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Spectroscopic Evidence for Electron Transfer Preceding or Accompanying Nucleophilic Aromatic Displacement Reactions on Nitrophthalic Systems with 4-Methylphenoxide Ion

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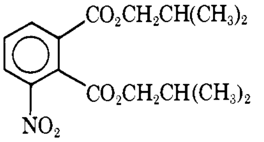
Abstract: The spectroscopically observed behavior of solutions containing the 4-methylphenoxide ion (**2**) and two different nitro aromatics, capable of undergoing nitro displacement, has been studied. In the case of **1**, the investigation mainly centered on the behavior under conditions where the nitro displacement did not proceed to any significant extent (although the behavior over an extended time interval during which very slow displacement occurred was also monitored). For **3**, where displacement is very much faster, spectral analyses were obtained during and subsequent to nitro displacement. The ^{13}C NMR, ^{1}H NMR, ESR, and UV evidence obtained strongly suggests that electron transfers occur prior to and in competition with the nitro displacement reactions.

The interaction of bases with nitro aromatics in solution has been reported to result in electron-transfer processes in which the radical anion of the nitro aromatic was formed.[1] These radical anions have been thoroughly characterized by electron spin resonance techniques in some cases[1] and proposed with good reason in others.[2]

During aromatic nucleophilic substitution (S$_N$Ar) reactions involving, for example, methoxide and a nitro-activated aromatic containing an appropriately placed leaving group, both components needed to produce the radical anion of the nitro aromatic are present. However, only a few reports of the observation of radical anions in such systems have appeared,[3] presumably because of the dominant interest by most investigators in the structures of the Meisenheimer intermediates, the products, and the kinetics of their formation and decomposition.[4] In the few reported cases, the radical anions were identified[3a] or detected[3b-d] *only by ESR* and were produced in very low yields (e.g., <1%[3a]).

During our studies[5] of aromatic nitro displacement reactions on nitrophthalic esters, we found that an intense deep red color was produced by combining diisobutyl 3-nitrophthalate (**1**) with sodium 4-methylphenoxide (**2**) in *N,N*-dimethylformamide (DMF) at ca. 25 °C, but that, *at this temperature,* no detectable nitro displacement occurred for many hours. This report summarizes our attempt to spectroscopically determine the nature of the substance or substances responsible for this phenomenon and to compare these results with those obtained by allowing **2** to interact with 4-nitro-*N*-methylphthalimide (**3**) under nitro displacement conditions.



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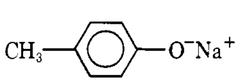

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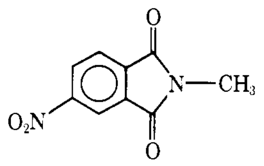

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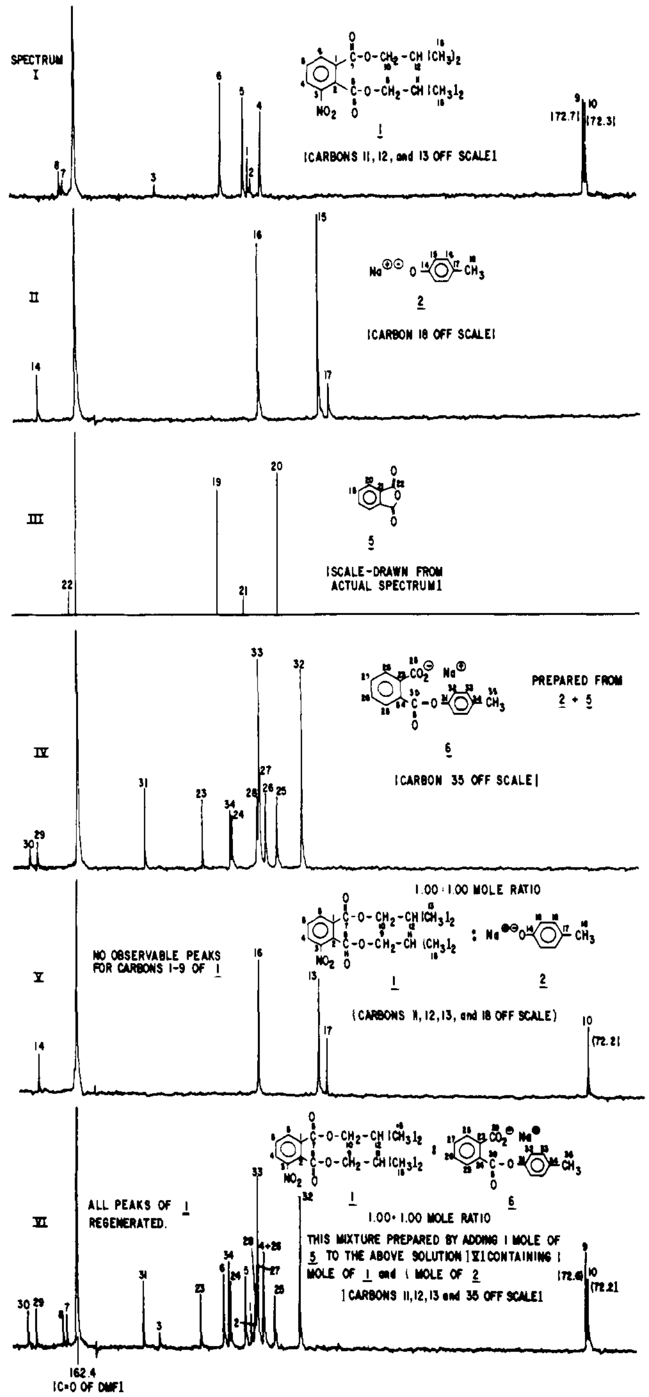


Figure 1. ^{13}C NMR spectra of 1, **2**, **5**, **2** + **5**, 1 + **2**, and 1 + **2** + **5**.

Results and Discussion

Diisobutyl 3-Nitrophthalate. When a DMF solution containing an equimolar mixture of diisobutyl 3-nitrophthalate (**1**) and sodium 4-methylphenoxide (**2**) was prepared at 25 °C and examined by ^{13}C NMR spectroscopy, it was surprising to find that the only peaks observed were those due to *one* of the methylene carbons of **1**, the methine carbons of **1**, the methyl carbons of **1**, and all of the carbons of **2**. Peaks for the six aromatic carbons, the carbonyl carbons, and *one* of the methylene carbons of **1** were not observed (see Figure 1, compare spectra I, II, and V), even at very high signal to noise ratios. Similarly, at other molar ratios of **1**:**2**, namely, 1.00:0.10, 1.00:0.50, and 1.00:2.00, the ^{13}C NMR spectral data were the same (see Figure 2,[6] spectra VII, VIII, and IX, respectively).

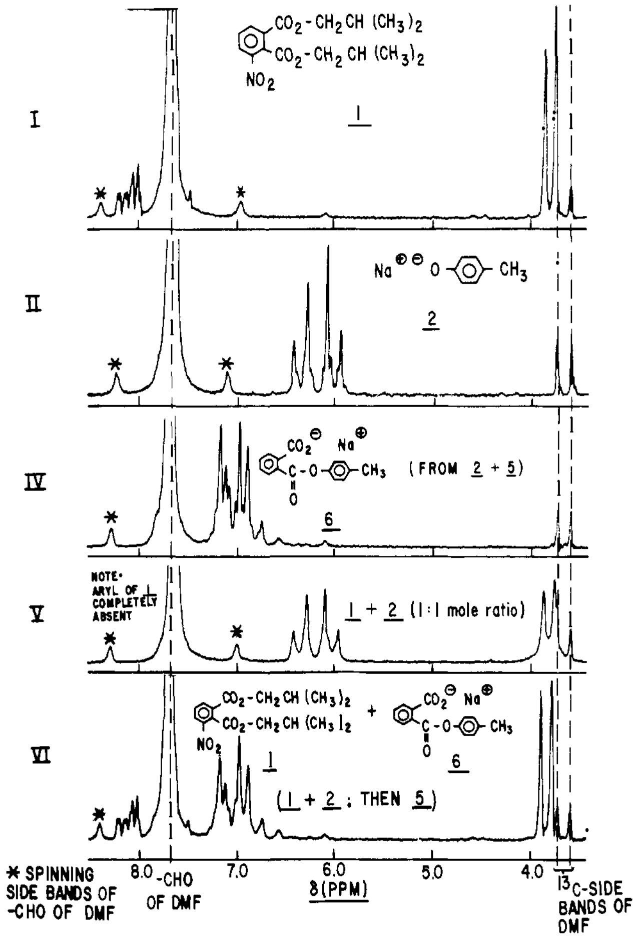
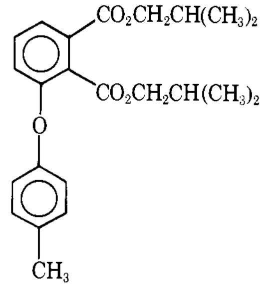


Figure 3. ^{1}H NMR spectra. Partial loss of ^{1}H NMR spectrum of 1, in presence of **2**, and complete reappearance on addition of phthalic anhydride **5**.

The same general phenomenon was observed by ^{1}H NMR spectroscopy. That is, in the equimolar solution of **1** and **2**, the aromatic proton multiplet for **2** was clearly present while that of **1** was completely absent (see Figure 3, compare spectra I, II, and V).

During the time at 25–38 °C necessary to obtain the above spectra, none of the nitro displacement reaction, which occurs readily at higher temperatures to produce **4**, could be detected.



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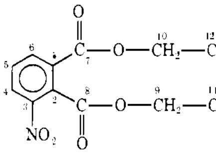
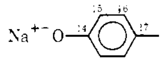
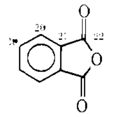
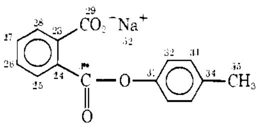
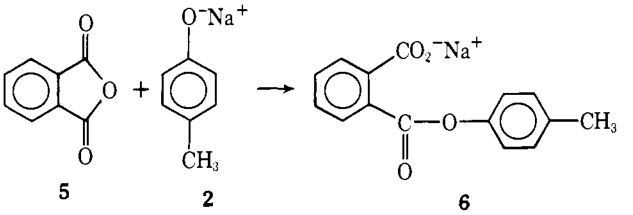
In separate ^{13}C NMR experiments, it had been demonstrated that phthalic anhydride (**5**) reacted rapidly in DMF at 25 °C with **2** to produce sodium 4-methylphenyl phthalate (**6**) (Figure 1, spectrum IV). Clearly, from known spectra (Figure 1, spectra II and III), **2** and **5** were completely consumed. The average difference between the observed and calculated chemical shifts for the 13 distinct carbons of **6** was only ±1.1 ppm, strong proof for its structure (see Table I and footnote *m*). The facility of this reaction was likewise dem-

Table I. Observed ^{13}C NMR Chemical Shifts[a] for Solutions of **1** + 2 with and without the Subsequent Addition of Phthalic Anhydride (**5**) in DMF Solutions at 35 °C

		Spectrum	I	II	III	IV	V[b]	VI[c,d]	VII[b]	VIII[b]	IX[b]
	Carbon atom	Mole ratio employed **1**	1.00	0	0	0	1.00	1.00	1.00	1.00	1.00
		2	0	1.00	0	1.00[d]	1.00	1.00	0.10	0.50	2.00
		5	0	0	1.00	1.00[d]	0	1.00	0	0	0
 1	1		130.9[e]				*f*	130.7[e]	*f*	*f*	*f*
	2		130.4[e]				*f*	130.2[e]	*f*	*f*	*f*
	3		147.2				*f*	147.2	*f*	*f*	*f*
	4		128.7				*f*	128.5[g]	*f*	*f*	*f*
	5		131.7				*f*	131.7	*f*	*f*	*f*
	6		135.7				*f*	135.5	*f*	*f*	*f*
	7		164.4[h]				*f*	164.2[h]	*f*	*f*	*f*
	8		165.0[h]				*f*	164.9[h]	*f*	*f*	*f*
	9		72.7				*f*	72.6	*f*	*f*	*f*
	10		72.3				72.2	72.2	72.2	72.2	72.1
	11		27.6[i]				27.5[i]	27.5[i]	27.5[i]	27.5[i]	27.5[i]
	12		28.0[i]				27.9[i]	27.8[i]	27.9[i]	27.8[i]	27.8[i]
	13		18.8				18.7	18.7	18.7	18.7	18.7
 **2**	14			169.4		*d*	169.2	*d*	*j*	169.1	169.2
	15			118.9		*d*	119.0	*d*	118.5	118.9	118.9
	16			129.4		*d*	129.4	*d*	129.4	129.4	129.4
	17			117.3		*d*	117.5	*d*	*j*	117.6	117.5
	18			20.0		*d*	20.1	*d*	20.2	20.1	20.0
 **5**	19				136.6	*d*		*d*			
	20				125.6	*d*		*d*			
	21				131.7	*d*		*d*			
	22				163.6	*d*		*d*			
 **6**[m]	23					139.6		139.7			
	24					134.3[e]		134.3[e]			
	25					126.4		126.5			
	26					128.4[k]		128.5[g,k]			
	27					129.4[k]		129.5[k]			
	28					129.9[k]		130.0[k]			
	29					169.7[l]		169.8[l]			
	30					171.1[l]		171.3[l]			
	31					149.8		149.8			
	32					122.1		122.2			
	33					129.6		129.6			
	34					134.6[e]		134.6[e]			
	35					20.2		20.3			

[a] In parts per million from external tetramethylsilane. [b] This mixture of 1 and 2 was prepared in DMF at 25 °C under nitrogen and the ^{13}C NMR spectrum was then immediately recorded at 35 °C during 1 h. [c] An equimolar mixture of 1 and **2** was prepared in DMF at 25 °C under nitrogen. *After this solution had remained at 25 °C for 1 h*, an equivalent of phthalic anhydride **5** was added and then the ^{13}C NMR spectrum was recorded at 35 °C during 1 h. [d] None of either 2 or **5** was detectable in this ^{13}C NMR spectrum. They reacted quantitatively to produce 6. [e] These two assignments within a column might be switched. [f] These peaks were totally absent from the ^{13}C NMR spectrum even though high signal to noise ratios were attained and those peaks (10–18) which were observed were very strong. [g] Overlap of two peaks. [h] These two assignments within a column might be switched. [i] These two assignments within a column might be switched. [j] These peaks were too weak to be observed since, in this solution, the total concentration of 2 was very small. [k] These three assignments within a column might be interchanged. [l] These two assignments within a column might be switched. [m] Note the agreement between the observed and calculated values (below) for this compound; the average difference is only ±1.1 ppm. The calculated values were determined by subtracting out known $-NO_2$ substituent effects from known values of the corresponding molecule containing a $-NO_2$ group on carbon 25 (ref 7) (carbon atom, calculated value given): 23, 140.0; 24, 137.1; 25, 126.3; 26, 129.8; 27, 129.0; 28, 130.6; 29 and 30, 165.7 and 167.8; 31, 149.4; 32, 122.0; 33, 129.7; 34, 135.2; 35, 20.2.



5 **2** **6**

onstrated by ^{1}H NMR spectroscopy (see Figure 3, spectra II and IV).

The addition of 1 equiv of phthalic anhydride to an equimolar solution of **1** and **2** gave **6** (see Figure 1, spectrum VI, and Figure 3, spectrum VI) and, at the same time, regenerated entire spectra of **1**. Careful examination of the ^{13}C NMR spectrum VI, Figure 1 (and data in Table I), shows that the expected peaks for all of the carbons of **1** and **6** were now present. Similarly, the ^{1}H NMR spectrum VI, Figure 3, shows the expected aryl multiplets for **1** and **6**. The NMR spectral observations are summarized in Scheme I.

When DMF solutions of **1** and **2** were prepared, a pronounced color appeared; the visible spectrum showed a λ_{max} at 423 nm (Figure 4)[6] whereas solutions of either **1** or **2** alone were virtually transparent above 400 nm. This absorption maximum was eliminated upon addition of phthalic anhydride, coincident with the reappearance of the entire NMR spectrum of **1**. (Solutions of **5** and **6** were also transparent above 400 nm.) However, another absorption maximum was now observed at 473 nm. It is not yet clear whether this arose from some additional minor species (besides **6**) generated upon addition of **5** or if it was present previously and was hidden under the tailing of the 423 nm maximum.

The ESR spectrum of a solution of **1** and **2** was also obtained (Figure 5A). It was virtually the same as the spectrum obtained (Figure 5B) for the radical anion **7** generated from **1** and Na in DMF solution. The observed hyperfine splitting constants

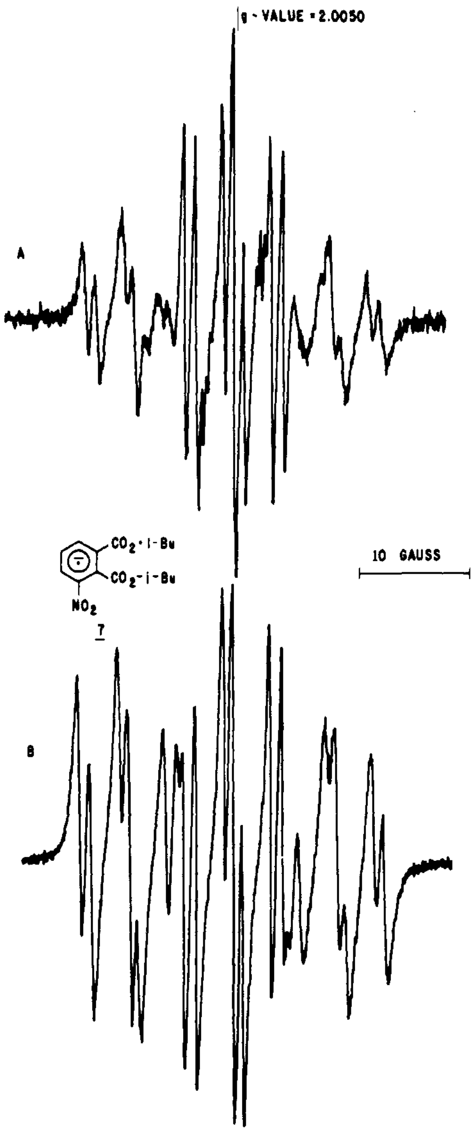
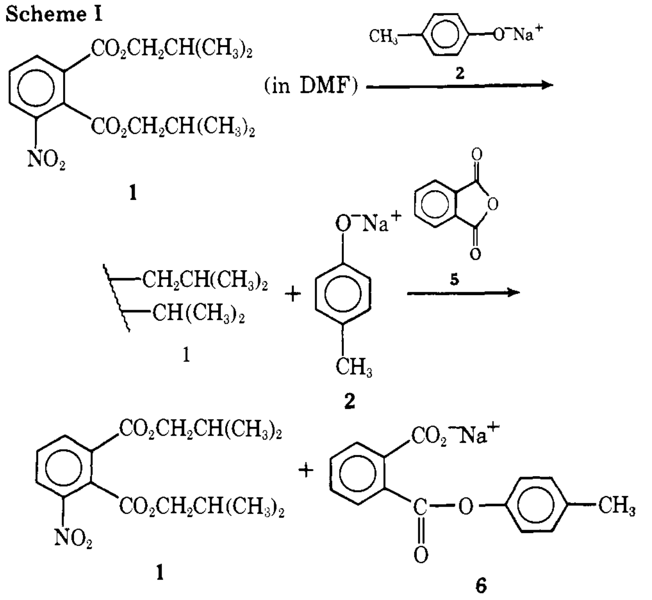
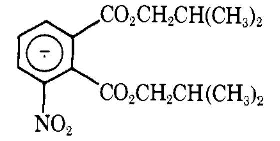


Figure 5. A: ESR spectrum of the radical anion **7** formed in a DMF solution containing equal amounts of **1** and **2** (~1.3 × 10^{-4} *m* concentration of spins). **B**: ESR spectrum of the radical anion **7** generated from 1 + metallic sodium in DMF solution (~3.4 × 10^{-3} *m* concentration of spins).

Scheme I



in both cases are in agreement with values expected for **7**.[8] By double integration of the spectrum produced in the solution



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of **1** + **2** and by comparison with a diphenylpicrylhydrazyl (DPPH) standard solution, it was possible to estimate that the concentration of spins (presumably **7**) in the solution of **1** + **2**, after 40 and 140 min, was approximately 0.8% of the initial concentration of **1** (see Table II).

^{13}C NMR and ^{1}H NMR spectral observations were also made for DMF solutions containing **1** + **7** prepared from **1** and a deficiency of sodium metal. In an experiment where the initial molar ratio of **1**:sodium was 100:8, the ^{1}H NMR spectrum recorded at 2, 25, and 43 h showed no aryl multiplet for **1**. The ^{13}C NMR spectrum after 30 h at 25 °C showed only *one* methylene carbon, both methine carbons, and the methyl carbons of **1** (Table III). This was exactly the same as observed for **1** in solutions containing **1** + **2**. At this same point in time (30 h), the doubly integrated ESR spectrum of another similar mixture of **1** and **7** (prepared from a 100:11 mixture of **1**:sodium in DMF) showed that there was only approximately 0.24% of **7** present based on the total amount of **1** originally present (Table IV).[6] This low level of **7** in the presence of **1** was apparently still sufficient to cause the ^{13}C NMR spectrum to be devoid of the aromatic carbons, the carbonyl carbons, and *one* of the methylene carbons of **1** and the ^{1}H NMR spectrum to be devoid of the aryl multiplet of **1**. Addition of phthalic anhydride **5** to this solution caused a rapid change in the color from dark red-brown to light brown and a simultaneous regeneration of the aryl multiplet (^{1}H NMR of **1**).

One possible explanation of the spectral phenomena displayed by solution of **1** and **2**, before and after addition of **5**, which is consistent with all of the observations above is displayed in Scheme II. Reversible formation of Meisenheimer intermediates such as **8** which do not lead to the eventual displacement products (**4** in this case) is not at all unusual. This behavior has been reported by several workers.[4d] Equilibrium electron transfer between **8** and another molecule of **1** could then give **7** plus the reasonably well-stabilized radical **9**.[10] Exchange between **1** and **7** could then proceed at an appropriate rate to give the observed spectra. Apparently **7** exchanged rapidly enough with **1** to allow every molecule to exist for a finite time as the paramagnetic species **7** during the NMR experiments. Electron exchange of this type is well known to lead to shifting and pronounced broadening of NMR lines as a result of very short relaxation times.[11] In the present case, this resulted in the partial spectrum described above. However, the effect was very specific here; namely, only the aryl multiplet in the ^{1}H NMR and the aromatic carbons, the carbonyl carbons, and one of the methylene carbons in the ^{13}C NMR spectrum were eliminated, whereas the rest of the alkyl carbons and hydrogens[12] were unchanged. This is consistent with the assumption that the excess electron density of **7** should be primarily in the π system, thereby causing only the aryl carbons and hydrogens and the carbonyl carbons to have very short relaxation times. Furthermore, it is probable that the one methylene carbon which was not observed by ^{13}C NMR spectroscopy was the one in the 2-carbobutoxy group. The potential proximity between this carbon and the expected region of highest excess electron density, the nitro group, argues in favor of this suggestion (see structure **10**).

Electron exchange was not rapid enough, however, to eliminate hyperfine splitting in the ESR spectrum. That is, on the ESR time scale, electron transfer between **1** and **7** was slow

Table II. Determination of the Concentration of Radical Anions Produced by the Interaction of Nitro Aromatics with Sodium 4-Methylphenoxide (**2**)

Initial sample composition (*m*)	Time at 25 °C since mixing, min	Area^{a} of the modulated ESR spectrum, cm^2	Spin concn,^{b} *m*	% radical anions^{b} [Spin concn/init nitro aromatic concn × 100]
DPPH (0.00245) in DMF		217^{c}	0.00245	
1 (0.0150) + **2** (0.0150) in DMF	40	11.7^{c}	0.000132	0.88
1 (0.0150) + **2** (0.0150) in DMF	140	10.4^{c}	0.000117	0.78
DPPH (0.0577) in DMF		425^{d}	0.0577	
3 (0.157) + **2** (0.157) in DMF	8	23.7^{d}	0.00322	2.05
3 (0.157) + **2** (0.157) in DMF	24	20.7^{d}	0.00281	1.79
3 (0.157) + **2** (0.157) in DMF	51	17.6^{d}	0.00239	1.52
3 (0.157) + **2** (0.157) in DMF	146	8.3^{d}	0.00113	0.72
3 (0.157) + **2** (0.157) in DMF	230	5.6^{d}	0.00076	0.48
3 (0.177) + **2** (0.160) in DMF	7	25.5^{d}	0.00346	1.96
3 (0.177) + **2** (0.160) in DMF	33	26.4^{d}	0.00358	2.02
3 (0.177) + **2** (0.160) in DMF	73	15.7^{d}	0.00213	1.20
3 (0.177) + **2** (0.160) in DMF	166	5.1^{d}	0.00069	0.39
3 (0.177) + **2** (0.160) in DMF	257	2.1^{d}	0.00029	0.16

[a] Determined by the numerical integration method of Wyard (ref 9). Since all of the spectrometer settings affect the area, the entire set used for the unknown solutions was identical with that used for the known samples to which the unknowns were being compared (see footnotes *c* and *d* below). [b] Because of the intrinsic errors in the method, these values should be considered accurate to only ±50%. [c] Spectrometer settings: modulation width 20 G; amplitude 36; response 0.1; sweep width ±100 G; sweep time 10 s; field intensity 3425.2 G; current 0.5 A. [d] Spectrometer settings: modulation width 20 G; amplitude 2; response 0.1; sweep width ±50 G; sweep time 10 s; field intensity 3425.9 G; current 0.5 A.

Scheme II

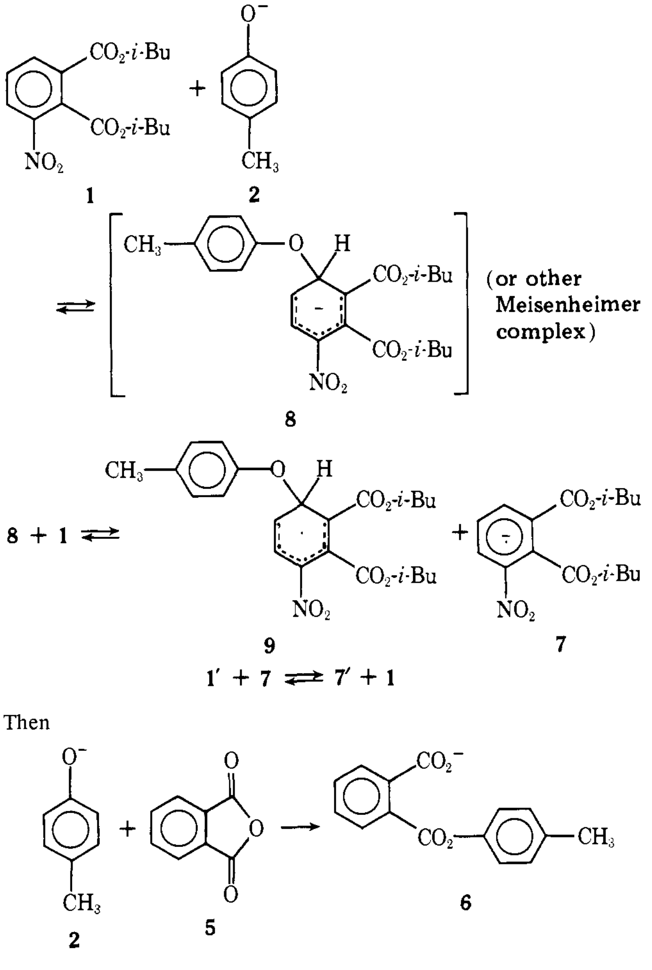
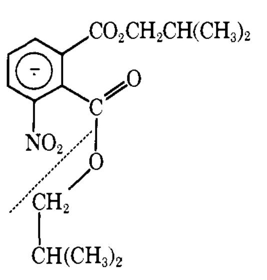


Table III. ^{13}C NMR Chemical Shifts^{a} of Mixtures of **1** and **7** in DMF Solution Which Was Initially Prepared to Be 92:8

Carbon atom^{b}	30 h	72 h
1	*c*	130.8^{d}
2	*c*	130.3^{d}
3	*c*	146.9
4	*c*	128.7
5	*c*	131.7
6	*c*	135.7
7	*c*	163.3^{e}
8	*c*	163.9^{e}
9	*c*	72.7
10	72.3	72.3
11	27.6^{f}	27.6^{f}
12	27.9^{f}	27.9^{f}
13	18.8	18.8

[a] Parts per million from external tetramethylsilane. [b] Numbers correspond to those given to structure 1 in Table I. [c] These peaks were totally absent from the spectrum. [d] These two assignments within a column might be switched. [e] Same as *d*. [f] Same as *d*.



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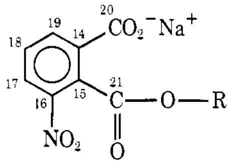
enough to allow the radical anion to be observed as a discrete species. It can be estimated[13] that there should have been approximately 10^8–10^9 encounters per second between **1** and **7** under these conditions. If it is assumed that electron transfer took place at most of these encounters, the spectroscopic observations are consistent with the experimental time scales involved, namely, ESR ~10^{10} s^{-1} and NMR ~10^6–10^7 s^{-1}.

The fact that the entire normal ^{1}H and ^{13}C NMR spectra of the 4-methylphenoxide ion **2** was always observed in these solutions is also significant and consistent with the mechanistic proposal of Scheme II.[14]

Equilibria are proposed throughout since no products resulting from the decomposition of **7** or any other intermediates have been detected in these solutions. The slight differences in the ESR patterns for **7** generated in these solutions and from

Table VI. ^{13}C NMR Chemical Shifts[a] and the Identification of the Products of the Decomposition of the Anion Radical **7** in DMF Solution by Comparison to Known Compounds



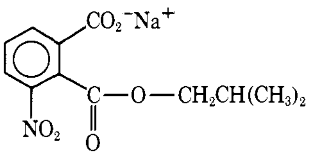
Carbon atom	R = $-^{22}CH_2CH(CH_3)_2$ (**11** obsd in this expt)	R = Ph[b] **12**	R = *p*-PhCH$_3$[b] **13**	HO–$^{23}CH_2$–$^{24}CH(CH_3)_2$[c]
14	141.0	141.0	140.9	
15	130.0	132.1	132.3	
16	146.4	146.3	146.3	
17	124.5	124.9	125.0	
18	129.4	129.9	129.9	
19	136.3	136.4	136.4	
20	167.4[d]	165.5[d]	165.7[d]	
21	168.3[d]	168.0[d]	167.8[d]	
22	71.8			
23	68.6			68.65
24	31.0			31.09

[a] Parts per million from external tetramethylsilane. [b] See ref 7. [c] Determined during this work. [d] These two assignments within a column might be switched.

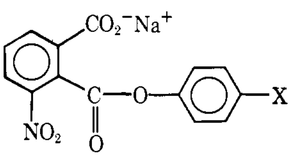
1 + sodium metal suggest the presence of another radical species. The ultraviolet maximum observed at 473 nm *after* the addition of phthalic anhydride is not inconsistent with some addend between **8** and phthalic anhydride. However, we have not yet been able to obtain any solid structural evidence for **8** or **9**.

Upon addition of phthalic anhydride **5** to the solution, all of the 4-methylphenoxy anion **2** was consumed to give **6**. This would displace each of the first two equilibria to the left, thereby reducing the level of the radical anion **7** sufficiently to allow the normal NMR spectra of **1** to be observed.[15]

Thermal Stability of 7. In addition to the above described interactions of **1** and **2** to produce **7** and the behavior of **7** produced from **1** + sodium, the stability of **7** (generated under the latter conditions) over longer periods of time in DMF solution was also followed. Thus, when the ^{13}C NMR spectrum of a DMF solution, initially containing *equimolar quantities* of **1** and sodium, was monitored at ca. 25 °C, it was found that (a) the aromatic, the carbonyl, and one of the methylene carbon peaks of **1** were not observable at 30 or 100 h, but they were at 200 h, and (b) a set of entirely new peaks due to decomposition products was present at 30 h and thereafter (Table V).[6] (Although similar behavior of the ^{13}C NMR spectra of **1**, in the presence of *small amounts* of **7**, was discussed above, the decomposition products of **7** were apparently too low in concentration to be detected.) The major decomposition product was identified as the sodium isobutyl 3-nitrophthalate isomer **11** by comparison of its ^{13}C NMR spectrum with those of known[7] structures **12** and **13**. The aryl and carbonyl chemical shifts of **11** appeared over the 124.5–168.3-ppm range, as did those of **12** and **13**. The average difference between the chemical shifts of discrete carbons of **11** and the corresponding carbons of **12** and **13** was ±0.68 and ±0.73 ppm, respectively. In addition, the methylene carbon of **11** was clearly observed at 71.8 ppm. The other major decomposition product was identified similarly by ^{13}C NMR as isobutyl alcohol (Table VI). No specific structural identity could be assigned to other minor decomposition products from the observed ^{13}C NMR peaks. However, it is quite likely from the chemical shifts that there were alkyl carbons attached to nitrogen in these products (39.5, 40.5, 41.2, and 42.9 ppm); the chemical shifts for the methyl groups in DMF are 30.9 and 36.0 ppm.



11



12, X = H
13, X = CH$_3$

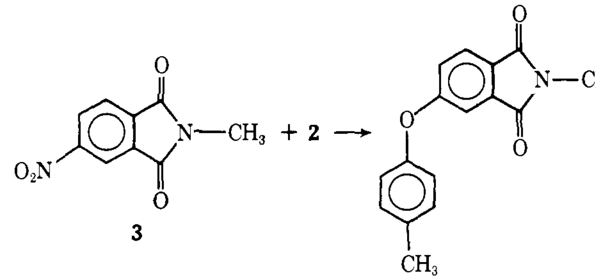
Once the level of radical anion (**7**) concentration had dropped enough to allow the entire spectrum of **1** to be observed (somewhere between 100 and 200 h), it was found at 200 h that the relative molar amounts of **11** and **1** were approximately 1:2, respectively.

The two major products, **11** and isobutyl alcohol, *cannot* be accounted for by a simple base (**7**) catalyzed hydrolysis reaction of **1** since the level of water in the DMF solvent was only approximately 100 ppm. In the actual experiment, approximately 1.7×10^{-3} mol of **1** was converted to **11** + isobutyl alcohol, whereas the total amount of water that could have been present was only approximately 4×10^{-5} mol. Furthermore, large amounts of water would have destroyed the radical anion as fast as it was formed. It was found, however, that some was present (^{13}C NMR broadening effects) even at 100 h.

Additional information bearing on this chemistry was obtained from solutions of **1** + **2**, prepared from the same batches of DMF and **1**, in which none of **11** was observed. If simple base-catalyzed hydrolysis of **1** were occurring, it should have occurred significantly also when the base was **2**. The failure to observe **11** in solutions of **1** + **2**, even after extended periods of time (see below), is consistent with the fact that the actual level of **7** was quite small in the **1** + **2** case but inconsistent with a base-catalyzed hydrolytic mechanism. The actual mechanistic explanation for the conversion of **7** to **11** + isobutyl alcohol + **1** in DMF solution is under investigation.

Long-Term Behavior of a Solution of 1 and 2. The suggestion (Scheme II) of the existence of an equilibrium electron transfer process to produce **7** and other intermediates (possibly **8** and **9**) raised the question as to whether decomposition products of these intermediates (for example, **11** + isobutyl alcohol from **7**) would be produced to any detectable extent over an extended period of time. To answer this question, a solution of **1** and **2** was allowed to remain at room temperature for a very long period (745 h) and was monitored at various times by ^{13}C NMR spectroscopy. The results are summarized in Figure 6[6] (and Table XI in the Experimental Section). After a considerable time at room temperature, the usual spectrum of a mixture of **1** and **2** began to show several additional peaks. These corresponded *exactly* to those of the strongest peaks (protonated carbons) in the known[5] spectrum of **4**. No other extraneous peaks (due to **11**, for example) could be detected. Careful acidification and ^{13}C NMR (see bottom spectrum in Figure 6[6]) and gas chromatographic/mass spectral analysis of the entire reaction mixture indicated that it contained only **1**, **4**, and 4-methylphenol (**14**). Thus, under these reaction conditions, either **7** and other intermediates did not undergo appreciable decomposition or the amount of products produced was too small to be detected. Very slow nitro displacement between **1** and **2** was the only significant reaction.

4-Nitro-*N*-methylphthalimide. Unlike **1**, when 4-nitro-*N*-methylphthalimide (**3**) was dissolved in a DMF or Me$_2$SO solution at approximately 25 °C containing an equimolar amount of **2**, the nitro displacement reaction leading to **15** proceeded to completion quite rapidly.[16] In order to examine the spectral behavior of **3** during and subsequent to displacement under these conditions, it was necessary to conduct the reaction nonstoichiometrically, so that some of **3** was always present.



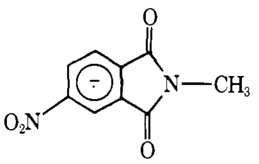
3

15

Thus, 0.5 equiv of **2** was added to a solution of **3** in Me$_2$SO. The resulting solution was monitored by ^{1}H NMR spectroscopy in the aromatic region. As can be seen from these spectra (Figure 7), **15** was produced quite rapidly while, initially, there was no indication of the presence of the excess **3**. Gradually, the spectrum for the excess **3** reappeared, first in a significantly broadened form and later in progressively more detail. Integration of the final mixture indicated that it contained **3**, **15**, and 4-methylphenol (**14**) in the molar ratio of 60:40:11. (The sample of **2** used in this and the following experiment in DMF was contaminated with a small amount of **14**.)

Similarly, addition of 0.5 equiv of **2** to a solution of **3** in DMF resulted in the same kind of ^{1}H NMR behavior (Figure 8).[6] **15** was produced rapidly and the excess **3**, initially not observable, gradually reappeared.

Once again, it appeared that electron transfer processes were occurring presumably to give the corresponding radical anion **16**. This was causing the ^{1}H NMR spectrum of those protons of **3** near the region of high spin density to be broadened to the extent that they were not initially observable. As **16** was consumed, either by the shifting of equilibria or by some decomposition path, the spectrum of **3** gradually appeared and sharpened. The distinction between this system and the one previously discussed (**1** + **2**) is that here electron transfers, etc., occurred competitively with the facile nitro displacement reaction.



16

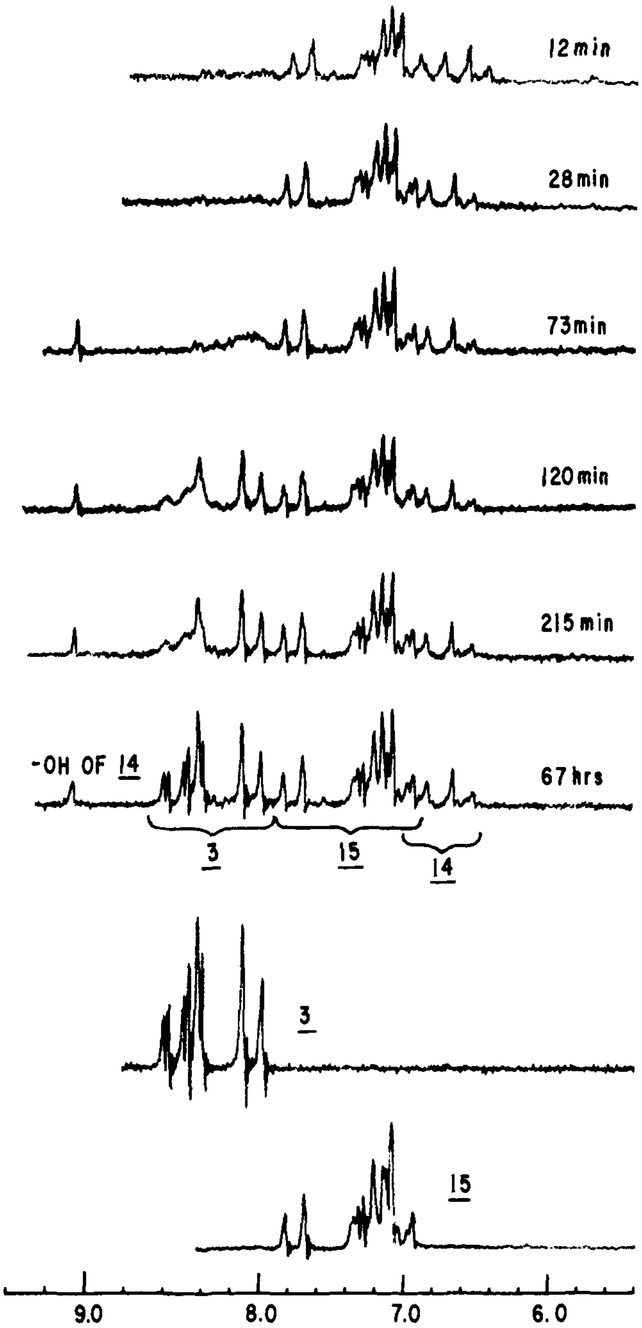


Figure 7. ^{1}H NMR spectrum of aryl region from the reaction of **3** with 0.5 equiv of **2** in ME$_2$SO (and revelant known spectra).

Further indication and evaluation of a radical ion was achieved by examining the ESR spectra of solutions prepared from **2** and **3** with either exact stoichiometry or off-stoichiometry (Table II). Spin concentrations as high as approximately 2% of the original concentratins of **3** were detected and were observed to fall off somewhat more rapidly[17] than in the case of **7** in DMF solution.

All of these spectral observations can be accommodated mechanistically by a scheme similar to that proposed in the previous case (**1** + **2**) except that most of the 4-methylphenoxide is removed from the system relatively rapidly by nitro displacement.

In a manner analogous to the behavior of solutions of (presumably) **16** prepared from **2** + **3**, a DMF solution of **16**, prepared from **3** + sodium, not only produced a strong ESR signal, but also led to the same kind of ^{1}H NMR spectral results; the aryl region was initially absent and gradually grew in.[18]

Experimental Section

All ^{13}C NMR spectra were recorded at 25.2 MHz utilizing complete ^1H decoupling at 100 MHz with a Varian Associates XL-100-15 spectrometer equipped for FT operation. The total pulse delay used was 2.0 s (0.8 s acquisition time + 1.2 s delay). Proton spectra were determined with a Varian T-60 spectrometer. Probe temperatures for ^{13}C and ^1H NMR were 35 and 38 °C, respectively.

Visible spectra were recorded on a Cary spectrophotometer. ESR spectra were obtained with a Jeolco JES-ME ESR instrument. **1** was prepared as described elsewhere.[5] Anhydrous DMF and Me_2SO were Burdick and Jackson reagent grade and were used without further purification. The DMF contained 100 ppm water; the Me_2SO contained 130 ppm water (K. Fischer titrations). VPC analyses were carried out using a 10% SE-30 column and programming from 150 to 290 °C at 10 °C/min. All transfers of reagents and solvents were carried out in a dry, nitrogen-filled glove box.

Preparation of Sodium 4-Methylphenoxide (2). Exactly 17.98 g (0.7817 mol) of sodium metal (freshly cleaned free of NaOH under hexane) was dissolved in 1000 mL of anhydrous methanol under nitrogen with external cooling. Then, 84.43 g (0.7817 mol) of freshly distilled 4-methylphenol was added. The resulting homogeneous solution was stirred in a hot water bath overnight while a steady stream of dry nitrogen was passed over it to remove essentially all of the methanol. The resulting white solid was heated in an oil bath at 100 °C under vacuum (approximately 2 mmHg) for 4 h and at approximately 25 °C for an additional 16 h. The dry product **2** was removed form the round-bottom flask in a dry nitrogen glove box and used and stored under dry nitrogen. The yield was 100.5 g (99%).

Interaction of 1 and 2 at 25–38 °C in Anhydrous DMF Solution under Nitrogen.

A. ^{13}C NMR Observations. The following solutions (I–IX) were prepared and their ^{13}C NMR spectra were recorded at 35 °C. The 65–175-ppm regions of the spectra are displayed in Figures 1 and 2,[6] and all of the spectral data are listed in Table I.

I. **1** (1.00 g, 0.0031 mol) in 5.0 mL of DMF (0.62 *m* solution).

II. **2** (0.30 g, 0.0023 mol) in 4.0 mL of DMF (0.58 *m* solution).

III. Phthalic anhydride **5** (1.36 g, 0.0092 mol) in 15.0 mL of DMF (0.61 *m* solution).

IV. **2** (1.19 g, 0.0092 mol) and 1.36 g (0.0092 mol) of phthalic anhydride **5** in 15.0 mL of DMF (resulting in a 0.61 *m* solution of sodium 4-methylphenyl phthalate **6**). This solution was stored at 25 °C for 1 h and then the spectrum was recorded.

V. **1** (2.05 g, 0.0063 mol) and 0.82 g (0.0063 mol) of **2** in 10.0 mL of DMF (0.63 *m* solution of each component); solution turned dark red immediately at 25 °C. The recording of the spectrum of this solution at 35 °C was begun as soon as the solution was prepared and required 1 h for data acquisition to achieve the signal to noise level shown in Figure 1. (About 1 h after this spectrum had been recorded, a sample was diluted with ether, extracted with dilute HCl, and dried with $MgSO_4$. VPC analysis of this ether solution showed that **1** and **2** were essentially the only components present in the reaction mixture; perhaps a trace (<1%) of the nitro displacement product **4** was detected.)

VI. **1** (3.10 g, 0.0096 mol) and 1.25 g (0.0096 mol) of **2** were dissolved in 15.0 mL of DMF (0.64 *m* solution of each component). This solution was stored at 25 °C for 1 h and then 1.42 g (0.0096 mol) of phthalic anhydride **5** was added. After another 1 h, the spectrum was recorded.

VII. **1** (0.60 *m* solution) and 0.06 *m* solution of **2** in DMF. Spectrum[6] was recorded as soon as solution was prepared.

VIII. **1** (0.60 *m* solution) and 0.30 *m* solution of **2** in DMF. Spectrum[6] was recorded as soon as solution was prepared.

IX. **1** (0.30 *m* solution) and 0.60 *m* solution of **2** in DMF. Spectrum[6] was recorded as soon as solution was prepared.

B. ^1H NMR spectra were obtained on the same solutions as used for the ^{13}C NMR spectra: I (**1**); II (**2**); IV (**2** + **5** → **6**); V (**1** + **2**); VI (**1** + **2**; + **5** → **1** + **6**). The δ 3.5–8.5 ppm regions of these spectra are shown in Figure 3.

The spectrum of solution V (see Figure 3) was the same whether it was recorded 5 min or 1 h after the solution was prepared. Integration of this spectrum showed aryl protons of **2**:$-CH_2-$ protons of **1**:CH_3- protons of **1** (4:4:12); care was taken to correctly subtract out the area of the ^{13}C side bands of the solvent from the integral for the $-CH_2-$ protons of **1**.

C. Visible spectra of 0.01 M solutions of each of the following were recorded: I (**1**); IV (**2** + **5** → **6**); V (**1** + **2**); VI (**1** + **2**; + **5** → **1** + **6** + an unidentified colored species). No visible spectra were obtained for **2** alone or **5** alone since solutions of these in DMF were virtually colorless (similar to IV). The spectra are shown in Figure 4.[6]

Table VIII

Time at 25 °C, min	Relative VPC peak heights	
	3 (t_R = 4.4 min)	**15** (t_R = 8.6 min)
7	7	93
33	1	99
73	0.5	99.5
209	0.2	99.8

D. The ESR spectrum was obtained for the dark solution prepared by mixing 0.0486 g (0.000150 mol) of **1** in 5 mL of DMF with 0.0195 g (0.000150 mol) of **2** in another 5 mL of DMF in a nitrogen glove box; the concentration of each component was 0.0150 *m*. An unmodulated spectrum was taken 30 min after mixing and is shown in Figure 5A (spectrometer settings: modulation width 0.5 G; amplitude 2000; response 0.3; sweep width ±25 G; sweep time 10 min; field intensity 3425.2 G); hyperfine splitting constants, 9.0 (3 lines), 3.5 (3 lines), and 1.1 G (2 lines). This spectrum is very similar to that shown in Figure 5B of the independently prepared radical anion **7**. The resolution is not as good partly because the spin concentration is more than an order of magnitude lower.

Fully modulated spectra were also recorded 40 and 140 min after the solution was prepared. These spectra were then doubly integrated using the method of Wyard[9] and compared to the integral for a known amount of spins in a DMF solution of diphenylpicrylhydrazyl (DPPH). The results are listed in Table II.

Preparation of 7. NMR Behavior of a Solution in Which the Initial Molar Ratio of 1:7 Was 92:8. A solution of 3.23 g (0.0100 mol) of **1** in 16 mL of DMF (0.63 *m* solution) was stirred at 25 °C under nitrogen with 0.0195 g (0.00085 mol) of sodium metal (cleaned and cut into small pieces under hexane and weighed out under N_2). The solution darkened rapidly as the metal dissolved and **7** was produced. After stirring for 2 h, and with the metal completely dissolved, a sample was removed and, maintaining it under nitrogen at 25–35 °C, it was monitored by ^{13}C and ^1H NMR spectroscopy over several days. The ^1H NMR spectra recorded at 2, 25, and 43 h were the same as found previously for the solution (V) containing a mixture of **1** and **2** except that the spectrum of **2** was absent. That is, the aromatic protons of **1** did not appear in these spectra. The ^1H NMR spectrum recorded after 67 h did show the aromatic protons of **1** but in a somewhat broadened form.

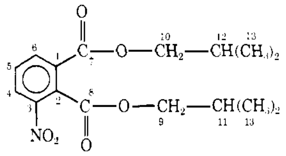
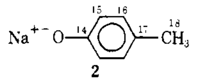
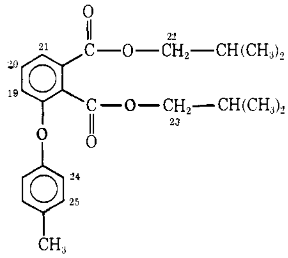
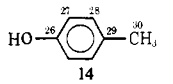
Similarly, the ^{13}C NMR spectrum at 30 h showed no aromatic or carbonyl carbons, only one methylene carbon, two methine carbons, and a single peak for the methyl carbons. This is also the same as displayed by the solution (V) containing **1** and **2** except that **2** is, of course, absent. At 72 h, the ^{13}C NMR showed all of the carbon shifts for **1**. The ^{13}C NMR data are listed in Table III.

Preparation of 7. ESR Spectral Variations with Time of a Solution in Which the Initial Mole Ratio of 1:7 Was ~89:11. Exactly 0.0128 g (0.000557 mol) of sodium metal was added to 1.62 g (0.00502 mol) of **1** in 10 mL of DMF. The solution darkened rapidly. A sample was removed after 6 h and its ESR spectrum was monitored. The ESR data are shown in Table IV.[6]

Effect of Phthalic Anhydride on the ^1H NMR Spectrum of the Solution Containing 1 and the Anion Radical 7. To a 9.28-g sample of the solution prepared in the previous experiment, 25 h after it was prepared (this sample could contain a maximum of 0.00041 mol of **7**), was added 0.070 g (0.00047 mol) of phthalic anhydride. The color of the solution changed instantly from dark red-brown to light brown and the ^1H NMR spectrum, recorded after another 20 min, displayed the entire spectrum for **1** including its well-defined aromatic multiplet.

^1H NMR Behavior of a Solution in Which the Initial Molar Ratio of 1:7 Was ~99:1. A solution with initial concentrations of **1** as 0.62 *m* and **7** as 0.0063 *m* was prepared by adding a precise amount of a freshly prepared solution of **1** + **7** in DMF to another solution of **1** in DMF. The final solution was then stored at 38 °C and monitored by ^1H NMR spectroscopy. After 10 min, the region for the aryl protons of **1** was completely blank. Between 20 and 45 min this region began to show a gradual increase in a broad, poorly defined peak. After 15 h, the entire well-defined spectrum of **1** was present.

Table XI. ^{13}C NMR Chemical Shifts in a DMF Solution of **1** and **2** as a Function of an Extended Period of Time at 25 °C^{a}

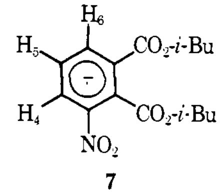
	Carbon atom	Time^{b} at 25 °C, h								After acidification
		5.3	28	53	97	183	243	376	735	
 **1**	1	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*i*
	2	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*i*
	3	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	147.1
	4	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	128.6
	5	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	131.7
	6	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	135.6
	7	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*i*
	8	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*i*
	9	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	72.6
	10	72.2	72.2	72.2	72.2	72.2	72.2	72.2	72.2	72.2
	11	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}	27.5^{d}
	12	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}	27.8^{d}
	13	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7	18.7
 **2**	14	169.2	169.1	169.1	169.0	169.0	168.9	168.8	168.7	*j*
	15	118.9	118.9	118.9	118.9	118.9	118.9	118.9	118.8	*j*
	16	129.4	129.4	129.4	129.4	129.4	129.4	129.4	129.3	*j*
	17	117.5	117.6	117.6	117.6	117.5	117.6	117.6	117.6	*j*
	18	20.1	20.1	20.1	20.1	20.1	20.1	20.1	20.1	*j*
 **4**	19					122.9^{e}	122.9	122.9	122.9	123.0
	20					131.0^{e}	131.0	131.0	131.0	131.1
	21					124.7^{e}	124.7	124.7	124.7	124.7
	22					71.4^{e,f}	71.5^{f}	71.5^{f}	71.5^{h}	71.5
	23					71.5^{e,f}	71.6^{f}	71.6^{f}	71.5^{h}	71.6
	24					*e,g*	*g*	*g*	119.0	119.0
	25					130.7^{e}	130.7	130.7	130.7	130.7
 **14**	26									155.7^{k}
	27									115.3^{k}
	28									129.8^{k}
	29									127.6^{k}
	30									20.1^{k}

[a] Compare results at early times with those given in Table I. [b] The time listed is the average time in which the spectrum was recorded. The actual times for recording, from start to finish, were 4.5–6.0, 26.5–29.5, 52.0–54.5, 92–98, 176–191, 241–244, 367–384, and 727–743, respectively. [c] These peaks were totally absent from the spectrum. [d] These two values within a column may be switched. [e] The shifts, obtained previously (ref 5) for an authentic sample, are 122.9, 131.0, 124.5, 71.1, 71.3, 118.7, and 130.5 ppm, respectively. Only the strong peaks for **4** are discernible. [f] These two values within a column may be switched. [g] This peak is buried by overlap with the strong one at 118.9 ppm for carbon 15 of **2**. [h] Overlapping peaks. [i] These nonprotonated carbon peaks were either buried or too weak to be observed in this spectrum. [j] Not present because all of **2** had been converted to **14**. [k] The shifts obtained for an authentic sample were 155.3, 115.4, 129.9, 127.6, and 20.2 ppm, respectively.

^{1}H NMR Behavior of a Solution in Which the Initial Molar Ratio of 1:7 Was 99.5:0.5. In this case, the "growing-in" of the well-defined aromatic multiplet of **1** was complete in less than 45 min.

^{13}C NMR Behavior of a Solution of the Anion Radical 7. A solution of 1.62 g (0.0050 mol) of **1** in 8 mL of DMF was stirred at 25 °C with 0.117 g (0.0051 mol) of sodium metal. The metal began to dissolve rapidly and the solution became very dark. Samples of the solution were removed after approximately 30, 100, and 200 h and analyzed by ^{13}C NMR spectroscopy. The results are tabulated in Table V.[6] Once again, the spectrum of **1** was only partially discernible for many hours and, then, completely present again. The identities of the observed products from the decomposition of **7** in this solution have been established with reasonable certainty by comparison of ^{13}C NMR shifts with those of known structures. This evidence is tabulated in Table VI.

ESR Behavior of a Solution of the Anion Radical 7. A solution of 0.1845 g (0.00057 mol) of 1 in 10 mL of DMF was stirred with 0.0131 g (0.00057 mol) of sodium at 25 °C. After 3 h, a sample was removed. The unmodulated ESR spectrum of this solution is shown in Figure 5B (spectrometer settings: modulation width 0.1 G; amplitude 710; response 0.1; sweep width ±25 G; sweep time 10 min; field intensity 3425.2 G). The hyperfine splitting constants are in agreement with structure **7**.



7

$a_N^{NO_2} = 9.4$; $a_{H_4} \sim a_{H_6} = 3.5$; $a_{H_5} = 1.1$ G (lit.[8] for 3-nitrophthalimide: $a_N^{NO_2} = 8.75$; a_{H_4} and a_{H_6} = 2.75 and 3.60; $a_{H_5} = 0.88$ G)

Data from recordings of the modulated spectrum are listed in Table VII.[6]

Reaction of 3 with 2 in DMF at 25 °C. VPC Analysis.[16] Exactly 0.5817 g (0.00447 mol) of **2** was added to a solution of 0.9218 g (0.00447 mol) of **3** in 30 mL of DMF. Small aliquots of the resulting homogeneous solution were removed at various times, worked up with CH_2Cl_2/H_2O, dried with $MgSO_4$, and analyzed by VPC. The results (Table VIII) indicate that this reaction is quantitative and quite rapid at 25 °C ($t_{1/2} \ll 7$ min).

Reaction of 3 with 0.5 Equiv of 2 in Me_2SO at 25 °C. ^{1}H NMR Behavior of the Resulting Solution at 38 °C. To a solution of 1.03 g (0.0050 mol) of **3** in 14 mL of Me_2SO was added 0.33 g (0.0025 mol) of **2**. The solution rapidly turned deep green and all of **2** had dissolved in ca. 10 min. A sample of the resulting solution was removed and monitored by ^{1}H NMR spectroscopy at 38 °C. The results are illustrated in Figure 7 along with known spectra of **3** and **15**.

Reaction of 3 with 0.5 Equiv of 2 in DMF at 25 ° C. ^{1}H NMR Behavior of the Resulting Solution at 38 °C. To a solution of 1.03 g

(0.0050 mol) of **3** in 10 mL of DMF was added, under N_2, 0.33 g (0.0025 mol) of **2**. The solution rapidly turned dark blue and became homogeneous. A sample was removed and monitored by ^1H NMR spectroscopy at 38 °C (probe temperature). The results are illustrated in Figure 8[6] and are very similar to those observed in Me_2SO (compare with results shown in Figure 7).

Reaction of 3 with 2 in DMF at 25 °C. ESR Analysis. A 0.6109-g sample (0.00470 mol) of **2** was added to a solution of 0.9680 g (0.00470 mol) of **3** in 30 mL of DMF at 25 °C. A sample of this homogeneous reaction mixture was examined periodically by ESR spectroscopy. This analysis suggests the presence of the radical anion **16** in the mixture. The results are listed in Table II.

This reaction was repeated at slightly off-stoichiometry: 1.9037 g (0.00530 mol) of **3**, 0.6182 g (0.00480 mol) of **2**, 30 mL of DMF. The ESR results are listed in Table II.

Preparation of the Anion Radical 16 in DMF and ^1H NMR Behavior of a Solution in Which the Initial Molar Ratio of 3:16 Was ~89:11. A solution of 1.03 g (0.0050 mol) of **3** in 10 mL of DMF was stirred at ca. 25 °C under N_2 and 0.0124 g (0.00054 mol) of sodium metal was added. The system rapidly became dark blue as the sodium dissolved. After 14 h, the ^1H NMR spectrum showed a slightly visible but very broadened aryl region and a sharp NCH_3 peak. After 87 h, the aryl region contained much more definition and was much stronger, but it was still significantly broadened by comparison with the spectrum of an authentic sample of **3**.

ESR Spectral Behavior of 16 in DMF. A very dark solution of the anion radical **16** was prepared in 10 mL of DMF from 0.0797 g (0.00039 mol) of **3** and 0.0089 g (0.00039 mol) of sodium metal. After 30 min, a sample was removed and monitored by ESR spectroscopy. The results show that significant radical ion concentrations were present to well over 7 h (Table IX[6]).

A plot of the reciprocal of the spin concentrations vs. time gave a straight line having a correlation coefficient of 0.998. This suggests that, at least in the final stages, the decay of **16** occurs with second-order kinetics. (A plot of the log (spin concentration) vs. time gave a decidedly curved line, i.e., not a first-order decay.)

ESR Spectral Behavior of 16 in Me_2SO. A solution of **16** was prepared by adding 0.0108 g (0.00047 mol) of sodium metal to a solution of 0.0967 g (0.00047 mol) of **3** in 10 mL of Me_2SO. After 20 min, a sample was removed and analyzed by following its ESR signal. The results are listed in Table X.[6]

Long-Term Monitoring of a Solution of 1 and 2 in DMF at 25 °C. Exactly 2.05 g (0.0063 mol) of **1** was added to a solution of 0.82 g (0.0063 mol) of **2** in 10.0 mL of DMF. The ^{13}C NMR spectrum of this homogeneous, dark red solution was recorded many times during the next 745 h. Selected spectra are displayed in Figure 6[6] and the spectral data are tabulated in Table XI.

The last of these spectra indicated that approximately 75% of the original amount of **2** was still present. Therefore, 0.47 g of 37% aqueous HCl (0.0047 mol of HCl) was added. The color lightened and fine solid particles (NaCl) appeared. A sample of the solution was centrifuged and again analyzed by ^{13}C NMR spectroscopy. This indicated that it contained only **1**, **4**,[5] and **14** (see bottom spectrum, Figure 6[6]). The mole ratio (NMR) of **1**:**4** was approximately 76:24.

Another sample of the reaction mixture was added to CH_2Cl_2, extracted with water to remove NaCl and $NaNO_2$, and submitted to gas chromatographic/mass spectral analysis. Similar to the previous ^{13}C NMR analysis, this showed only **1**, **4**[5], and **14**.

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Supplementary Material Available: Figures 2 (^{13}C NMR spectra of **1** + **2**), 4 (visible spectra), 6 (^{13}C NMR spectra of **1** + **2** as a function of time), and 8 (^1H NMR spectra from reaction of **3** with **2**) and Tables IV (ESR data for **7**), V (^{13}C NMR of mixtures of **1** and **7**), VII (ESR data for **7**), IX (ESR data for **16**), and X (ESR data for **16**) (7 pages). Ordering information is given on any current masthead page.

References and Notes

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(10) An alternative mechanism could also be suggested in which electron transfer occurred reversibly between **1** and **2** to give **7** directly and a 4-methylphenoxy radical which rapidly led to **9** or some other complex. An equilibrium involving **8** could then become a possibility also.

(11) (a) R. W. Kreilick in "NMR of Paramagnetic Molecules. Principles and Applications", G. N. LaMar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N.Y., 1973, pp 603–604; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, pp 145–146.

(12) A careful examination of the methylene protons of **1** in the solution of **1** + **2** showed that, although the signal was slightly broadened, no loss in the total integral (four protons) resulted (see Figure 3, spectrum V). It was necessary, of course, to subtract out the integral for the low-field half of the low-field ^{13}C side bands of the *N*-methyl groups of the solvent.

(13) M. J. Povich, *J. Phys. Chem.*, **79**, 1106 (1975).

(14) For example, the presence of the 4-methylphenoxy radical could have resulted in rapid electron exchange with unreacted **2** and thus broadened and shifted its spectrum. This was not observed.

(15) Another path by which the concentration of **7** could have been reduced was via electron transfer to phthalic anhydride **5** (see control in the Experimental Section).

(16) Nitro displacement by **2** from **3** is at least 10^3 more rapid than from **1**. See ref 5, and F. J. Williams and P. E. Donahue, *J. Org. Chem.*, in press.

(17) H. M. Relles and D. S. Johnson, unpublished results.

(18) No information has yet been obtained on the nature of the decomposition products in this case.