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Selectivity of Attack in Nucleophilic Alkylation of Nitroarenes with Grignard Reagents. Reactivity of Some Substituted Nitrobenzenes and Nitronaphthalenes

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Reactivity of some substituted nitrobenzenes and nitronaphthalenes with RMgX has been investigated. In all reactions C-alkylation products have been obtained. The entering alkyl group exhibits a great tendency to attack at unsubstituted positions. Examples of nucleophilic displacement of a nucleofugic group by an alkyl group are also reported. Our findings are discussed and compared with analogous studies on relative reactivities of differently substituted aromatic carbons toward nucleophiles. Anomalous behavior has been observed for reactions of methoxy derivatives which yield nitrocyclohexadienic or cyclohexenic compounds and lesser amounts of the expected nitroso derivatives. This unusual reactivity can be accounted for by a rapid aci–nitro tautomerization which prevails over decomposition to nitroso compounds.

It has been accepted[2] for a long time that the action of any type of Grignard Reagents on mononitroarenes could exclusively lead to N-alkylation products through 1,2 addition to the nitro group. Examples[3] of conjugate addition were confined to polynitro compounds.

We recently reported[4] that treatment of mononitroarenes with alkylmagnesium halides results in nucleophilic alkylation at ortho or para positions. Thus, the reactivity of alkyl and aryl[5] reagents has now been differentiated.

Our reaction is thought[6] to proceed through a conjugate addition (1,4 or 1,6) of RMgX to the nitroarenic system leading to adducts whose structure are similar to those postulated by Bunnett[7] for σ-anionic intermediates in nucleophilic aromatic substitution. The adducts can be decomposed to alkylnitroso compounds by adding concentrated hydrochloric acid or boron trifluoride.

Our results are strongly supported by a recent paper[8] in which this type of reactivity is extended to lithium alkyl compounds.

More recently we started studying the possibility of alkylating the substituted aromatic carbon. In a short paper,[9] we reported that the presence of a methyl group in *p*-methylnitrobenzene does not prevent attack of the entering alkyl group at the para position.

These interesting preliminary results prompted us to examine the influence of substituents on reactivity. In this paper we report the results obtained with reactions of some substituted nitrobenzenes and nitronaphthalenes.

Results

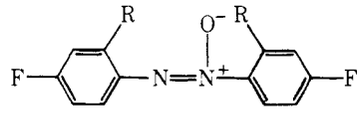
Reactivity of nitrobenzene (**1**) and *p*-phenoxy (**2**), *p*-(phenylthio) (**3**), *p*-(methylthio) (**4**), *p*-fluoro (**5**), *p*-chloro (**6**), *p*-methoxy (**7**), and *p*-(*N*,*N*-dimethylamino) derivatives with methyl- (**a**), *n*-butyl- (**b**), (2-phenylethyl)- (**c**), *sec*-butyl- (**d**), and benzyl- (**e**) magnesium halides in tetrahydrofuran or diethyl ether was investigated. Similar studies were performed on 1-nitro-2-methoxy- (**8**) and on 1-methoxy-2-nitro (**9**) naphthalenes.

Each experiment was performed with the same experimental procedure used for *p*-methylnitrobenzene,[9] which utilizes concentrated hydrochloric acid (33%) to decompose the adducts.

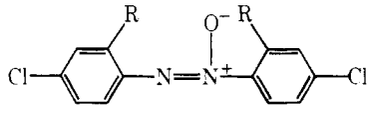
Investigated reactions and isolated products are summarized in Table I. The reported yields are those of pure products, obtained through chromatographic separation on silica gel columns, except for **1** for which the overall yield is given. This was calculated based on the mixture of both isomers **10** and **11** after preliminary purification from tars and other secondary products. ^{1}H-NMR analysis of this mixture gives approximately a 2:1 ratio value for ortho/para alkylation.

For the whole series of *p*-Z-nitrobenzenes, with the exception of **7**, the main reaction product is a 2-alkyl-4-Z-nitrosobenzene.

Reactions are often accompanied by formation of tars and trace amounts of byproducts, mainly arising from decomposition of nitroso derivatives (azoxy, nitro, etc.). In the reactions of **5** and **6**, the presence of azoxy compounds in the reaction products is considerable. They have been identified as 2,2′-dialkyl-4,4′-difluoro- (**17**) and 2,2′-dialkyl-4,4′-dichloro- (**18**) azoxybenzenes, respectively.



17a, R = CH_3
b, R = *n*-C_4H_9



18c, R = $PhCH_2CH_2$

Under identical experimental conditions, **7** yields mainly 1-nitro-4-methoxy-6-alkyl-1,3-cyclohexadiene (**19**) and lesser amounts of the expected nitroso compound (**20**). Similar re-

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Table I. Products and Yields of Reactions between RM_gX and Some Substituted Nitrobenzenes and Nitronaphthalenes

substrate	R in RMgX	products	yields, %	eluent[a]
1	n-C_4H_9	**10b**	64[b]	CH–EA (9:1, v/v)
		11b		
2	CH_3	**12a**	53	CH–EA (9:1, v/v)
2	n-C_4H_9	**12b**	51	CH–EA (9:1, v/v)
3	CH_3	**13a**	65	CH–EA (9:1, v/v)
4	CH_3	**14a**	73	CH–EA (9:1, v/v)
5	CH_3	**15a**	38	CH–B (20:1, v/v)
		17a[c]	17	
5	n-C_4H_9	**15b**	44	CH–B (20:1, v/v)
		17b[c]	15	
6	$PhCH_2CH_2$[d]	**16c**	35	CH–B (10:1, v/v)
		18c	18	
7	CH_3	**20a**	8	CH–EA (8:1, v/v)
		19a	48	
7	n-C_4H_9	**20b**	6	CH–EA (8:1, v/v)
		19b	54	
8	n-C_4H_9	**21b**	64	B
8	$PhCH_2CH_2$	**21c**	56	B
9[e]	CH_3	**24a**	95	CH–EA (10:1, v/v)
9[e]	n-C_4H_9	**24b**	73	CH–EA (10:1, v/v)
9[e]	$CH_3CH_2CH(CH_3)$–	**24d**	69	CH–EA (10:1, v/v)
9[e]	$PhCH_2$	**24e**	85	CH–EA (10:1, v/v)

[a] CH = cyclohexane; EA = ethyl acetate; B = benzene. [b] The yield refers to a mixture of both isomers. [c] Another azoxy compound was isolated in lesser amounts. This compound was tentatively identified as 2-alkyl-4,4′-difluoroazoxybenzene by means of ^1H NMR and mass spectra. [d] Large amounts of tars. [e] Using dilute hydrochloric acid (5%) to decompose the adduct.

Table II. ^1H NMR Spectral Parameters[a] of 1-Nitro-4-methoxy-6-R-1,3-cyclohexadienes in $CDCl_3$ at 30 °C

	chemical shifts in ppm from Me_4Si			coupling constants, Hz	
	R = Me	R = n-Bu		R = Me	R = n-Bu
2	7.56	7.57	2–3	6.8	7.0
3	5.15	5.11	2–6	0.3_5	0.3
5	2.22	2.40	3–5	1.8	1.9
5′	2.95	2.83	3–5′	0.4	0.3_5
6	3.29	3.18	5–5′	−17.2	−17.1
Me	1.15		5–6	1.8	1.8
CH_3–		0.90	5′–6	8.9	8.8
–CH_2–		1.2–1.6	6-Me	7.2	
–OMe	3.77	3.75	6-CH_2		6.2

[a] The spectra have been analyzed as ABX systems for the aliphatic protons. Splitting due to the long-range couplings has been corrected for insufficient resolution to get more reliable $4J_{H-H}$ values. The signs of the coupling constants have not been determined; therefore absolute values are reported although they are thought to be negative.[26]

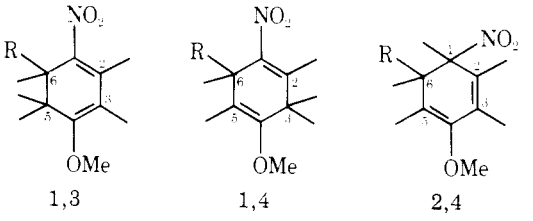


Figure 1.

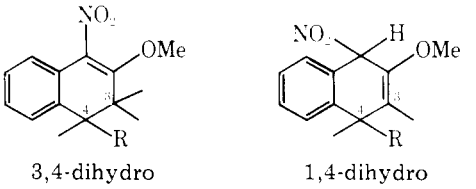


Figure 2.

sults have been obtained with **8**, which leads to 1-nitro-2-methoxy-4-alkyl-3,4-dihydronaphthalene (**21**).

19 and **21** can be quantitatively converted to their corresponding aromatic nitro derivatives **22** and **23** by treatment with DDQ.

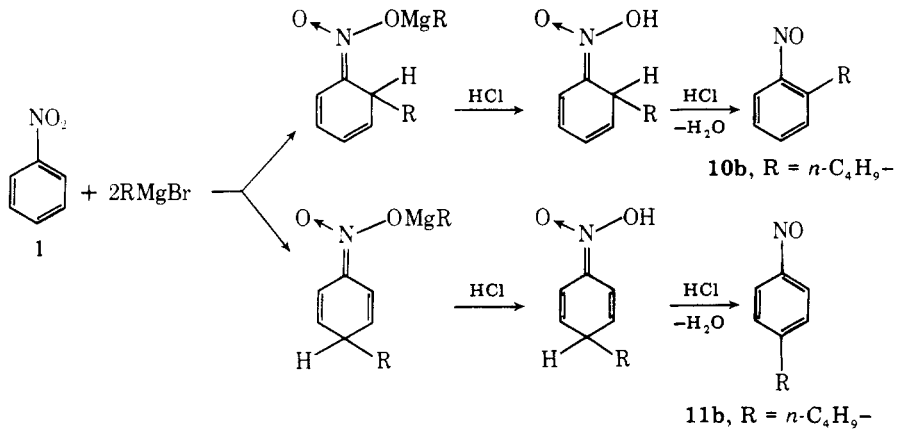
Reaction of 1-methoxy-2-nitronaphthalene results in substitution of the methoxy group by the alkyl group. The use of more dilute HCl (5%) actually increases the yields. High yields were obtained both with primary and secondary Grignard reagents. Under identical experimental conditions, the *N,N*-dimethylamino compound produced an intractable mixture. Likewise, attempts to decompose the adducts with NH_4Cl or dilute HCl were unsuccessful.

Characterization of Products. Nitroso, nitro, and azoxy compounds were easily identified by common analytical procedures. The structure of **19** has been assigned as follows. Elemental analysis, IR, and mass spectra indicated that this compound should have a cyclohexadienic structure. In addition, reaction with DDQ was used to pinpoint the site of substitution. However, some uncertainties remained concerning the dienic system. The ^1H-NMR spectrum at 100 MHz (see Table II) indicates that **19** must have a 1,3-cyclohexadienic structure (Figure 1). A 1,4-cyclohexadiene should have two olefinic protons, 2-H and 5-H, very weakly coupled, and a 2,4 structure should have three olefinic resonances. The actual ^1H NMR spectra show two olefinic resonances only, which are strongly coupled. In addition, the measured coupling values are only in full agreement with the assigned structure.

Likewise, the ^1H NMR spectrum provides conclusive evidence for the 3,4-dihydro structure **21** (see Figure 2). In fact, the presence of three aliphatic resonances and the values of coupling constants (see Experimental Section) are in accord with the assigned structure and inconsistent with a 1,4-dihydro compound.

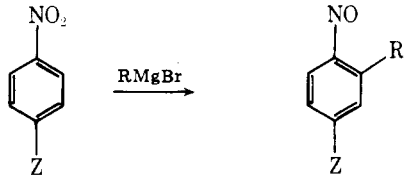
The visible spectrum of **19** shows a strong absorbance at about 360 nm. These findings indicate that strong conjugation exists between nitro and methoxy groups and that the dipolar structure is a major contributor to the ground state. ^1H NMR data confirm these conclusions. Proton 2 is deshielded by 1.8 ppm, and proton 3 is shielded by 0.8 ppm, with reference to the corresponding protons of unsubstituted 1,3-cyclohexa-

Scheme I



10b, R = n-C_4H_9-

11b, R = n-C_4H_9-



2, Z = PhO-
3, Z = PhS-
4, Z = MeS-
5, Z = F-
6, Z = Cl-

12a, Z = PhO-; R = CH_3-
12b, Z = PhO-; R = n-C_4H_9-
13a, Z = PhS-; R = CH_3-
14a, Z = MeS-; R = CH_3-
15a, Z = F-; R = CH_3-
15b, Z = F-; R = n-C_4H_9-
16c, Z = Cl-; R = $PhCH_2CH_2$-

diene. The observed perturbations follow the trend of chemical shift variations induced by the same substituents on the corresponding hydrogens of benzene.

For 2-methyl-4-methoxynitrobenzene (**22**) proton 6 (corresponding to 2-H) is deshielded by 0.6 ppm while proton 5 (corresponding to 3-H) is shielded by 0.6 ppm. Assuming that identical anisotropic effects must be present for the same substituents in both systems, we can deduce that the large difference in chemical shift variations is due to the greater dipolar character of **19**. A similar conclusion can be drawn for **21**.

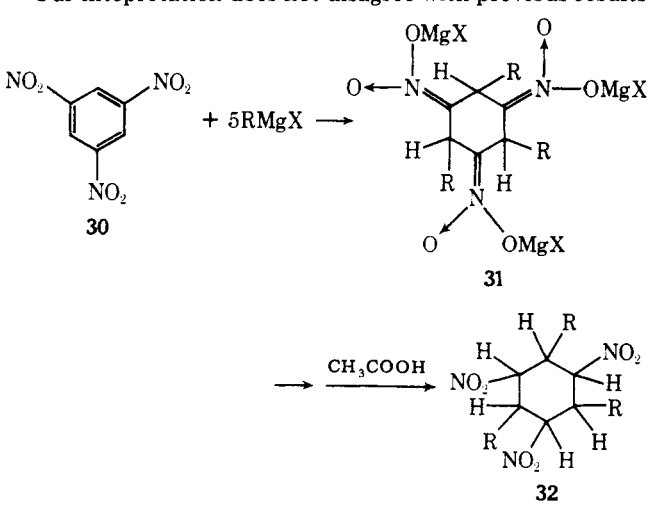
Discussion

The results show that these reactions occur with a large number of different substrates. All the compounds investigated, except *p*-(*N*,*N*-dimethylamino)nitrobenzene, lead to C-alkylation products through conjugate addition to the nitroarene system. The results allow some insight into the mechanism of the reaction and the selectivity of attack of the entering alkyl group.

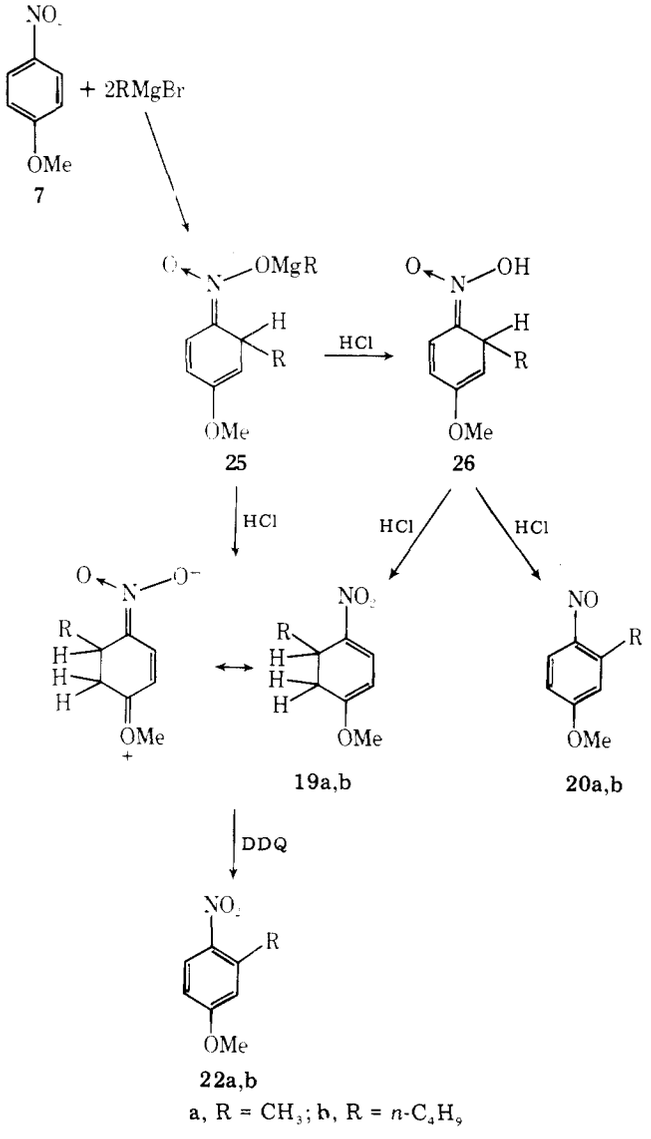
On decomposition in acid, the adducts resulting from attack of the Grignard alkyl group at unsubstituted positions lead to products which are different from those derived from the corresponding adducts formed by attack at substituted positions. Moreover, substituents in ortho and para positions to the nitro group appear to affect the decomposition pathway.

Attack at Unsubstituted Positions. Previous results[4] obtained from a wide range of unsubstituted nitroarenes showed adducts arising from attack at a C_{Ar}–H position decomposed to nitroso compounds in strong acidic medium. Electron-attracting or weakly electron-donating substituents do not change this reactivity pattern, while strong electron donors *ortho* or *para* to the nitro group bring about a different decomposition pathway; in fact nitronate adduct **25** leads mainly to C-protonation product **19** and only to small amounts of nitroso compound **20**, whereas **27** gives exclusive formation of C-protonation product **21**. The amount of tautomerization to the nitro form was found to decrease with increasing acidity of the medium and to increase when the nitro form exhibits greater stability relative to the nitronate or acid form.[10] Thus, it might be inferred that the action of concentrated hydrochloric acid on nitronate adducts generally affords nitronic acids, from which nitroso compounds are immediately formed by acid-induced elimination of water (see Scheme I). However, the presence of a strongly electron-donating group such as -OMe at the end of a conjugate nitrodienic or nitroolefinic system provides a considerable stabilizing effect on **19** and **21**, respectively, while its effect on nitronate adducts **25** and **27** and on nitronic acid **26** and **28** is less stabilizing (see Schemes II and III). This observation could explain the prevailing C-protonation reaction in the cases of **7** and **8** and the formation of the most stable isomers. It would have been very useful to substantiate our interpretation by the reaction on *p*-(*N*,*N*-dimethylamino)nitrobenzene. Unfortunately, as already mentioned, this substituent is incompatible with the reaction.

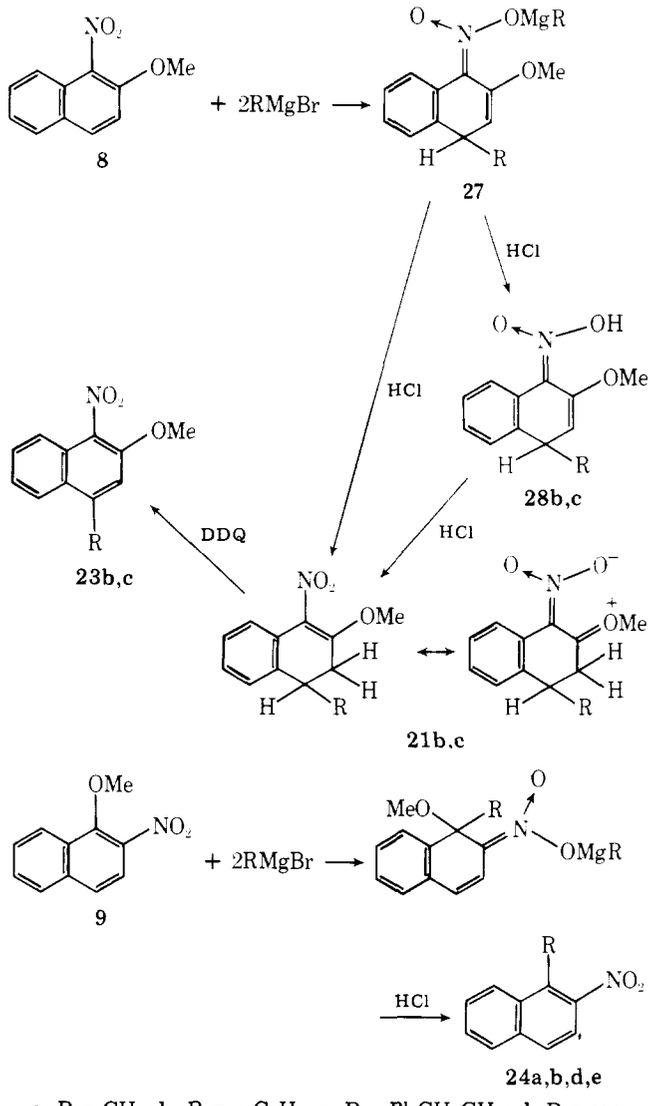
Our intepretation does not disagree with previous results



Scheme II



Scheme III



of Severin and co-workers[3] involving polyaddition of RMgX to di- and trinitrobenzenes. These authors have found that the action of dilute acetic acid (5%) on adduct **31** gives trialkyltrinitrocyclohexane (**32**). On the basis of the above discussion prevailing C-protonation can be accounted for by the low acidity of the medium.

Attack at Substituted Positions. When attack by an alkyl group occurs at a carbon atom carrying a leaving group such as –OMe, the action of the mineral acid on the adduct causes expulsion of methoxide ion leading to a substitution product (see Scheme III). To our knowledge,[11] the reactivity of 1-methoxy-2-nitronaphthalene represents the first example of a nucleophilic displacement of a leaving group by an alkyl group.

A different decomposition pathway has previously[9] been observed when the substituent at the electrophilic center is not a good leaving group. Adducts arising from attack at the para position of *p*-methylnitrobenzene under identical experimental conditions undergo conversion of the nitronate to a carbonyl function, leading to 4-methyl-4-alkyl-2,5-cyclohexadien-1-one.

Selectivity of Attack. Nitrobenzene undergoes nucleophilic attack by entering alkyl groups at both ortho and para positions. The ratio of ortho/para alkylation is predicted by statistical factors (2:1). This indicates that neither position is priviledged in the absence of substituents. Conversely, attack at unsubstituted positions appears to be strongly preferred in a large number of substituted nitrobenzenes. This selectivity has also been confirmed by the reactivity pattern observed in naphthalenes. It has been previously demonstrated[4a] that in a bicyclic system the condensed ring exhibits an effect similar to that generally shown by the nitro group so that attack takes place at the 1 position when the nitro group is bound to the 2 position. Conversely both 2 and 4 positions exhibit comparable chances of being attacked when the nitro group is in the 1 position. Therefore, in compound **9** the alkyl group is forced to attack the C_1–OMe carbon; indeed this is the only reaction observed. On the contrary, the unsubstituted position (C_4–H) is favored in compound **8**.

When comparing these results with established reactivity patterns in S_NAr substitution reactions, irreversibility of the alkylation process must be taken into account. The reactivity of the same substrate with nucleophiles such as RO^-, RS^-, amines, etc., cannot be compared since the attack by these nucleophiles to give σ-anionic intermediates is a reversible process.[12] For the reaction to proceed to substitution product a nucleofugic group must be expelled from the intermediate (Cl^- and F^- but not H^-). Recently, it has been possible to measure with suitable techniques the reactivity of carbon atoms not carrying nucleofugic groups in strongly activated systems.[13] There is already a large body of reliable evidence[14] showing the enhanced reactivity at unsubstituted positions.

Table III. Analytical and Physical Data of Some 2-Alkyl-4-Z-Nitrosobenzenes

compd no.	anal.,[a] % C	H	N	mp, °C	ν_{NO}, cm^{-1}	λ_{max}[b] (log ϵ)	δ
10b	73.59 74.15	8.03 8.21	8.58 8.32	36–37[f]	1490[c]	775 (1.57)	0.85–2.3 and 3.85–4.2 (7 H and 2 H, m, n-C_4H_9), 6.1–6.35 and 7.1–7.8 (4 H, m, H-3, H-4, H-5, and H-6) (CCl_4)
11b	73.59 73.65	8.03 8.17	8.58 8.61	oil	1460[d]	745 (1.64)	0.8–2.0 and 2.6–2.95 (7 H and 2 H, m, n-C_4H_9), 7.3–7.45 and 7.75–7.9 (2 H and 2 H, AB system, J = 8.5 Hz, H-2, H-3, H-5, and H-6) (CCl_4)
12a	73.99 73.31	5.77 5.80	6.16 5.99	75–76[f]	1480[c]	750 (1.67)	2.55 and 3.4 (3 H and 3 H, s, CH_3 and CH_3), 6.4 (1 H, d, $J_{5,6}$ = 9.0 Hz, H-6), 6.8 (1 H, dd, $J_{2,6} \sim 2$ Hz, H-5), 7.05 (1 H, d, H-3), 2.55, 7.15, and 7.4 (3 H, 2 H and 2 H, s and AB system, J = 8.5 Hz, p-$CH_3C_6H_4O$) (CCl_4)
12b	75.81 76.05	7.11 7.18	5.20 5.28	oil	1480[d]	750 (1.65)	0.9–2.1 and 3.75–4.1 (7 H and 2 H, m, n-C_4H_9), 6.35 (1 H, d, $J_{5,6}$ = 9.0 Hz, H-6), 6.75 (1 H, dd, $J_{2,6} \sim 2.0$ Hz, H-5), 7.15 (1 H, d, H-3), 2.5, 7.1, and 7.35 (3 H, 2 H and 2 H, s and AB system, J = 8.5 Hz, p-$CH_3C_6H_4O$) (CCl_4)
13a	68.09 67.85	4.84 4.71	6.11 6.21	oil	1480[d]	770 (1.53)	3.0 (3 H, s, CH_3), 5.95 (1 H, d, $J_{5,6}$ = 7.5 Hz, H-6), 6.3 (1 H, dd, $J_{3,5} \sim 1$ Hz, H-5), 6.7 (1 H, d, H-3), 6.7–7.1 (5 H, m, C_6H_5S) (CCl_4)
14a	57.95 57.35	5.37 5.58	8.27 8.52	67–68[f]	1490[d]	770 (1.72)	2.4 (3 H, s, SCH_3), 3.05 (3 H, s, CH_3), 5.90 (1 H, d, $J_{5,6}$ = 8.0 Hz, H-6), 6.5 (1 H, dd, $J_{3,5} \sim 1$ Hz, H-5), 6.8 (1 H, d, H-3) ($CDCl_3$)
15a	60.42 61.12	4.36 4.53	10.01 9.57	61–62[f]	1490[c]	760 (1.44)	3.35 (3 H, s, CH_3), 6.25 (1 H, dd, $J_{5,6}$ = 9.0 Hz, $J_{6,F}$ = 6.0 Hz, H-6), 6.75 (1 H, m, $J_{5,3} \sim 2$ Hz, $J_{5,F}$ = 10 Hz, H-5), 7.15 (1 H, dd, $J_{3,F}$ = 10 Hz, H-3) ($CDCl_3$)
15b	66.27 65.62	6.69 6.78	7.73 8.02	oil	1490[d]	760 (1.59)	0.75–2.15 and 3.65–3.95 (7 H and 2 H, m, n-C_4H_9), 6.1 (1 H, dd, $J_{5,6}$ = 9.0 Hz, $J_{6,F}$ = 6.0 Hz, H-6), 6.6 (1 H, m, $J_{5,3} \sim 2$ Hz, $J_{5,F}$ = 10 Hz, H-5), 7.1 (1 H, dd, $J_{3,F}$ = 10 Hz, H-3) (CCl_4)
16c	68.42 68.97	4.93 4.81	5.70 5.48	58–59[f]	1270[c,e]	775 (1.40)	3.0–3.3 and 3.9–4.2 (2 H and 2 H, m, CH_2CH_2), 6.0 (1 H, d, $J_{5,6}$ = 9.0 Hz, H-6), 6.8–7.2 (6 H, m, C_6H_5 and H-5), 7.35 (1 H, d, $J_{3,5} \sim 2$ Hz, H-3) ($CDCl_3$)
20a	63.56 64.21	6.00 5.95	9.27 9.23	oil	1490[d]	750 (1.63)	3.45 (3 H, s, CH_3), 4.05 (3 H, s, OCH_3), 6.50 (1 H, d, $J_{5,6}$ = 9.0 Hz, H-6), 6.7 (1 H, dd, $J_{3,5} \sim 2.5$ Hz, H-5), 7.05 (1 H, d, H-3), (CCl_4)
20b	68.37 67.78	7.82 7.89	7.25 7.35	oil	1490[d]	745 (1.45)	0.8–2.2 and 3.6–3.9 (7 H and 2 H, m, n-C_4H_9), 3.9 (3 H, s, OCH_3), 6.2 (1 H, d, $J_{5,6}$ = 9.0 Hz, H-6), 6.55 (1 H, dd, $J_{3,5} \sim 2.5$ Hz, H-5), 6.95 (1 H, d, H-3) (CCl_4)

[a] Upper line required. Lower line found. [b] In $CHCl_3$. [c] In KBr. [d] In CCl_4. [e] Dimer in the solid state. [f] From hexane.

For example, Todesco and Di Nunno[15] reported that in a series of 4-nitro-7-Z-benzofurazans the attack of MeO^- at C_5–H takes place more rapidly than at the C_7–Z position by factors which are respectively: Z = OMe, 25; Cl, 662; and F, 2. Among the few examples of irreversible attack,[10] one in full agreement with our results is the reaction between chloronitrobenzenes[16] and dimethyloxosulfonium ylide in Me_2SO. In this instance attack occurs at the ortho C–H rather than at the C–Cl position.

Experimental Section

IR and UV spectra were recorded with Perkin-Elmer 257 and 402 spectrophotometers, respectively. Mass spectra were recorded with a JEOL-100 instrument.

^1H NMR were recorded with JEOL-60 MHz and Varian 100 MHz spectrophotometers (tetramethylsilane as internal standard). THF and diethyl ether were purified as previously described.[4]

Starting Materials. p-Fluoro- and p-chloronitrobenzene are commercial products (Carlo Erba). Literature references for other compounds follow: **2**,[17] **3**,[18] **4**,[19] **7**,[20] **8**,[21] **9**.[22]

Reaction Procedure. A solution of alkylmagnesium halide (0.02 mol) in THF or diethyl ether (50 mL) was added dropwise at the appropriate temperature (0 °C for the naphthalene series and −40 °C for other compounds) under nitrogen to a solution of nitro compound in the same solvent. Immediately after addition was completed, 5 mL of hydrochloric acid (36%) was added. The reaction mixture was diluted with cold water and then immediately extracted with CH_2Cl_2. The organic layer was washed several times with water, dried, and evaporated at reduced pressure. The residue was subjected to chromatographic separation or purification on a silica gel column. Since nitroso and cyclohexadienic compounds show a high tendency to decompose in solution and during chromatographic separation, all operations must be carried out quickly.

Investigated reactions, isolated products, yields, and eluant mixtures used in each experiment are collected in Table I.

In the reaction of **1**, elution with cyclohexane–ethyl acetate (10:1 v/v) gave a mixture of both isomers **10b** and **11b**. Small amounts of the pure products can be obtained by submitting the mixture to chromatographic separation on a silica gel column using pentane as eluant. Analytical and physical data for unknown nitrosocompounds are collected in Table III.

Data for other compounds follow.

17a: mp 106–107 °C (from ethanol); $\nu_{-O^+N=N}$ (CCl_4) 1260 cm^{-1}; H NMR (CCl_4) δ 2.35 and 2.6 (3 H and 3 H, s, CH_3 and CH_3), 6.75–8.85 (6 aromatic H, m); M^+· 262. Anal. Calcd for $C_{14}H_{12}N_2OF_2$: C, 64.10; H, 4.62; N, 10.68. Found: C, 64.22; H, 4.57; N, 10.69.

17b: pale yellow oil; $\nu_{-O^+N=N}$ (CCl_4) 1260 cm^{-1}; H NMR (CCl_4) δ 0.4–3.1 (18 H, m, 2 × C_4H_9), 6.55–8.7 (6 aromatic H, m); M^+· 346. Anal. Calcd for $C_{20}H_{24}N_2OF_2$: C, 69.33; H, 6.99; N, 8.09. Found: C, 69.51; H, 7.02; N, 8.02.

18c: mp 130–132 °C (from petroleum ether); $\nu_{-O^+N=N}$ (CCl_4) 1320 cm^{-1}; H NMR ($CDCl_3$) δ 2.7–3.2 (8 H, m, 2 × CH_2CH_2), 6.85–7.6 and 8.45 (16 aromatic H, m); M^+· 474. Anal. Calcd for $C_{28}H_{24}N_2OCl_2$: C, 70.73; H, 5.09; N, 5.89. Found: C, 70.85; H, 5.21; N, 5.72.

H NMR data for **19a** and **19b** are collected in Table II. Other data follow.

19a: mp 59–60 °C (from pentane); ν_{NO_2} (CCl_4) 1490 and 1320; $\nu_{C=C}$ 1650 cm^{-1}; λ_{max} (hexane) 362 nm (log ϵ 3.96); M^+· 169. Anal. Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 8.72; N, 8.28. Found: C, 57.01; H, 6.48; N, 8.46.

19b: mp 40–41 °C (from pentane); ν_{NO_2} (CCl_4) 1490 and 1320; $\nu_{C=C}$ 1650 cm^{-1}; λ_{max} (hexane) 362 nm (log ϵ 3.96); M^+· 211. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.21; N, 6.53. Found: C, 62.71; H, 8.15; N, 6.71.

Reactions of **8** gave exclusively compound **21.**

21b: mp 67–68 °C (from CH_2Cl_2–hexane); ν_{NO_2} (KBr) 1520 and 1370; $\nu_{C=C}$ 1660 cm^{-1}; H NMR ($CDCl_3$)[23] δ 0.85–1.26 (9 H, m, C_4H_9), 1.51 (1 H, m, $J_{3,3'} \simeq 16$ Hz, $J_{3',4} \simeq 3.5$ Hz, H-3), 1.62 (1 H, m, $J_{3,4} \simeq 8.5$ Hz, H-3), 2.54 (1 H, m, H-4), 3.80 (3 H, s, OMe), 6.98–7.26 (4 H, m, H-5, H-6, H-7, and H-8); M^+· 261. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 70.11; H, 7.42; N, 5.38.

21c: mp 84–85 °C (from CH_2Cl_2–hexane); ν_{NO_2} (KBr) 1510 and 1360; $\nu_{C=C}$ 1650 cm^{-1}; H NMR ($CDCl_3$)[23] δ 1.81 (1 H, m, $J_{3,3'} \simeq 16$ Hz, $J_{3',4} \simeq 3.5$ Hz, H-3'), 1.92 (1 H, m, $J_{3,4} = 8.5$ Hz, H-3), 2.56 (1 H, m, H-4), 2.52–2.75 (4 H, m, CH_2CH_2), 3.71 (3 H, s, OMe), 6.98–7.26 (9 H, m, C_6H_5 and H-5, H-6, H-7, H-8); M^+· 309. Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.99; H, 6.47; N, 4.40.

Reactions of **9** gave exclusively compound **24.**

24a: mp 60–61 °C (lit.[24] mp 58–59 °C); ν_{NO_2} (KBr) 1500 and 1350 cm^{-1}; H NMR ($CDCl_3$) δ 3.65 (3 H, s, CH_3), 7.2–8.15 (6 aromatic H, m).

24b: pale yellow oil; ν_{NO_2} (in film) 1520 and 1350 cm^{-1}; H NMR (CCl_4) δ 0.8–2.1 and 2.85–3.3 (7 H and 2 H, m, n-C_4H_9), 7.3–8.2 (6 aromatic H, m). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.27; H, 6.41; N, 6.01.

24d: pale yellow oil; ν_{NO_2} (CCl_4) 1520 and 1360 cm^{-1}; H NMR (CCl_4) δ 0.7–2.4 and 3.45 (8 H and 1 H, m, $CH_3CH_2CH(CH_3)$–), 7.35–8.6 (6 aromatic H, m). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.20; H, 6.51; N, 6.14.

24e: mp 107–108 °C (from ethanol); ν_{NO_2} (KBr) 1510 and 1350 cm^{-1}; H NMR (CCl_4) δ 4.6 (2 H, s, CH_2), 6.9–7.25 (5 H, m, C_6H_5), 7.3–8.15 (6 aromatic H, m). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.43; H, 5.32; N, 5.53.

Reactions of 19a,b and 21b,c with DDQ. 19a,b and **21b,c** were quantitatively converted into the corresponding aromatic nitro compounds **22a,b** and **23b,c** by treatment with a slight excess of DDQ in refluxing dry benzene for 48 and 6 h, respectively.

22a: mp 54–55 °C (lit.[25] mp 55 °C); ν_{NO_2} (KBr) 1490 and 1340 cm^{-1}; H NMR (CCl_4) δ 2.75 (3 H, s, CH_3), 4.0 (3 H, s, OCH_3), 6.85–7.10 (2 H, m, H-3 and H-5), 8.20 (1 H, d, $J_{5,6} = 9.5$ Hz, H-6).

22b: yellow oil; ν_{NO_2} (CCl_4) 1500 and 1340 cm^{-1}; H NMR (CCl_4) δ 0.8–2.0 and 2.85–3.20 (7 H and 2-H, m, n-C_4H_9), 4.0 (3 H, s, OCH_3), 6.8–7.0 (2 H, m, H-3 and H-5), 8.05 (1 H, d, $J_{5,6} = 10$ Hz, H-6). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.32; H, 7.41; N, 6.59.

23b: mp 98–100 °C (from ethanol); ν_{NO_2} (KBr) 1530 and 1350 cm^{-1}; H NMR ($CDCl_3$) δ 0.92–1.65 and 3.01 (7 H and 2 H, m, n-C_4H_9), 3.96 (3 H, s, OCH_3), 7.62–7.94 (4 H, m, H-5, H-6, H-7, and H-8), 7.11 (1, H, s, H-3). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.49. Found: C, 69.65; H, 6.71; N, 5.63.

23c: mp 97–98 °C (from ethanol); ν_{NO_2} 1520 and 1350 cm^{-1}; M^+· 307. Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.38; H, 5.61; N, 4.70.

Registry No.—**1,** 98-95-3; **2,** 620-88-2; **3,** 952-97-6; **4,** 701-57-5; **5,** 350-46-9; **6,** 100-00-5; **7,** 100-17-4; **8,** 4900-66-7; **9,** 4900-62-3; **10b,** 7137-58-8; **11b,** 34645-50-6; **12a,** 69745-23-9; **12b,** 69745-24-0; **13a,** 69745-25-1; **14a,** 69745-26-2; **15a,** 69745-27-3; **15b,** 69745-28-4; **16c,** 69745-29-5; **17a,** 69745-30-8; **17b,** 69745-31-9; **18c,** 69745-32-0; **19a,** 69745-33-1; **19b,** 69745-34-2; **20a,** 69745-35-3; **20b,** 69745-36-4; **21b,** 69745-37-5; **21c,** 69745-38-6; **22a,** 5367-32-8; **22b,** 69745-39-7; **23b,** 69745-40-0; **23c,** 69745-41-1; **24a,** 63017-87-8; **24b,** 69745-42-2; **24d,** 69745-43-3; **24e,** 69745-44-4.

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