Tetrahedron Vol 33, pp 2321 to 2327 Pergamon Press 1977 Printed in Great Britain

HOMOLYTIC SUBSTITUTIONS IN INDOLINONE NITROXIDE RADICALS—II

REACTION WITH ORGANIC PERACIDS

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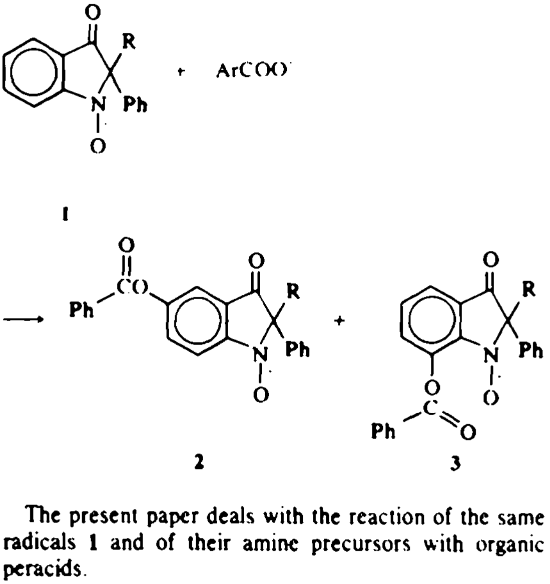
(*Received in UK 28 February 1977; Accepted for publication 17 March 1977*)

Abstract—The reactions of indolinone nitroxides **7** and of the corresponding amine precursors **15** with organic peracids were studied, and were found to give substitution products at the aromatic nucleus, i.e. 5-aroyloxy- and 7-aroyloxynitroxides **8** together with N-oxides **10** and with 7-hydroxynitroxides **9**. Structures were assigned on the basis of ESR and ^{1}H NMR spectra. A reaction scheme was proposed involving a homolytic substitution which accounts for the products obtained and is supported by an experimental proof.

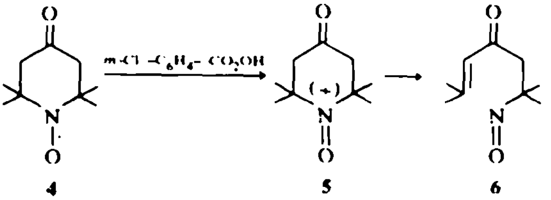
In previous papers we reported on the synthesis[1a] of indolinone nitroxides **1** and their reaction[1b] with aroyloxyl radicals leading to the substitution compounds **2** and **3**



1 **2** **3**

The present paper deals with the reaction of the same radicals **1** and of their amine precursors with organic peracids.

It is known[2] that 2,2,6,6-tetramethylpiperidine-1-oxyl **4** by treatment with *m*-chloroperbenzoic acid gives the nitroso derivative **6** via the intermediate formation of the oxoammonium ion **5**, whilst the analogous pyrrolidine nitroxides do not react:



4 **5** **6**

The verdazyl radicals too, by treatment with *p*-nitroperbenzoic acid are oxidised to ammonium salts which undergo a Hoffman type decomposition leading to 1,3,5-triphenyl-1-formylformazanes.[3] On the other hand, the oxidation of aliphatic and aromatic secondary amines with perbenzoic acids is a well-known synthetic route to nitroxides;[4] Rassat *et al.* applied this method extensively to aromatic amines[5] also but they did not mention the formation of reaction products deriving from a substitution at the aromatic nucleus.

The indolinone nitroxide radicals **7** react in benzene at room temperature for several hours with organic peracids in a 1:1 molar ratio giving compounds **8**, **9** and **10** via a substitution at the aromatic nucleus.

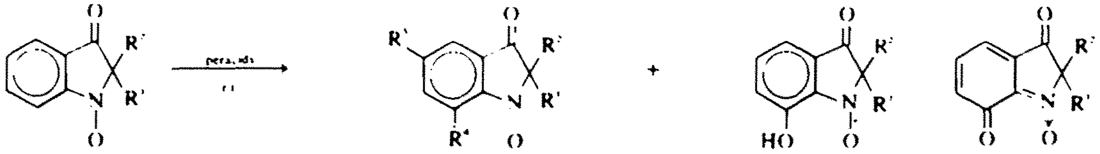
The organic peracids used were both aromatic and aliphatic, i.e. perbenzoic, *m*-chloro- and *p*-nitroperbenzoic, perlauric and trifluoroperacetic acid: scheme.

In all cases the principal reaction products were the N-oxides **10** (20–40% yield) which contain small quantities of the nitroxide radicals **9**, whilst compounds **8** bearing at the aromatic nucleus the acyloxy group deriving from the used peracid were always obtained in low yield (Table 1). Sometimes we were not able to isolate compounds **8** in the pure solid state, but highly purified solutions of them gave satisfactory IR and ESR spectra which were used for their identification and characterisation (Tables 2 and 3).

Compounds (**8a**, **b**, **d**, **e**, **f**, **g**, **h**) were identified by comparison (m.p., mixed m.p., IR and ESR spectra) with the identical products obtained in the reaction of indolinone nitroxides **7** with aroyl oxyl radicals.[1b]

Compounds (**8c**, **i**, **m**, **n**, **o**) were assigned the reported structure on the basis of the tight similarity of their ESR spectra with those of the above mentioned nitroxides **8**. In the case of these compounds, as for **8f**, we were able to observe the formation of only one isomer, even if the second one was probably formed although in too low yield to be isolated. The compound obtained was assigned the structure of 7-acyloxy- and not the isomeric one of the 5-acyloxy-derivative, because in all previously studied reactions the 7-isomer considerably predominates over the 5-isomer (see also Ref. 1b).

In the case of the lauryl derivatives, both isomers could be obtained, so the structure assignment was possible by means of the ESR value of a^N and of the greater a^H, which corresponds either to the 5-H or 7-H. As we pointed out in the previous paper,[1b] in the ESR spectra of 7-acyloxy derivatives (such as **8b**, **e**, **h**) a^N is lower than for 5-isomers (9.2 against 9.5 G approx.), and $a^{7\text{-}H}$ is greater than $a^{5\text{-}H}$ (3.2 against 3.0 G approx). The ESR spectrum of the lauryl derivative isolated in a greater amount exhibits $a^N = 9.23$ G and $a^H = 3.22$ G, while the



7a–e **8a–p** **9a–e** **10a–e**

a: R^1 = Me; R^2 = Ph
b: R^1 = Et; R^2 = Ph
c: R^1 = R^2 = Ph
d: R^1 = CH_2Ph; R^2 = Ph
e: R^1–R^2 = $(CH_2)_4$

a: R^1 = Me; R^2 = Ph; R^3 = $PhCO_2$; R^4 = H
b: R^1 = Me; R^2 = Ph; R^3 = H; R^4 = $PhCO_2$
c: R^1 = Me; R^2 = Ph; R^3 = H; R^4 = m-Cl—C_6H_4—CO_2
d: R^1 = Et; R^2 = Ph; R^3 = $PhCO_2$, R^4 = H
e: R^1 = Et; R^2 = Ph; R^3 = H; R^4 = $PhCO_2$
f: R^1 = Et; R^2 = Ph; R^3 = H; R^4 = p-NO_2—C_6H_4—CO_2
g: R^1 = R^2 = Ph; R^3 = $PhCO_2$; R^4 = H
h: R^1 = R^2 = Ph; R^3 = H; R^4 = $PhCO_2$
i: R^1 = R^2 = Ph; R^3 = H; R^4 = m-Cl—C_6H_4—CO_2
j: R^1 = R^2 = Ph; R^3 = R^4 = m-Cl—C_6H_4—CO_2
k: R^1 = R^2 = Ph; R^3 = CH_3—$(CH_2)_{10}$—CO_2; R^4 = H
l: R^1 = R^2 = Ph; R^3 = H; R^4 = CH_3—$(CH_2)_{10}$—CO_2
m: R^1 = R^2 = Ph; R^3 = H; R^4 = CF_3
n: R^1 = CH_2Ph; R^2 = Ph; R^3 = H; R^4 = m-Cl—C_6H_4—CO_2
o: R^1–R^2 = $(CH_2)_4$; R^3 = H; R^4 = m-Cl—C_6H_4—CO_2
p: R^1–R^2 = $(CH_2)_4$; R^3 = R^4 = m-Cl—C_6H_4—CO_2

a: R^1 = Me; R^2 = Ph
b: R^1 = Et; R^2 = Ph
c: R^1 = R^2 = Ph
d: R^1 = CH_2Ph; R^2 = Ph
e: R^1–R^2 = $(CH_2)_4$

Table 1. Reactions of compounds 7 and 15 with peracids

Compound[a]	peracid[a]	products (%)[b]			
7a	$PhCO_2OH$	7a	8a	8b (10)	9a–10a (19)
7a	m-Cl-C_6H_4-CO_2OH	7a	—	8c	9a–10a
7b	Ph-CO_2OH	7b	8d	8e (9)	9b–10b (28)
7b	p-NO_2-C_6H_4-CO_2OH	7b	—	8f	9b–10b
7c	Ph-CO_2OH	7c	8g	8h (10)	9c–10c (25)
7c	m-Cl-C_6H_4-CO_2OH	7c (6)	8i (9)	8j	9c–10c (47)
7c	CH_3-$(CH_2)_{10}$-CO_2OH	7c	8l	8k	9c–10c (24)
7c	F_3C-CO_2OH	7c	—	8m	9c–10c (30)
7d	m-Cl-C_6H_4-CO_2OH	7d	—	8n	9d–10d
7e	"	7e	8p	8o	9e–10e
15a	"	7a (13)	—	8c (8)	9a–10a (28)
15b	p-NO_2-C_6H_4-CO_2OH	7b (5)	—	8f (3)	9b–10b (40)
15c	m-Cl-C_6H_4-CO_2OH	7c	—	8i (6)	9c–10c (28)
15d	"	7d	—	8n	9d–10d
15e	"	7e (15)	8p	8o	9e–10e (5)

[a] a molar ratio substrate/peracid 1:1 and 1:2 was used for compounds 7 and 15, respectively; [b] products 8 and 10, for which percentages are set out in parenthesis, were isolated either in the solid state or as uncrystallizable oils; other compounds, for which yields are not indicated, were obtained in solution and identified by means of their IR and/or ESR spectra.

spectrum of the other derivative exhibits $a^N = 9.5$ G and $a^H = 2.94$ G, so they were assigned structures **8l** and **8k**, respectively.

Compounds **8j** and **8p** show ESR spectra simpler than those of all other radicals **8**, from which only one a^N and two equal a^H values can be obtained (Table 3): the lack of an hfcc value of approx. 3 G strongly suggests the lack of both 5-H and 7-H, so a double substitution structure was assigned.

Compounds **10** were assigned the reported structures on the basis of the ^1H NMR spectra of **10a** and **10e**. The latter, recorded at 100 MHz, exhibits in the aromatic hydrogen region a quartet centered at 7.25δ, a doublet at 6.8δ and another doublet at 6.5δ; from this spectrum two

Table 2. Analytical and spectroscopic data of compounds **7e**, **8** and **10**

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
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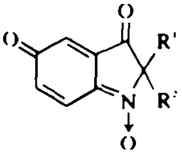
coupling constants can be obtained, J – 6.4 Hz and J = 9.5 Hz, respectively. The third coupling constant is too small to be detected, even if it may be suggested by a small line broadening. These coupling constant values led us to exclude structures **11** isomeric with **10**, which should exhibit one *ortho*, one *meta* and one *para* J_{HH}; in fact, whilst values of approximately zero Hz for the J^{para}_{HH} and of 9.5 Hz for the J^{ortho}_{HH} are acceptable, a value of 6.4 Hz is by far too great for a J^{meta}_{HH}.[6] On the contrary, the experimental J values are in agreement with structures **10** which should present two not fully equivalent J^{ortho}_{HH} and one J^{para}_{HH}, the assignment of the experimental values being: $J_{H_4H_5} = 6.4$ Hz; $J_{H_5H_6} = 9.5$ Hz; $J_{H_4H_6} = 0$ Hz approx.[6]



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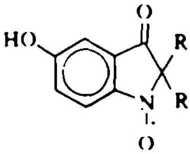

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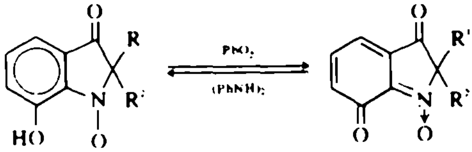
Compound **10a** exhibits in the aromatic hydrogen region an NMR spectrum at 100 MHz analogous with the spectrum of **10e** (with the extra signal for the phenyl group, which fortunately appears as a broad singlet), from which two J values of 9.5 Hz and 6.6 Hz, respectively, could be obtained.

Compounds **9** were assigned the reported structure on the basis of their ESR spectra (Table 3), and with the aid of the following chemical proofs:

(i) Treatment of the reaction mixture **9–10** with PbO$_2$ causes the disappearance of the ESR signal because of the oxidation of **9** to **10**:



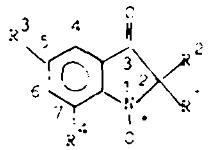
9 **10**

(ii) Treatment of the mixture **9–10** with a small quantity of 1,2-diphenylhydrazine causes a very sharp *increase* of the intensity of the ESR signal, because of the reduction of **10** to **9**.[7]

The isomeric structure **12** was also ruled out because each compound **9** exhibits an ESR spectrum which is identical to the ESR spectrum shown by the reduction product of the corresponding compound **10**, for which structure **11** was ruled out. Moreover, oxidation of **9** gave **10** as the unique reaction product.

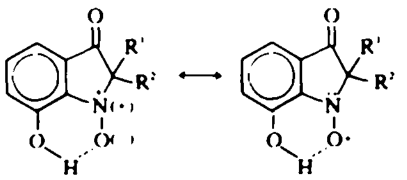
Compounds **9a–e** exhibit in the ESR spectra an a^N value of approx 10.6 G, considerably greater than the corresponding value for compounds **8** (9.2–9.5 G). This fact is in full agreement with the assigned structure of 7-OH derivatives, because it can be easily explained by the formation of an intramolecular H-bond which favours the more polar limit structure **13** against the less polar one **14**.

Table 3. Hfccs of nitroxides **7e**, **8** and **9**



	a^N	a^{5-H}	a^{7-H}	$a^{4-H} = a^{6-H}$ (2H)	a^{H_R}
7e*	9.75	3.01	3.01	----	------
8c	9.64	3.39	----	1.05	$a^{H_{Me}}$ = 0.11 (3H)
8i	9.30	3.19	----	1.01	------
8j	9.17	----	----	1.00	------
8k	9.50	----	2.94	1.03	------
8l	9.23	3.22	----	1.00	------
8m	8.85	2.90	----	1.00	a^F = 3.90 (3F)
8n	9.06	3.25	----	1.01	$a^{H_{CH_2Ph}}$ = 0.5 (1H)
8o	9.40	3.29	----	1.28	$a^{H_{(CH_2)_4}}$ = 0.48 (2H); $a^{H_{(CH_2)_4}}$ = 0.27 (2H).
8p	9.34	----	----	1.25	$a^{H_{(CH_2)_4}}$ = 0.50 (2H); $a^{H_{(CH_2)_4}}$ = 0.26 (2H).
9a	10.68	3.29	----	0.78	$a^{H_{OH}}$ = 0.53
	(10.60)	(3.25)	----	(0.75)	------
9b	10.53	3.29	----	0.95	$a^{H_{OH}}$ = 0.48; $a^{H_{Et}}$ = 0.36 (1H)
9c	10.58	3.23	----	0.80	$a^{H_{OH}}$ = 0.52
	(10.58)	(3.27)	----	0.80	------
9d	10.50	3.32	----	0.93	$a^{H_{OH}}$ = 0.86; $a^{H_{CH_2Ph}}$ = 0.49 (1H)
9e*	10.68	3.29	----	----	------

* the ESR spectra of 7e and 9e are not resolved, so a^{4-H}, a^{6-H} and a^{H_R} values could not be obtained. The hfccs in parenthesis refer to the products in $CDCl_3$ solution treated with D_2O.



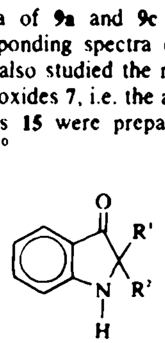
13 **14**

so enhancing the a^N value.[8]

The percentage of compounds **9** in the reaction mixture **9**–**10** was determined by means of a quantitative analysis based on the integration[9] of their ESR signal and the comparison with the ESR signal of a solution at known concentration of a 100% radical, the 2,2-diphenyl-3-indolinone-1-oxyl.[14]

The resulting percentage was only 1–2%, which can explain, together with band broadening caused by the intramolecular H-bond, the absence of the OH band in the IR spectra of the **9**–**10** mixture. Nevertheless, the presence of the OH group in compounds **9** was demonstrated by treatment of their $CDCl_3$ solutions with D_2O, which caused a very sharp modification in the ESR spectra because of the disappearance of the hfcc due to the H-atom of the OH group; in Figs. 1 and 2 the ESR spectra of **9a** and **9c** are set out together with the corresponding spectra obtained after addition of D_2O.

We also studied the reaction of the amine precursors of nitroxides **7**, i.e. the amines **15**, with organic peracids. Amines **15** were prepared according to literature methods.[10]



a: R¹ = Ph; R² = Me
b: R¹ = Ph; R² = Et
c: R¹ = Ph; R² = Ph
d: R¹ = Ph; R² = CH_2Ph
e: R¹-R² = $(CH_2)_4$

15a–e

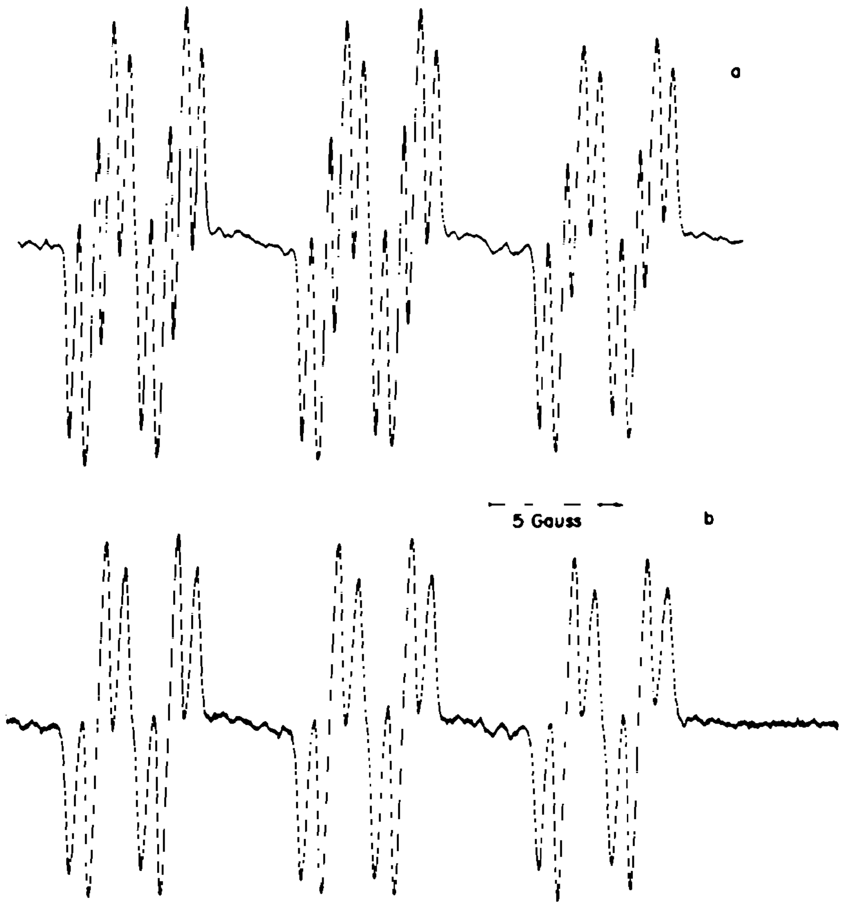


Fig. 1. (a) ESR first-derivative spectrum of the nitroxide **9a** in $CDCl_3$ solution. (b) ESR first-derivative spectrum of **9a** in $CDCl_3$ solution after treatment with D_2O

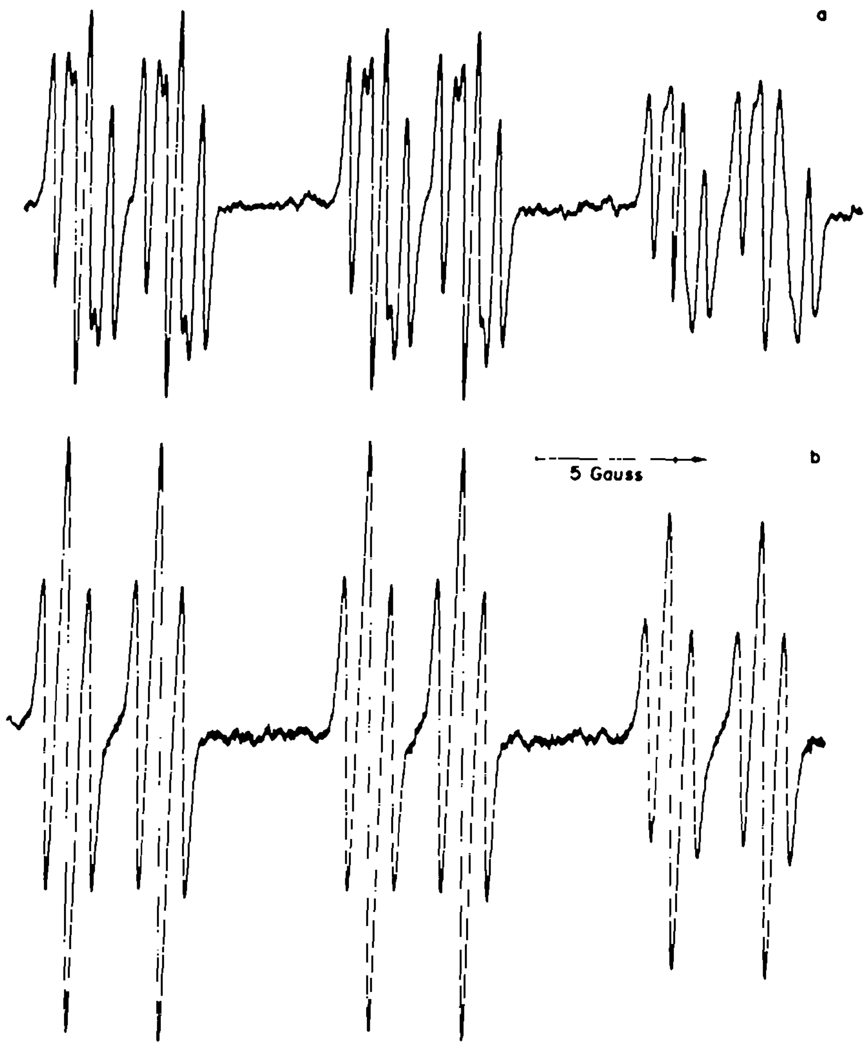
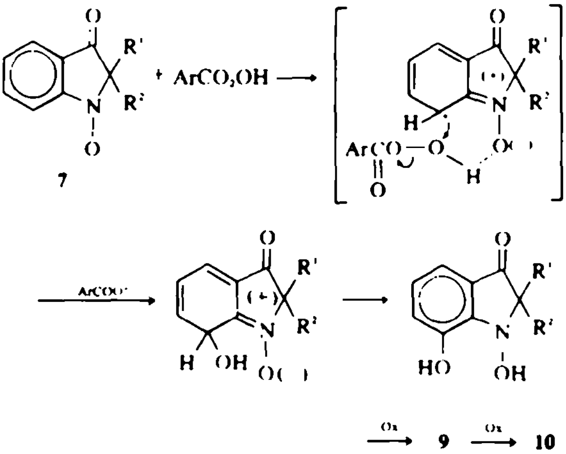


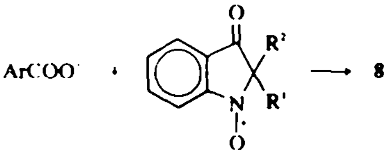
Fig. 2. (a) ESR first-derivative spectrum of the nitroxide **9c** in $CDCl_3$ solution. (b) ESR first-derivative spectrum of **9c** in $CDCl_3$ solution after treatment with D_2O.

The reaction of **15** with organic peracids in a molar ratio amine/peracid of 1/2 led to the very rapid formation of the corresponding nitroxide radicals **7** and, after a longer reaction time, to the compounds **8**, **9** and **10** in the same experimental ratio and apparently at the same rate observed for the reaction with the nitroxide radicals (Table 1). Therefore in our opinion the observed formation of **8**, **9** and **10** proceeds from the nitroxides and not from the amines.

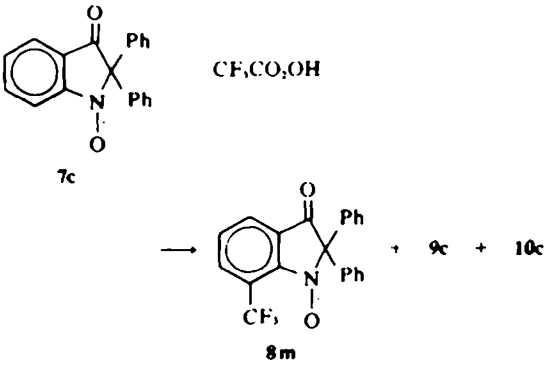
As far as the mechanism of these substitutions is concerned, we have some evidence that the reaction proceeds through the formation of free radicals by decomposition of the organic peracids, perhaps induced by the nitroxide radicals.[11] The isolation between the reaction products of compounds **10**, whilst the isomeric compounds **11** could never be obtained, suggests that a cyclic transition state may be involved in the reaction pathway:



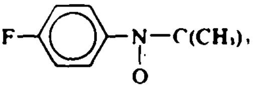
The R-COO· radicals react with the indolinone nitroxides at C-5 and C-7, leading to the aroyloxy-derivatives, as we demonstrated in a previous research.[16]



via a homolytic substitution reaction. The experimental proof which supports the proposed homolytic reaction scheme is the isolation of **8m** in the reaction of **7c** with trifluoroperacetic acid:



The CF_3 group must derive from the decarboxylation of the $CF_3COO^\cdot$ radical[12] and its presence in **8m** was demonstrated by the ESR spectrum of this compound, which shows a hfcc of 3.90 G due to three equivalent fluorine atoms of a CF_3 group. This coupling constant value is in agreement with the value of 3.5–4.25 G for a F-atom directly bonded at the aromatic nucleus in **16**[13] and **17**,[14] respectively:[15]



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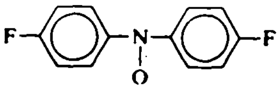


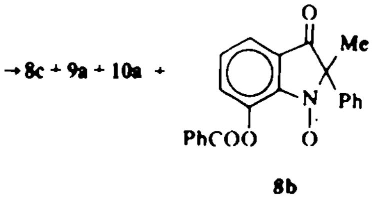
17

whilst it seems far too great to be attributed to the F-atom of a CF_3COO group linked at the aromatic nucleus. In fact it must be noted that in radicals **8** in which R^3 or R^4 is a RCOO group, we never observed an hfcc attributable to the H-atoms of the R group. Moreover, the low value of a^N in radical **8m** (8.85 G against a value of 9.2–9.5 G for other radicals **8**) confirms the presence of the strong electron-attracting group CF_3 on the aromatic nucleus.[16]

It is worthy of note that, contrary to the $CF_3COO^\cdot$ and in agreement with $ArCOO^\cdot$ radicals, lauryl radical $CH_3(CH_2)_{10}COO^\cdot$ does not decarboxylate in the reaction conditions (as indicated by the CO band in the IR spectra of **8k**, **l**, Table 2), even if it is known that aliphatic acyloxyl radicals decarboxylate faster than the aromatic ones.

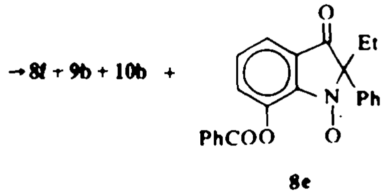
Finally we studied the reaction of **7a**, **b** with *m*-chloro- and *p*-nitro-perbenzoic acids in the presence of benzoic acid; besides the usual products, i.e. **8c**, **9a**, **10a** and **8f**, **9b**, **10b**, respectively, also **8b** and **8e** were obtained in low yields:

7a + $m-Cl-C_6H_4-CO_3H + PhCOOH$



8b

7b + $p-NO_2-C_6H_4-CO_3H + PhCOOH$



8e

These reactions were easily interpreted by admitting that benzoic acid can be oxidised to benzoyl oxyl radical by oxyl radicals:

$$PhCOOH + ArCOO^\cdot \rightarrow PhCOO^\cdot + ArCOOH$$

which occurrence we demonstrated in the reactions of **7** with benzoyl peroxide in the presence of carboxylic acids.[16]

EXPERIMENTAL

The m.ps are not corrected. The IR spectra were recorded using a Perkin-Elmer 257 apparatus; the ^{1}H NMR spectra were recorded on a Joel 100 MHz apparatus in CD_3COCD_3 using TMS as internal standard; the ESR spectra were recorded in $CHCl_3$ using a Varian E-4 apparatus. Compounds **7**,[1a] **15**[10] and $PhCO_2OH$[17] were prepared as described in the literature. m-Cl-C_6H_4-CO_2OH and p-NO_2-C_6H_4-CO_2OH were commercial products.

A *Oxidation of* **7a–e** *and* **15a–e** *with aromatic peracids and peralauric acid.* 2 Mmoles of **7a–e** in 20 ml benzene and 2 mmoles peracids in 20 ml Et_2O were mixed at room temp. and after standing for 15–20 hr (3 days in the case of perlauric acid), the mixture was treated with Na_2CO_3 aq. The organic layer, washed with water many times, was separated, dried on Na_2SO_4 and evaporated to dryness. The residue was chromatographed on SiO_2 column or on SiO_2 preparative TLC using benzene, or petrolether/ethylacetate 9:1 or benzene/acetone 9:1 as eluents. The same results were obtained in the oxidation of compounds **15a–e** using a molar ratio compound/peracid 1:2.

The isolated products and the corresponding yields are set out in Table 1; analytical and spectroscopic data are set out in Tables 2 and 3.

B *Oxidation of* **7c** *with* CF_3CO_2OH. 4 ml of CF_3COOH and 6 ml of 35% H_2O_2 were added to 300 mg of **7c** in 20 ml of CH_2Cl_2 at room temp and kept overnight under stirring. The reaction solution worked up as described in A gave the products indicated in Table 1; the hfccs of product **8m** are set out in Table 3.

C *Oxidation of* **7a** *and* **7b** *with peracids in the presence of benzoic acid.* 1 Mmole of **7a**, 1 mmole of m-Cl-C_6H_4-CO_2OH and 3 mmoles of PhCOOH in 20 ml of a mixture of benzene/ether 1:1, were kept standing for 15 hr at room temp. The reaction solution worked up as described above in A gave **8c**, **9a**, **10a** and **8b**. The reaction between **7b**, p-NO_2-C_6H_4-CO_2OH and PhCOOH was carried out under the same conditions; the isolated products were **8f**, **9b**, **10b** and **8e**. All products were identified by their ESR and IR spectra.

D *Spectroscopic proofs of the equilibrium* **9⇄10**. Addition of PbO_2 to a 10^{-3} M chloroform soln of **10**, from which the characteristic ESR signal of compound **9** had been recorded, caused the immediate disappearance of the signal. When an half equimolar amount of $(PhNH)_2$ was added to same soln, the intensity of the characteristic ESR signal of **9** was increased over 80 times.

E *Treatment of* **9** *with* D_2O. 10^{-2} M $CDCl_3$ solns of the **9–10** mixture were shaken with an equal volume of D_2O. The $CDCl_3$ layer was separated and dried on Na_2SO_4; from this soln the new ESR signal was recorded (Figs. **1b** and **2b**).

F *Assessment of the percentage of radical* **9** *in the mixture* **9–10**. The percentage of radical in the **9–10** mixture was determined by comparing the ESR signals of approx 10^{-3} M benzene solns of this mixture with the ESR signal of 2,2-diphenyl-3-indolinone-1-oxyl **7c** benzene soln. Double integration of the signal was carried out numerically according to Wyard[9] and the radical content proved to be about 1-2%.

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