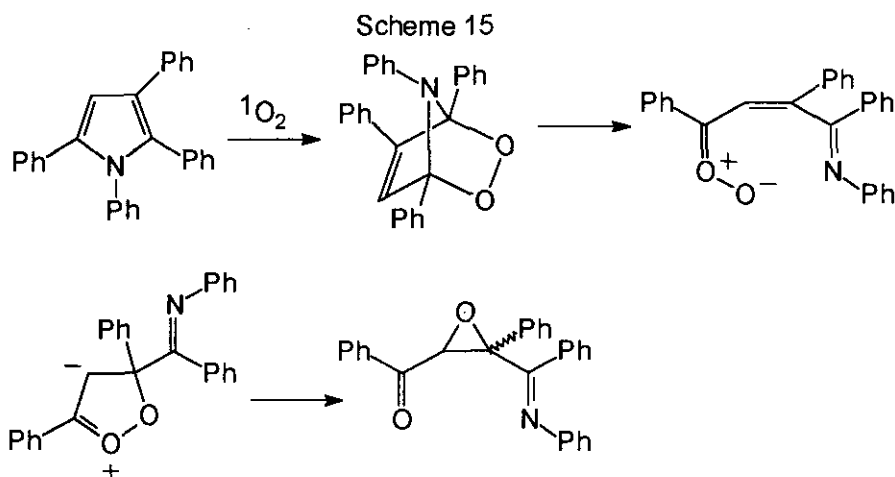
Scheme 13



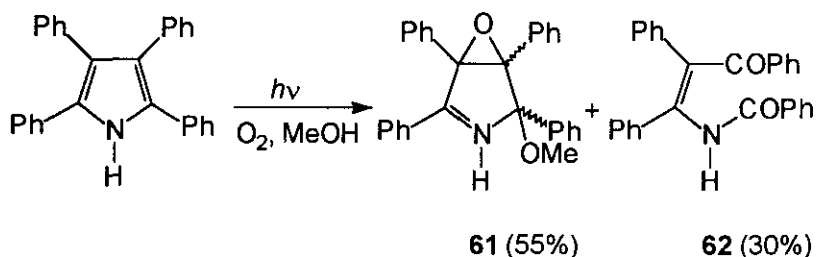
Scheme 14



The photochemical behaviour of tri- and tetraphenylpyrroles was found to be more unusual. Thus, 2,3,5-triphenyl-*N*-methylpyrrole gave **58** in 65% yield, while 1,2,3,5-tetraphenylpyrrole gave the compound (**59**) and (**60**) in 70% yield.^{55,56} The formation of compounds (**59**) and (**60**) can be understood on the basis of the reactions depicted in Scheme 15.



Analogous product was obtained using as substrate 1-benzoyl-2,3,4,5-tetraphenylpyrrole.⁵⁷ 2,3,4,5-Tetraphenylpyrrole also underwent oxidation under the same conditions. In 1957 the author was not able to isolate any product, but in 1960 Wasserman reported that compound (**61**) and (**62**) can be obtained.^{58,59} Successively, the hydroperoxide was obtained.⁶⁰⁻⁶²



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