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N–N BOND CLEAVAGE AND REARRANGEMENTS OF ARYLHYDRAZONES AND ARYLHYDRAZIDES—RECENT DEVELOPMENTS

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INTRODUCTION

Derivatives of hydrazine are known since a long time to undergo rearrangements with N–N bond fission. Among them the best known are the benzidine and related rearrangements and the Fischer indole synthesis, both catalysed by acids.

The aim of this review is to offer a general outlook of the results, achieved in the last 5 years and only partially published, we obtained investigating initially some new aspects of the indole synthesis and then considering the behaviour towards Lewis acids of some non indolizable arylhydrazones.

Our contribution in the field of the indole synthesis has disclosed some new aspects, in an area formerly vastly and extensively explored; in our opinion, however, the most interesting results come from investigation of non indolisable arylhydrazones, which undergo a surprising variety of unexpected rearrangements some of which even exploitable in synthetic chemistry.

II. FISCHER INDOLE SYNTHESIS: NEW FINDINGS

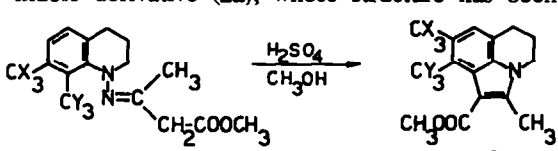
The behaviour of 2,6-alkyldisubstituted arylhydrazones in the Fischer indole synthesis has been scantly explored:[1] indole derivatives were known to be formed by migration of an alkyl group (usually a Me group) to the adjacent C atom (1,2-shift)[2,3,4] or to the C atom in the *para* position (1,4-shift).[5]

In some cases a Me group was observed to be detached but its fate was not established.[6,7]

Our attention has been devoted initially to the study of the behaviour of this class of compounds.

(a) *Double 1,2-shift of a substituent*

The obtainment under Fischer conditions of the indole derivative (**2a**), whose structure has been ascertained by independent synthesis, starting from arylhydrazone (**1a**), shows that the rearrangement occurs with a formal 1,3-migration of a Me group.

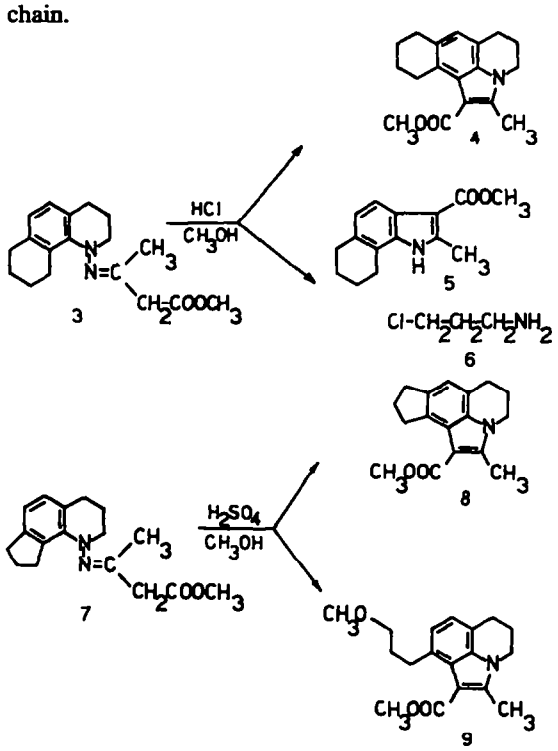


1
a : X = Y = H
b : X = D Y = H

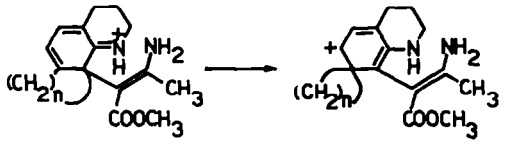
2
a : X = Y = H
b : X = H, Y = D
c : X = D, Y = H

Under the same conditions the deuterated hydrazone (**1b**) gave an about 1:1 mixture of the two isomeric indole derivatives (**2b** and **2c**), as deduced from its NMR spectrum, thus proving that the rearrangement occurred through a double 1,2-shift of the Me group.[8]

The same reaction mechanism has to be invoked for the formation of indoles (**4** and **8**) starting from the derivatives **3** and **7**[9,10] carrying a cycloaliphatic chain.



The intermediates originating the above products present the spirocyclopentane and spirocyclobutane structures (**11a** and **11b**) respectively, the more difficult formation of the latter being in accord with the isolation, from the second reaction, of the indole derivative (**9**), carrying the methoxypropyl chain, nearby (**8**).[10]



10 11

a : n=4
b : n=3

Product **9**, whose structure has been ascertained by independent synthesis, originates from the nucleophilic attack of methanol on the cyclohexadienoneimine (**10b**), in competition with the 1,2-shift of the substituent.

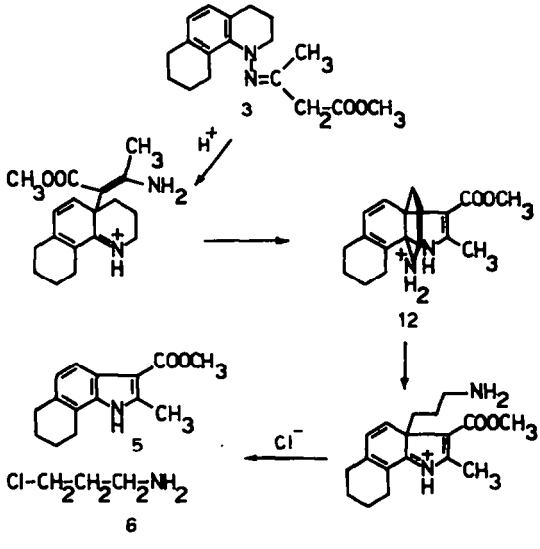
(b) *Loss of a substituent*

The detachment of a substituent *ortho* to the hydrazine chain has been frequently observed by previous workers.[6,7] The fore-going example relative to the indole (**9**) represents a case in which the detachment occurs by capture of a nucleophile present in the reaction medium, the latter being retained in the final product.

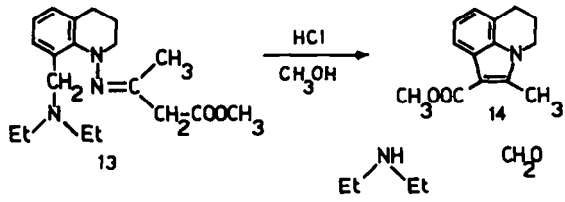
Our results in many other different instances have shown that the loss of a substituent always occurs by capture of a nucleophile.

Remarkable is the formation of some indole derivatives[11] from N-aminotetrahydroquinoline hydrazones which occurs with the loss of the whole aminotrimethylene chain. So, hydrazone (**3**) afforded, nearby **4**, also the indole **5** and γ-chloropropylamine (**6**), arising from the detachment of the aminotrimethylene chain.

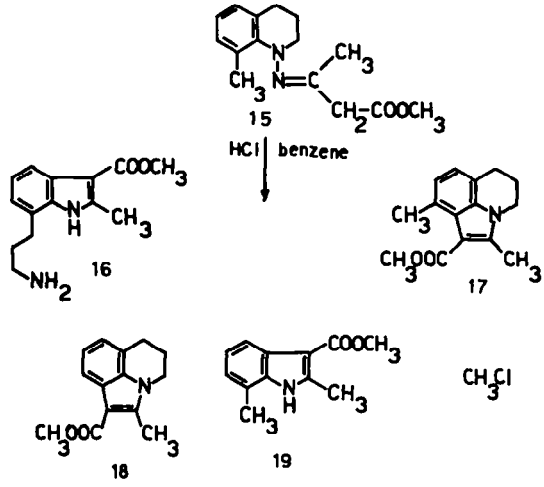
The proposed mechanism invokes the intermediacy of a propellane structure **12** and accounts satisfactorily for the observed products:



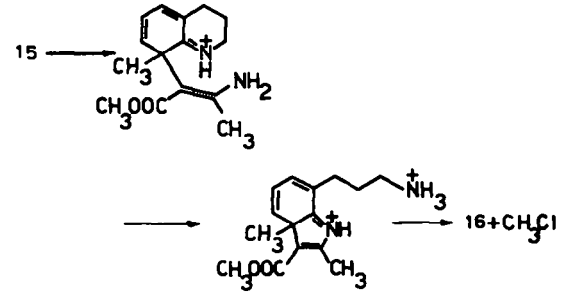
We have pursued the idea that the detachment reaction should be favoured over the 1,2-shift of the substituent whenever the latter, when lost, is capable of originating a particularly stable carbonium ion. The hypothesis has found full experimental support: substrate **13** gave exclusively the indole product **14**, nearby formaldehyde and diethylamine, originated from the substituent lost during the cyclisation:[12]



A special case of substituent detachment simultaneous with the opening of the tetrahydroquinoline ring has been observed with hydrazone **15**, which afforded the products shown in the scheme:[13]

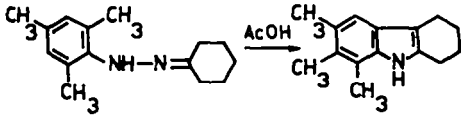


The different products were isolated and characterised either by independent synthesis or following their spectroscopic characteristics. Products **17** and **18** come from known routes; the origin of compound **19** is similar to that discussed above for the formation of **5** from **3**; instead the formation of the aminopropylindole (**16**) can only be accounted for by a novel pathway:

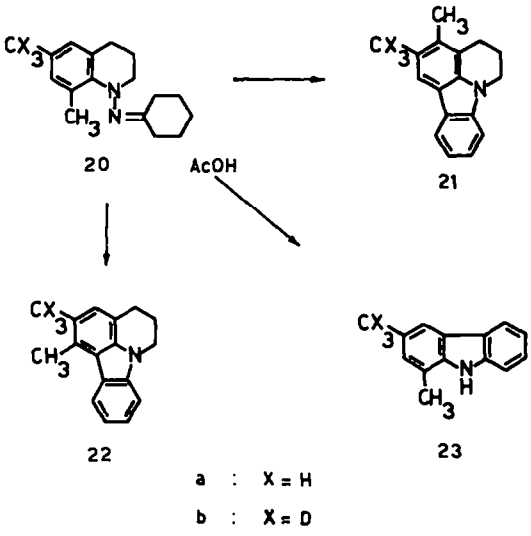


(c) 1,4- *and* 1,5-*Shifts of a methyl group*

Carlin reported in 1959[5] the first example of a 1,4-shift of a Me group during a Fischer indolisation: we have further investigated the scope and the mechanism of this migration.



We observed analogous rearrangements in many other cases: for instance the hydrazone (**20a**) gave the carbazole (**21a**), and nearby other products (**22a** and **23a**) which can be accounted for by known reaction pathways.

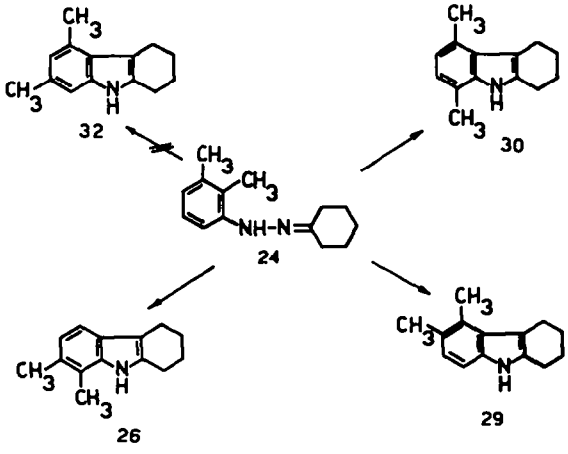


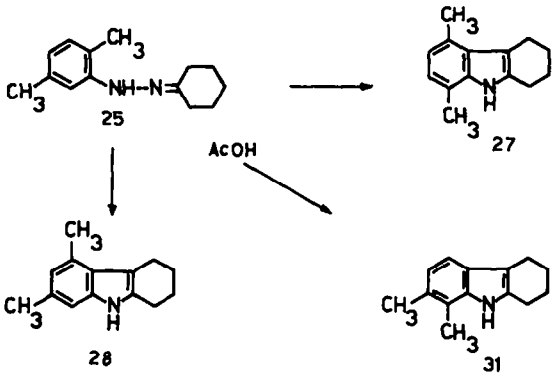
The deuterated hydrazone (**20b**) then has been submitted to the rearrangement in order to check whether the scrambling of the Me with the deuteromethyl group was possible.[14] Such a scrambling would have supported the hypothesis that the 1,4-shift is actually the result of three subsequent shifts of the Me group clockwise if referred to our depiction of formulas. The NMR of the reaction mixture showed instead that no scrambling occurs, thus invalidating the mechanism previously proposed by other Authors.[15]

In 1977 Miller reexamined the matter and gave some evidence that the apparent 1,4-migration could be satisfactorily accounted for by three subsequent anticlockwise 1,2-shifts of the substituent.[16]

Our recent findings are in accord with Miller's hypothesis, although the alternative mechanism envisaging a first [1,5]-sigmatropic shift, followed by a second 1,2-shift, cannot be excluded.[17]

Reactions which suggested us this conclusion are shown in the following schemes:





Both the hydrazones under study (**24** and **25**) have an unoccupied position *ortho* to the hydrazine residue and for this reason in both cases indoles (**26** and **27**), which originate by cyclisation at this position, are by far the predominant products in the reaction mixture.

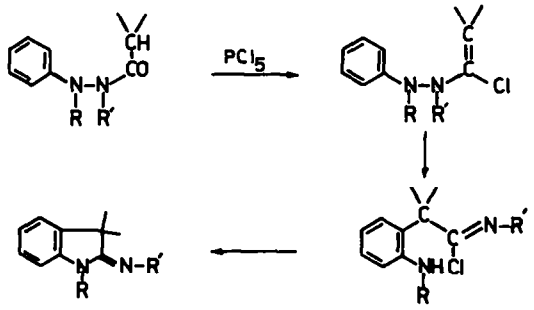
However, concentrating sufficiently the by products and isolating them either as tetrahydrocarbazole or as carbazole derivatives, it has been possible to identify all of them by comparison with authentic samples independently synthesised. We established the presence of products arising from the attack at the substituted position followed by 1,2-shift (**28**) and double 1,2-shift (**29**) of the Me group according to the pathways already outlined; in both cases however there are present products derived from cyclisation at the occupied position and migration of the Me group to the other *ortho* position. These are products **30** and **31** respectively, while product **32**, which would derive from a direct 1,4-migration of the Me in the starting hydrazone (**24**), is totally absent.

These are the first two cases in which it has been established the migration of a substituent from one *ortho* to the other *ortho* position during the indole synthesis. This migration could be the result either of a [1,5]-sigmatropic (Woodward–Hoffmann allowed) rearrangement or alternatively of two subsequent 1,2-shifts of the Me group which should go through the position of the ring to which the N atom is bonded. This second possibility is believed to be less likely.

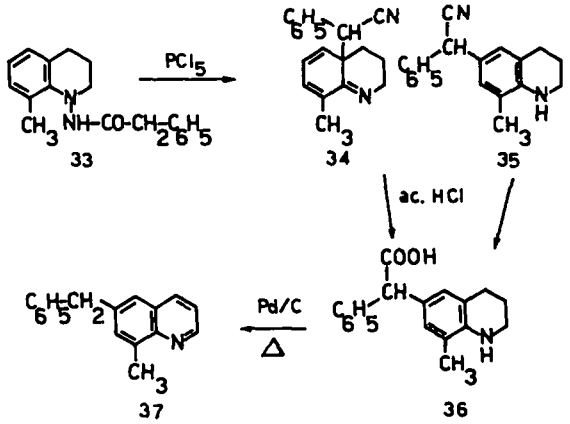
The above findings appear to contribute to the knowledge of the mechanism of the apparent 1,4-migration of the Me group, formerly observed by Carlin: it can be the result of a triple 1,2-shift, as proposed by Miller, or of two subsequent shifts, the first [1,5] and the second [1,2].

III. REARRANGEMENTS OF PHENYL- AND DIPHENYLACETIC ACID 2,6-DISUBSTITUTED ARYLHYDRAZIDES

Kost has recently shown[18] that 2-aminoindoles are obtained upon treating aliphatic acid arylhydrazides with phosphorous oxychloride or pentachloride, along a reaction path which at first involves similar intermediates as the Robinson's mechanism for the Fischer indole synthesis.[19]



We have further investigated this reaction starting from 2,6-disubstituted arylhydrazides derived from phenyl and diphenylacetic acids.[20] Upon treatment with phosphorous pentachloride in benzene solution, the hydrazide (**33**), derived from 8-methyl-N-aminotetrahydroquinoline, gave two compounds (**34** and **35**):

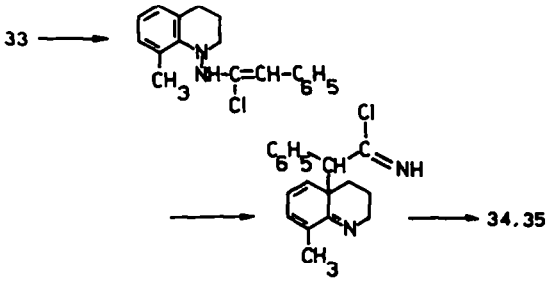


The structure of **35** has been established by hydrolysis to the corresponding acid (**36**), followed by aromatisation and simultaneous decarboxylation promoted by palladized charcoal to give a benzyl-8-methylquinoline.

The position of the benzyl residue, as reported in formula **37**, has been established by independent synthesis of the three isomeric 5-, 6-, and 7-benzyl-8-methylquinolines.

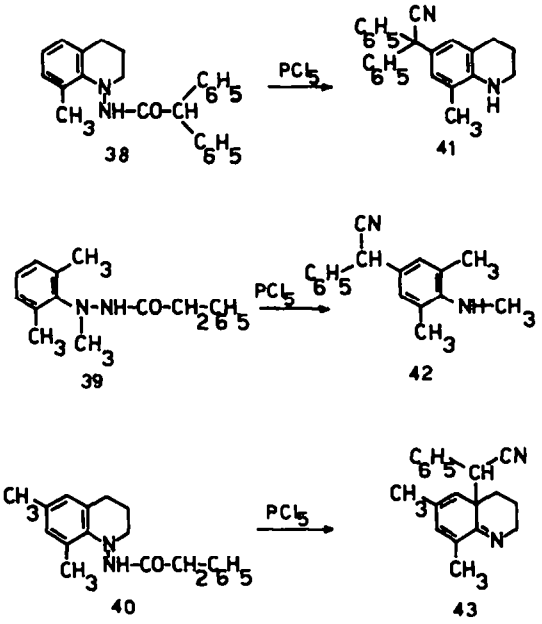
The structure of the cyclohexadienoneimine derivative (**34**) has been established on the basis of analytical and spectroscopic data; furthermore acqueous hydrochloric acid promotes in **34** a 1,3-sigmatropic shift of the cyanobenzylic group and hydrolysis of the nitrile function to the same acid (**36**) derived from the hydrolysis of **35**.

The mechanism proposed for the formation of the two compounds (**34** and **35**) is outlined in the following scheme:



The formation of **35** from a cyclohexadienoneimine intermediate isomeric of **34** but carrying the α-cyanobenzyl group in position 8 of the tetrahydroquinoline ring, cannot be excluded; in this case such an intermediate should be far less stable than **34**.

The results obtained with three other different hydrazides (**38**, **39** and **40**) are shown in the scheme reported below: while in the first two cases only the products originated through the 1,3-sigmatropic shift (**41** and **42**) could be isolated, in the third case, where this rearrangement is prevented, the cyclohexadienonimine derivative (**43**) only, and fission products thereof, are formed[21]:



IV. REARRANGEMENTS OF ARYLHYDRAZONES OF AROMATIC AND ARYLALIPHATIC CARBONYL COMPOUNDS

A general procedure for promoting rearrangement reactions in these derivatives and those here to follow is reported below.

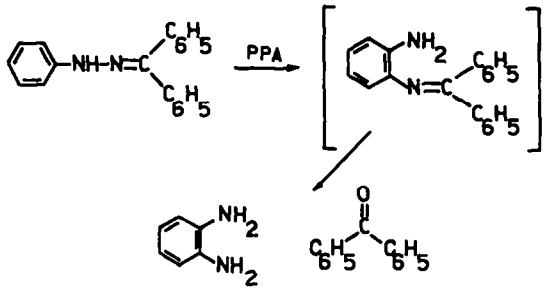
The hydrazone is added, under stirring, to a large excess (usually a 10 fold excess in weight) of polyphosphoric acid (PPA) preheated at 60°–80°, then the mixture is heated at 100°–120° for ½–1 hr. The reaction is often exothermic: in every case a short heating period is sufficient to complete the reaction.

Among the acid promoters we have examined, the polyphosphoric acid is the most efficient one: in few cases analogous results have been obtained using other acid media (H_2SO_4, $HClO_4$).

Column chromatography has been extensively used to separate the different reaction products.

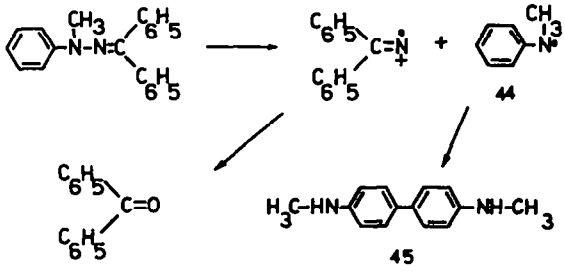
(a) *Benzophenone*

o-Phenylenediamine and benzophenone have been obtained in good yields starting from benzophenone phenylhydrazone.



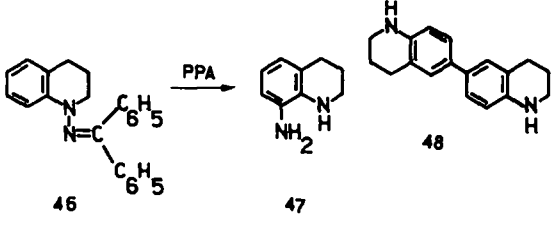
The reaction may be interpreted as an intramolecular migration of the protonated benzophenoneimine group from the nitrogen to the *ortho* position of the benzene ring.

Benzophenone-N-methyl-phenylhydrazone behaves differently, affording in moderate yields N,N'-dimethylbenzidine (**45**). This unusual benzidine formation may be interpreted assuming a dimerisation of the radical intermediate (**44**; or its protonated form).

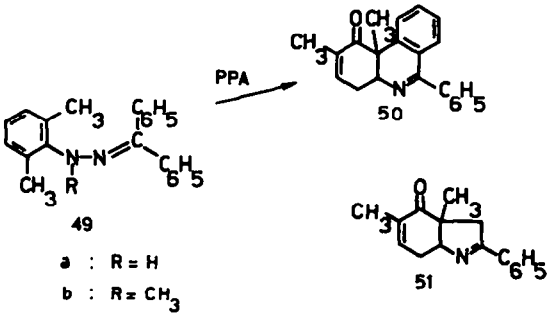


The fate of the N atom of the radical cation evolving to benzophenone has not been established so far.

Both the above reaction paths are presented by the hydrazone (**46**) derived from benzophenone and N-amino-tetrahydroquinoline, giving the products **47** and **48**:



The 2,6-dimethyl-phenylhydrazone (**49a**) of benzophenone unexpectedly gave in modest yields (15%) nearby benzophenone (60%) and some other unidentified products, an interesting compound to which we have assigned the structure **50**.

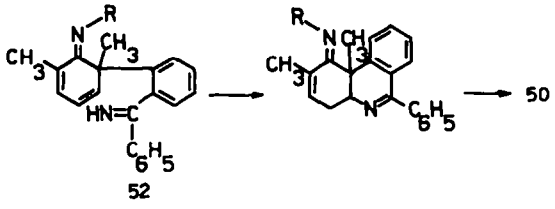


Such an assignment is based on the similarity of the NMR peaks of this compound with those presented by compound **51**, obtained by Carlin upon rearrangement of the 2,6-dimethyl-phenylhydrazone of acetophenone and whose structure has been unequivocably established by the same Author.[22]

Chemical evidences supporting proposed structure have been achieved also through catalytic and chemical reduction of **50**.

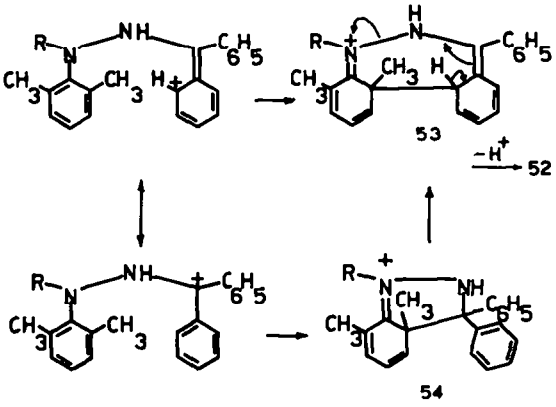
We arrived at the same product and with analogous yields starting from benzophenone-N-2,6-trimethyl-phenylhydrazone (**49b**).

Concerning the mechanism of formation of **50** it is evident that the immediate precursor of the final product should be the cyclohexadienonimine derivative **52**

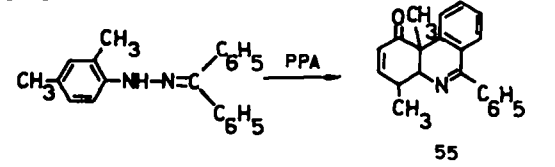


in turn possibly formed by ring opening of the cyclic precursor **53**. This latter could be formed either directly by cyclisation of the protonated substrate, or alternatively in two steps, through a ring enlargement of a 5-membered ring intermediate (**54**).

The two hypotheses are shown in the following scheme:



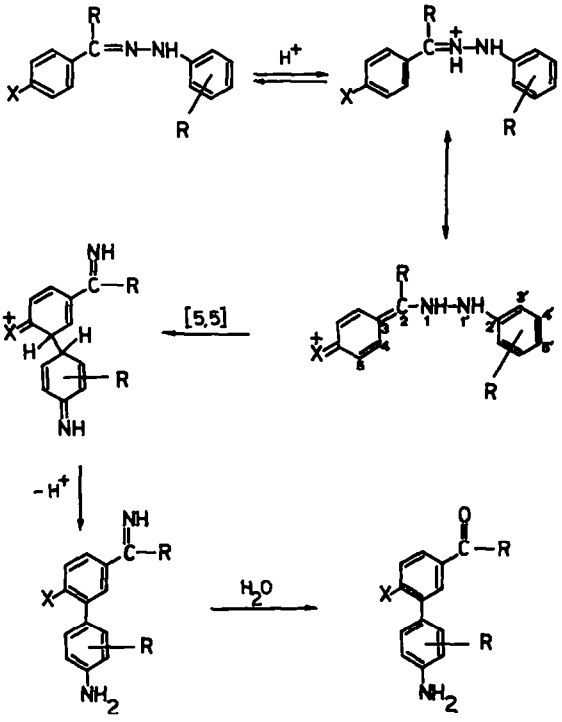
Benzophenone-2,4-dimethyl-phenylhydrazone gave, upon treatment with PPA, a complex mixture of products from which we could isolate, in low yields, compound **55**, whose structure is quite similar to that of **50**. The structural assignment to the compound, which appears to be only one of the possible stereoisomers, reposes on the interpretation of its spectral data and the mechanism of its formation appears to be the same as that previously proposed for **50**.



(b) *Benzophenones and other aromatic carbonyl compounds carrying electrodonating substituents*

The behaviour towards PPA of arylhydrazones of aromatic and arylaliphatic carbonyl compounds presenting electrondonating substituents in the aryl ring is remarkably different from that shown by substrates so far considered. It has been observed that in general these compounds are transformed into diphenyl derivatives and, for some of them, the yields are so high that this reaction presents considerable preparative interest.

Its mechanistic course, which is reported in the following scheme has some analogy with the benzidine rearrangement and should be classified as a [5,5]-sigmatropic rearrangement.



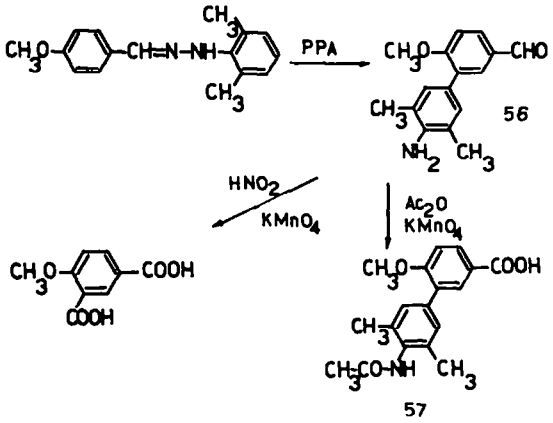
X = electron donating substituent

The protonate substrate can be written with the positive charge delocalized on the hetero atom in position *para* to the CO group: a numbering assigns the formal butadienylic sistems connected to the N atoms of the hydrazine residue. The rearrangement can be looked at as a concerted process which involves the N–N bond breaking and the C–C bondformation between positions 5 and 5': this is indeed a [5,5]-sigmatropic rearrangement. Aromatisation of the ring leads to a ketimine (which has been sometimes isolated) and then, after hydrolysis, to the final product.

Other interesting pathways have been found in some cases affording terphenyl derivatives, diarylethers and in a unique case, a deoxybenzoin.

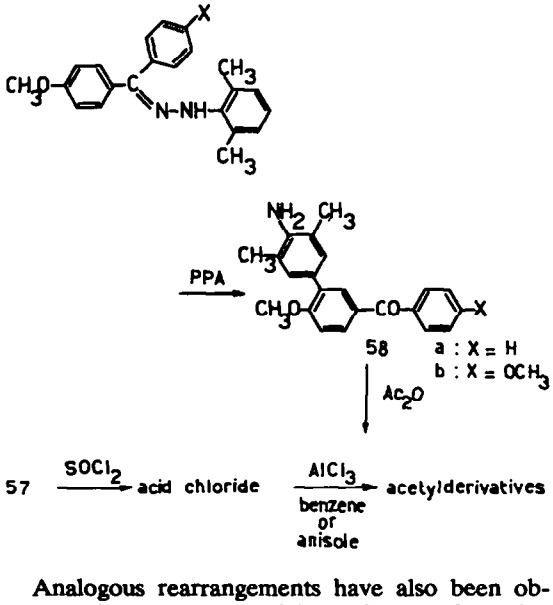
(1) *Anisaldehyde.* PPA treatment of aromatic aldehyde arylhydrazones affords complex reaction mixtures: however anysaldehyde 2,6-dimethylphenylhydrazone gave in a 35% yield a rearranged product **56**, whose structure has been elucidated as 2-methoxy-5-formyl-3',5'-dimethyl-4'-aminodiphenyl.[23] This compound in fact shows NMR equivalence of the aromatic Me groups and can be oxidized to 4-methoxy-isophtalic acid.

The scheme reported below shows also the conversion into the corresponding acetylamino acid (**57**), a reaction which allowed us to interrelate the structure of the product obtained from anisaldehyde with those of other products arising from rearrangements of similar substrates (see below).



(2) *Methoxy substituted benzophenones.* The 2,6-dimethyl-phenylhydrazones of 4-methoxy-, and of 4,4'-dimethoxybenzophenone undergo an analogous rearrangement, leading to the diphenyl derivatives **58a** and **58b**, in high yields.

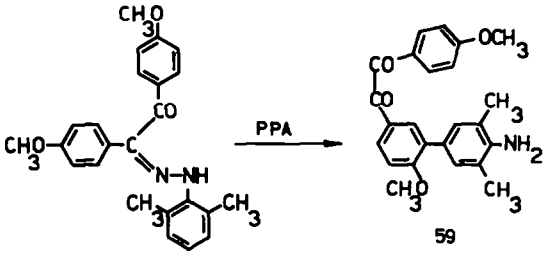
These compounds can also be obtained as N-acetyl-derivatives starting from acetylamino acid (**57**), through its chloride and final F.C. condensation with benzene or anisole respectively.



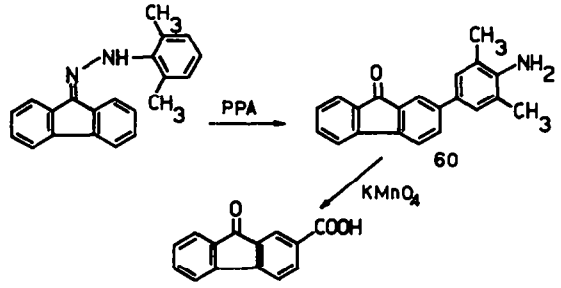
Analogous rearrangements have also been observed, in comparable yields, with the following benzophenone derivatives: 2-methyl-phenylhydrazone and phenylhydrazone of the 4-methoxybenzophenone; phenylhydrazone, *p*-chloro- and *p*-bromo-phenylhydrazone of 4,4'-dimethoxybenzophenone.

In the last two cases the rearrangement occurs with the loss of the halogen atom.(†)

(3) *Anisil.* The α-diketone (**59**) has been similarly obtained from the mono-2,6-dimethylphenylhydrazone of anisil:



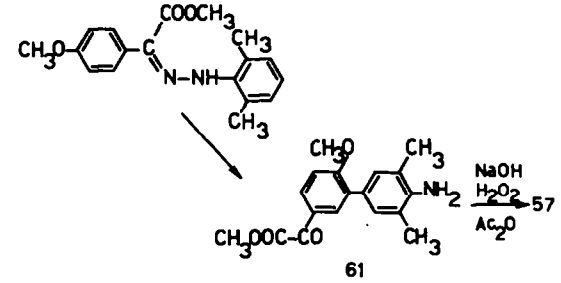
(4) *Fluorenone.* The following scheme shows that the 2,6-dimethyl-phenylhydrazone of fluorenone undergoes an analogous rearrangement, affording product **60**, whose structure has been determined by oxidation to the fluorenone-2-carboxylic acid:



In this case, electron delocalizing ability of the fluorene system fully compensates the lack of electrondonating substituents on the carbonyl mojety of the substrate.

(5) *4-Methoxy-phenylglyoxylic acid esters.* Another series of substrates undergoing the same rearrangement are the arylhydrazones of 4-methoxyphenylglyoxylic acid esters; we have tested the phenylhydrazone, the 2,6- and the 3,5-dimethylphenylhydrazone, and have obtained in every case the corresponding diphenyl derivatives in very high yields.

The scheme shows the chemical evidence for the assignment of the proposed structure in the case of the product (**61**) obtained from the 2,6-dimethyl-phenylhydrazone.



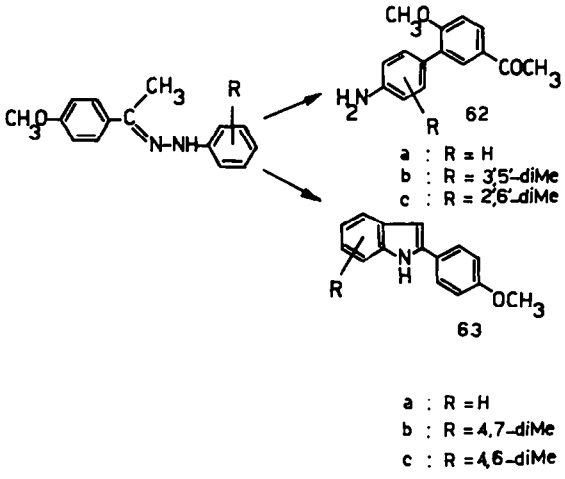
† Many examples are known of reductive loss of a halogen atom during the Fischer indolization of haloarylhydrazones.[24]

(6) *4-Methoxyacetophenone.* Once verified the ease to carry out the above [5,5]-rearrangement, the theme has been extended to arylhydrazones derived from acetophenones, carrying in the *para* position electron-donating substituents. The reason of this choice was to check whether the foregoing rearrangements could be competitive with the usual Fischer indole synthesis.

Results obtained clearly show that the two processes are competitive and assign the role played by substituents upon the reaction path.

Substrates we have considered were three arylhydrazones derived from 4-methoxyacetophenone; the phenylhydrazone, the 2,6-dimethyl- and 3,5-dimethyl-phenylhydrazone.[25]

Results are summarised in the following scheme:

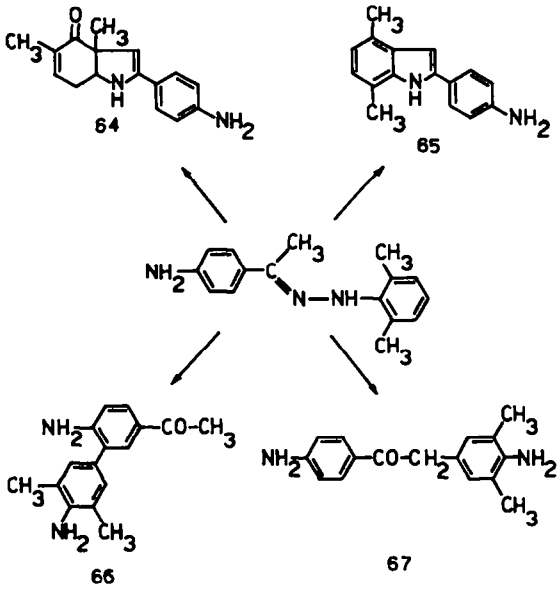


It is evident that in every case both reaction pathways are followed, although the product spread varies because of the substituent effects. The phenylhydrazone afforded the indole derivative (**63a**) nearby a 10% of the product originating from the [5,5]-rearrangement (**62a**); the 3,5-dimethylphenylhydrazone gave approximately equal amounts of the products **63c** and **62c** of the two paths; finally the 2,6-dimethyl-phenylhydrazone gave almost exclusively the [5,5]-rearranged product **62b** accompanied by small amounts of the indole derivative **63b**, in which a 1,2-Me shift has occurred.

The above results suggest the following conclusions: (a) the [5,5]-sigmatropic rearrangement occurs even in substrates capable of undergoing the Fischer indole synthesis. (b) the presence of electrondonating Me groups on the ring of the arylhydrazine favours the [5,5]-rearrangement.

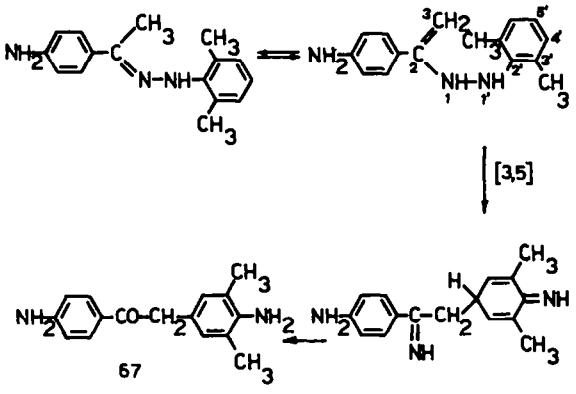
(7) *4-Aminoacetophenone.* The case of the 2,6-dimethyl-phenylhydrazone of 4-aminoacetophenone is particularly interesting because the four products isolated from the reaction mixture constitute the evidence of four concurrent reaction paths.

It is clear that compound **66** derives from the [5, 5]-rearrangement; compound **65** arises from the indole condensation with 1,2-shift of a Me group; compound **64** originates from an already mentioned reaction path known for the acetophenone

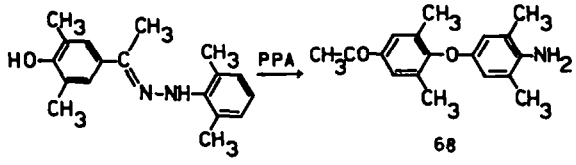


2,6-dimethyl-phenylhydrazone,[22] and verified by us on many 2,6-dimethyl-phenylhydrazones derived from acetophenones substituted at the *para* position with electron withdrawing groups; finally, compound **67** arises from a totally new rearrangement.

The scheme shows the mechanism we propose for the formation of this deoxybenzoin derivative: according to the Woodward–Hoffmann rules, we code this new reaction, found so far in this case only, as a [3,5]-sigmatropic rearrangement



(8) *4-Hydroxyacetophenones and benzophenones.* PPA induces another new rearrangement in arylhydrazones of *p*-hydroxyacetophenones and benzophenones. While the 4-hydroxybenzophenone-2,6-dimethyl-phenylhydrazone undergoes the usual [5,5]-rearrangement, the 2,6-dimethyl-phenylhydrazone of 3,5-dimethyl-4-hydroxyacetophenone affords product **68**, arising from coupling of the *para* position of the arylhydrazine ring with the phenolic oxygen:

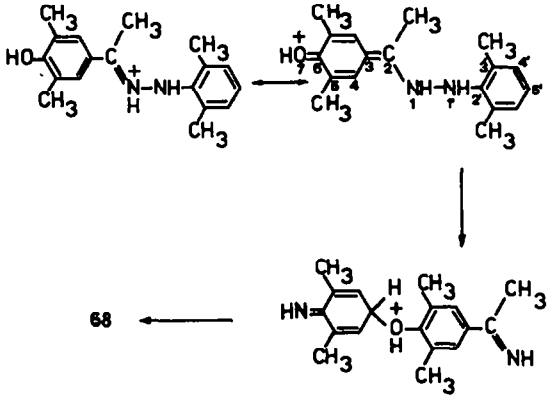


The structure of product **68** was proved by independent synthesis: in fact, condensation of 4-fluoro-2,6-dimethyl-nitrobenzene with the 4-hydroxy-3,5-dimethylacetophenone afforded a diarylether which gave **68** upon reduction of the nitro group.

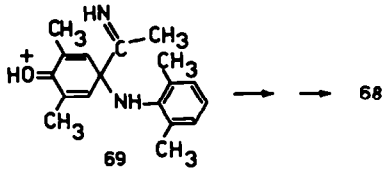
Analogous rearrangements have been observed for the 3,5-dimethyl-phenylhydrazones of 4-hydroxy-3,5-dimethylacetophenone and 4-hydroxy-3,5-dimethylbenzophenone.

In the case of 4-hydroxyacetophenone-2,6-dimethyl-phenylhydrazone the new rearrangement is competitive with the [5,5]-sigmatropic process.

To account for the formation of the diarylethers, two alternative mechanisms can be considered; according to the first one the reaction can be envisaged as a one step [5,7]-sigmatropic rearrangement, as shown in the scheme referred to the formation of **68**:



According to the second one, the reaction develops through two successive steps, the first affording a "quinamine" intermediate (**69**): the latter could rearrange to a diarylether along the lines already known in the literature for this class of compounds.[26]

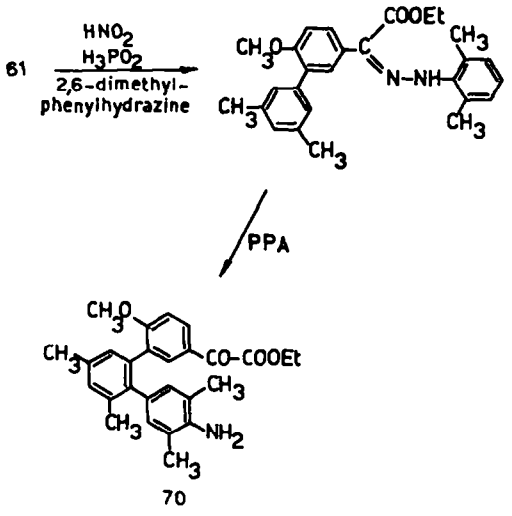


It is remarkable that this rearrangement occurs, analogously to the [5,5]-sigmatropic one, preferentially and often exclusively in those substrates which could undergo the Fischer indole synthesis under the same conditions.

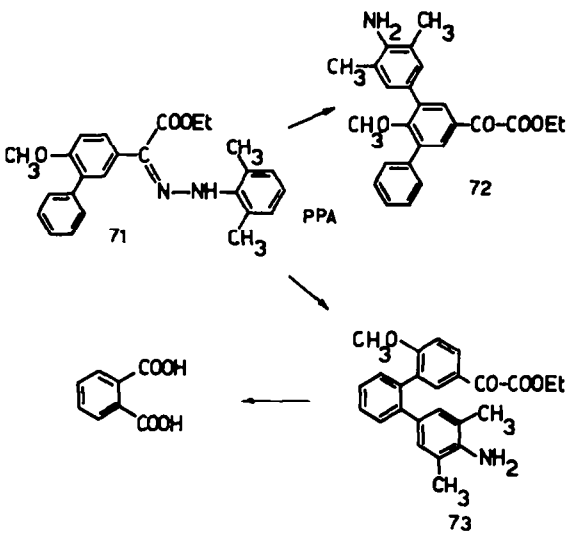
(9) *3-Aryl-4-methoxyacetophenone and 3-aryl-4-methoxy-phenylglyoxylic acid esters.* Another new rearrangement has been observed by reacting with PPA a few arylhydrazones of title compounds: so the above described diphenyl-ketoester (**61**) has been deaminated (through the diazonium salt), then transformed into the corresponding 2,6-dimethyl-phenylhydrazone, and finally treated with PPA.

The isolated product showed four aromatic Me groups in the NMR, two equivalent (those *ortho* to the nitrogen) and two presenting different chemical shifts. The compound could not therefore arise

from the [5,5]-rearrangement and the only other possible structure was the *ortho*-ter phenyl arrangement present in **70**.

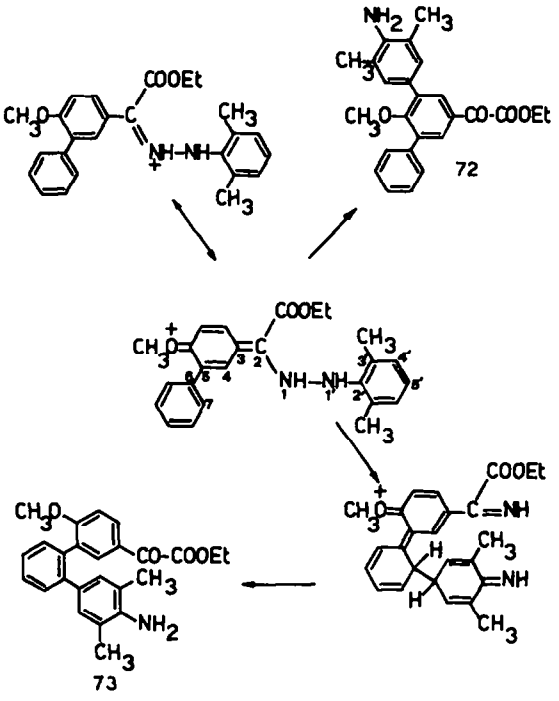


To further check this result, the hydrazone **71** has been treated with PPA to give a mixture of two isomeric rearranged products (**72** and **73**). Evidence for the assigned structures came from the analysis of the spectral data. Furthermore the *ortho*-terphenylic structure of **73** was proved as follows: the product was hydrolysed with hydrobromic acid and then oxidised with permanganate: phthalic acid was detected among the oxidation products.



Compound **72** is the result of the [5,5]-sigmatropic rearrangement already observed, while compound **73** and **70** as well originates from a new process which can be coded as a [5,7]-sigmatropic rearrangement. The reaction paths are reported in the scheme.

Small numbers label the two conjugated systems which mutually interact: in the [5,7]-rearrangement the butadienylic system of the arylhydrazine moiety reacts with the hexatrienylic counterpart of the other moiety of the molecule.

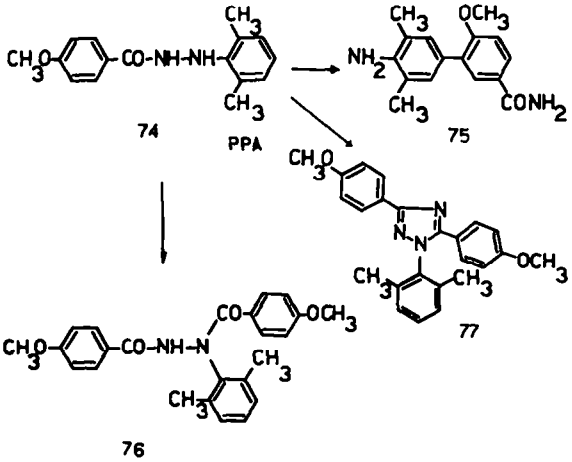


In the present case the [5,7]-and the [5,5]-rearrangements are competitive, while, in the preceding one, the [5,7]-rearrangement is favoured over the [5,5]-one: this might be related to a greater activation induced by two Me groups on the benzene ring.

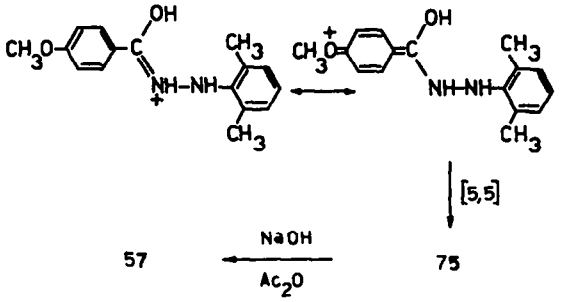
The [5, 7]-sigmatropic rearrangement has been observed also in the case of the 2,6-dimethylphenylhydrazone of 2-methoxy-5-acetylbiphenyl.

V. REARRANGEMENT OF OTHER SUBSTRATES: *p*-ANISIC ACID 2,6-DIMETHYL-PHENYLHYDRAZIDE

The new rearrangements described in this review do not appear to be confined to arylhydrazones. As an example of its extension to other substrates we report here the results obtained from the PPA treatment of *p*-anisic acid 2,6-dimethylphenylhydrazide (**74**), which gave the carboxy amide (**75**), nearby the side products (**76** and **77**).

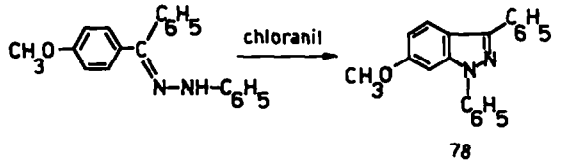


The amide **75** clearly originates from a [5,5]-sigmatropic rearrangement as shown in the scheme, which also reports, as chemical proof of its structure, the correlation with acetylamino acid (**57**).



VI. SIDE REACTIONS

The formation of indazole derivatives when reacting arylhydrazones with PPA, has been frequently observed by us, even though generally in very low yields. An example of this side reaction is the formation of the indazole derivative (**78**) from



the 4-methoxybenzophenone phenylhydrazone symultaneous with the occurrence of the usual [5,5]-rearranged product.

The same indazole (**78**) has been obtained by an independent synthesis by oxidation of the starting phenylhydrazone with chloroanil.

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