Addition and Redox Processes in the Reaction of Grignard Reagents with 1,4-Dinitrobenzene. Factors affecting Product Distribution

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1,4-Dinitrobenzene (**1**) reacts smoothly and irreversibly with alkyl-magnesium or -lithium reagents to give at first the nitroarene radical anion (**3**) (redox product) and 6-alkyl-2-nitro-5-*aci*-nitrocyclohexa-1,2-diene (**4**) (addition product). Intermediate (**4**) undergoes an immediate addition to the nitro function by a second mole of RMgX or RLi to give *trans*-4,5-dialkyl-3,6-di-*aci*-nitrocyclohexene (**5**), which can be converted into the corresponding *trans*-5,6-dialkyl-1,4-dinitrocyclohexa-1,3-diene (**6**) by oxidation with sodium hypochlorite or dichlorodicyanobenzoquinone. The addition process is favoured by lower temperatures and weakly polar and highly viscous solvents, while steric hindrance in the magnesium reagent enhances radical anion (**3**) formation. These findings are interpreted in terms of a single electron-transfer mechanism in which all factors delaying a geminate recombination of the radical pair [originating from one electron donated from the reagent RM to (**1**)] favour the redox process to the detriment of addition. The almost absolute stereoselectivity of the double alkylation process is attributed to steric control on the direction of attack of RM to the ene-nitro function of (**4**) exerted by the axial alkyl group. A detailed e.s.r. study of 1,4-dinitrobenzene radical anion is also reported.

The ability of nitroaromatic compounds to undergo a facile electron-transfer reaction from bases is well documented.[1] However, in contrast with the previous evidence, it has been recently established[2] that the normal reactivity of an alkyl-lithium or -magnesium reagent results in conjugate addition to the nitroarene system. The redox process can compete only at high temperatures[3] and in the presence of strong steric hindrance in both the substrate and the carbanionic reagent:[4] a well thought-out choice of reaction conditions can favour conjugate addition. In 1971, it was reported[5] that dithianyl-lithium is quantitatively oxidized to its dimer by halogeno substituted nitrobenzenes at 0 °C in tetrahydrofuran (THF). Fifteen years later, in mechanistic investigations[6,7] on the factors affecting product distribution, more suitable experimental conditions for obtaining predominant addition were identified.[3]

Since conjugate addition of Grignard reagents to nitroarenes represents one of the more significant procedures for alkylating those aromatic systems which do not enter into the Friedel–Crafts reaction,[8] further investigations are needed to clarify the parameters controlling the distribution of products. In this work we analyse the effect on the reaction when the electron affinity of the nitroarene substrate is dramatically increased by introducing a second nitro group into the *para* position.

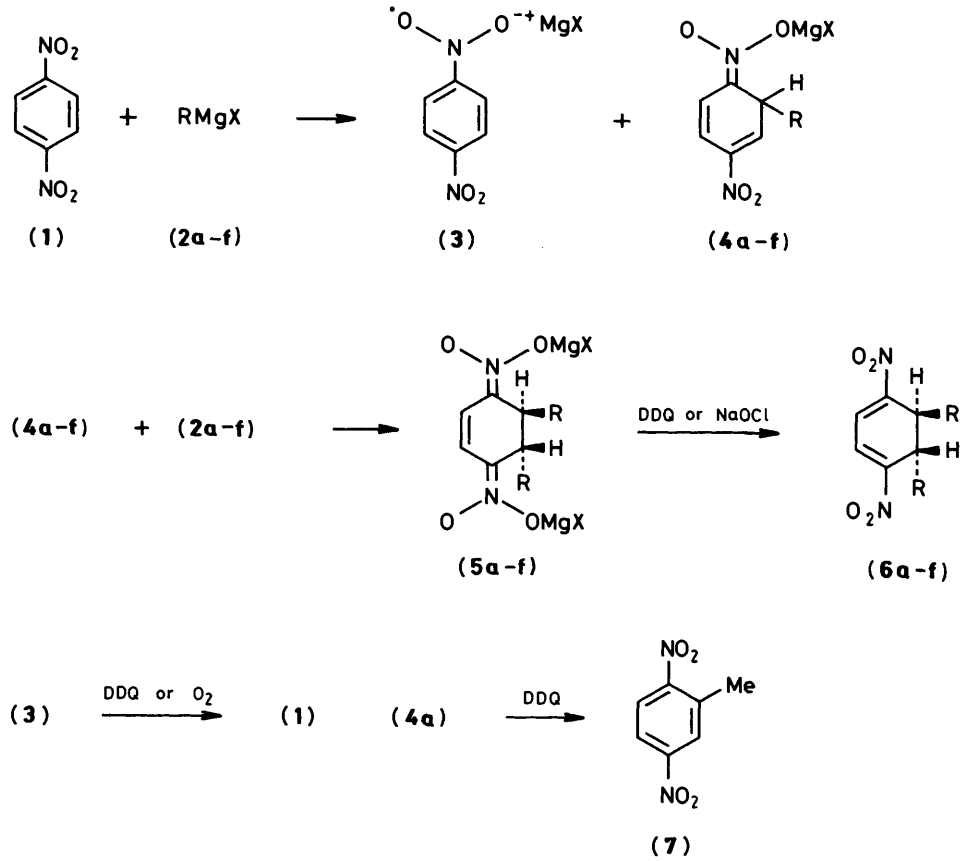
Results

When 1,4-dinitrobenzene (**1**) was allowed to react with two moles of methylmagnesium chloride (**2a**) at −70 °C for 10 min in THF, the radical anion (**3**) (redox product) and the *aci*-nitro (**5a**) (diaddition product) were formed predominantly (Scheme 1). In fact, on treatment of the reaction mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[9] (procedure A), compounds (**3**) and (**5a**) were oxidized to the initial dinitrobenzene (**1**) (32%) and *trans*-5,6-dimethyl-1,4-dinitrocyclohexa-1,3-diene (**6a**) (56%), respectively. No traces of the corresponding *cis*-isomer were detected by g.c.–m.s. analysis. In contrast with closely related reactions, no products arising from substitution of the nitro group were observed.[8a,b] The use of an excess of Grignard reagent and/or the prolongation of the reaction time (60–90 min) did not modify the yields nor the relative amounts of products (**1**) and (**6a**). Furthermore, it was very difficult to perform a quantitative chromatographic separation of the two compounds on a silica gel column (see the Experimental section). However, because of the different degree of oxidation on treatment with atmospheric oxygen and also the solubility of di-*aci*-nitro compound (**5a**) in a weakly acidic medium, an alternative and more profitable procedure is available. On quenching the reaction mixture with aqueous ammonium chloride with oxygen bubbled through it, the radical anion (**3**) is immediately oxidized to (**1**),[10,†] while compound (**5a**) remains unaffected and dissolves in the aqueous layer. Dinitrobenzene can be removed by extraction with diethyl ether and, after filtration on silica gel, was recovered. On the other hand, the unstable compound (**5a**) was easily oxidized to cyclohexadiene (**6a**) by treatment of its aqueous solution with sodium hypochlorite (procedure B). The usual work-up gave (**6a**) of 98% purity. Following this procedure, the two products can be isolated without resorting to tedious chromatographic techniques and a readily available oxidizing agent can be successfully employed instead of the expensive DDQ.

Double alkylation has been observed in the reaction of *m*-dinitrobenzene with RMgX;[11] however no information was given on the stereoselectivity of the reaction and on the occurrence of redox side reactions.

The relative proportions of (**6a**) and (**1**) depends on the experimental conditions employed. By decreasing the reaction temperature, the yield of addition product (**6a**) increases to the

† The oxidation of nitroarene radical anion with DDQ or oxygen is immediate and quantitative. Therefore the amount of recovered starting material provides a more accurate measure of the radical-anion concentration than quantitative e.s.r. measurements which are generally affected by large errors.



Scheme 1. **a**, R = Me; **b**, R = Et; **c**, R = $PhCH_2$; **d**, R = $PhCH_2CH_2$; **e**, R = CH_2=$CH(CH_2)_2$; **f**, R = Me_3SiCH_2.

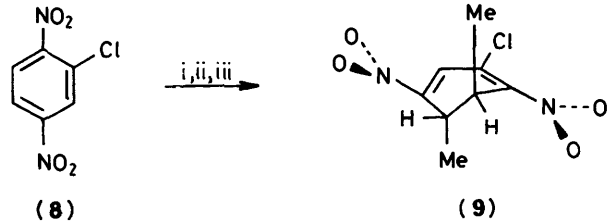
detriment of the redox product (**1**). An analogous finding was obtained for the reaction in less polar solvents. Cyclohexadiene (**6a**) is inert towards oxidizing agents; use of DDQ in benzene at reflux, lead tetra-acetate in dichloromethane,[12] or any other method gave no reaction. The reaction can be successfully applied to other Grignard reagents (**2b–f**). In all cases, the simpler procedure B was employed except for the reaction with but-3-enylmagnesium halide in which hypochlorite can affect the exocyclic double bond. All the results obtained are summarized in the Table.

In order to verify the possibility of introducing two different alkyl chains by adding two Grignard reagents consecutively, the reaction of dinitrobenzene (**1**) with a stoicheiometric amount of (**2a**) was carried out in THF at −70 °C, followed by oxidation of the mixture with DDQ. G.l.c. analysis of the reaction mixture revealed 62% starting material, 24% cyclohexadiene (**6a**) and only 4% 2,5-dinitrotoluene (**7**) (Table, entry 1). The formation of (**7**) suggests that double alkylation proceeds in two steps *via* a monoalkyl *aci*-nitro intermediate (**4**). In consequence, the explanation for regiocontrol of the reaction is obvious. In fact, in an intermediate like (**4**) attack of the carbanionic moiety of RMgX can occur only at the ene-nitro function, since the α,β-unsaturated *aci*-nitro framework is practically inert towards this type of attack. Furthermore, the second attack can occur faster than the first in which the aromatic ring is destroyed, if the negative charge does not interfere with the ene-nitro group. In other words, the magnesium ion and the oxygen atoms of the *aci*-nitro function must be linked by a strong co-ordination bond.

Therefore, the use of a less powerful metal counter-ion such as lithium must lead to an increase of monoalkyl product. 12% Dinitrotoluene (**7**) was recovered under the same experimental conditions (Table, entry 15), while the reaction carried out with two moles of methyl-lithium gave a product distribution (Table, entry 16) very similar to that of the methylmagnesium derivative.

Assignment of Structure.—Generally, the structure of cyclohexadienes is easily assigned on the basis of their ^{1}H n.m.r. spectra,[13] since the values of the coupling constants of the hydrogen atoms bonded to the sp^3 carbons are well known and significatively different (J_{aa} *ca.* 16, J_{ae} *ca.* 7, J_{ee} *ca.* 2 Hz).[14] Unfortunately, as compounds (**6a–f**) are symmetrical, H-5 and -6 have identical chemical shifts, and thus no information on the structure can be obtained from their coupling constants.

For assignment purposes, therefore, we synthesized the unsymmetrical 2-chloro-5,6-dimethyl-1,4-dinitrocyclohexa-1,3-diene (**9**) starting from 2-chloro-1,4-dinitrobenzene (**8**) (Scheme



Scheme 2. *Reagents:* i, MeMgX–THF, −70 °C; ii, aq. NH_4Cl; iii, 8% NaOCl.

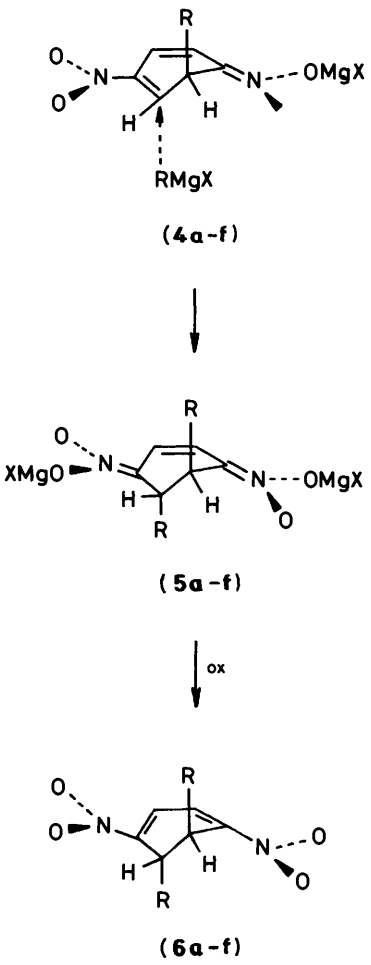
2). It is interesting to note that chlorine is not displaced in this reaction. This finding confirms that when unsubstituted and heterosubstituted reactive positions are present in the substrate, only the former are attacked by Grignard reagents.[2]

Compound (**9**) has $J_{5,6}$ 1.4 Hz in agreement with a pseudo-equatorial/pseudo-equatorial relationship. On the other hand,

Table. Product distribution from reaction of 1,4-dinitrobenzene (**1**) and some alkyl Grignard reagents (**2a–f**) or MeLi[a] in various solvents and at various temperatures, followed by oxidation of the unstable intermediates.

Entry	RM	Solvent	Temp./°C	Procedure[b]	Monoaddition product (%)	Diaddition product (%)[c]	Recovered (**1**) (%)[c]
1	(**2a**)[d]	THF	−70	A	4[e]	24[e]	62[e]
2	(**2a**)	THF	−70	A	—	58[e]	35[e]
3	(**2a**)	THF	−70	B	—	56	31
4	(**2a**)	THF	−50	B	—	45	42
5	(**2a**)	THF	−30	B	—	33	59
6	(**2a**)[f]	Et_2O	−50	B	—	62	27
7	(**2a**)[f,g]	Bu^{t}Ph–PhH	−30	B	—	65	22
8	(**2b**)	THF	−70	B	—	30	37
9	(**2c**)	THF	−70	B	—	20	53
10	(**2d**)	THF	−70	B	—	34	38
11	(**2e**)	THF	−70	A	—	36	37
12	(**2f**)	THF	−70	B	—	18	50
13	(**2f**)	THF	−70	A	—	17	53
14	(**2f**)[f,g]	Bu^{t}Ph–PhH	−30	B	—	24	41
15	MeLi[d]	THF	−70	A	12[e]	15[e]	68[e]
16	MeLi	THF	−70	B	—	50[e]	40[e]

[a] The reaction was carried out by adding two moles of organometallic reagent to (**1**) unless otherwise mentioned. [b] See text. [c] Yields calculated for pure isolated products. [d] Reaction carried out with an equimolar amount of (**2a**). [e] G.l.c. yields. [f] Reaction carried out by adding (**1**) to (**2**) in a 1:2 molar ratio. [g] (**2**) was prepared in Et_2O, the solvent removed by vacuum and dry Bu^{t}Ph was added to dissolve the solid Grignard–ether complex.



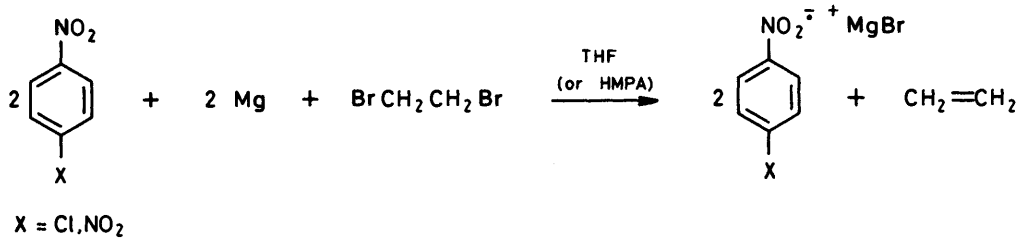
Scheme 3.

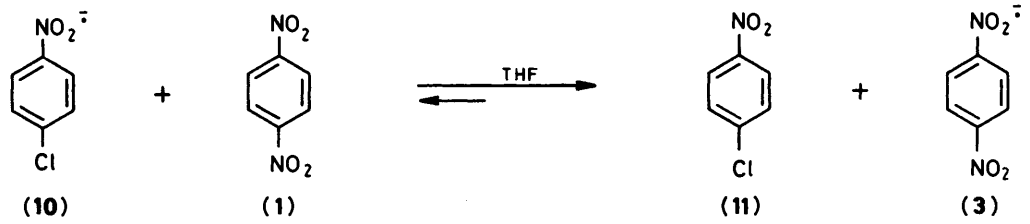
the stereocontrol of the reaction should lead to the *trans* isomer, and each alkyl group must assume an axial conformation to minimize steric repulsions with each other and with the vicinal nitro group.

It has been established that, in cyclic systems like (**4**), a bulky substituent on a tetrahedral carbon atom adjacent to an exocyclic double bond preferentially assumes an axial conformation so as to minimize its steric repulsion with atoms or groups linked to the exocyclic double bond[15] (Scheme 3). The axial orientation of the R group in (**4**) may distinguish the position of attack by the carbanionic moiety of RMgX on the ene-nitro function. On account of steric factors, it may be expected that RMgX attacks the electrophilic carbon atom from the axial direction opposite to the bulky R group, leading exclusively to compound (**5**) in its more stable conformation. Oxidation of (**5**) to (**6**) does not modify the relative geometries of the two alkyl groups.

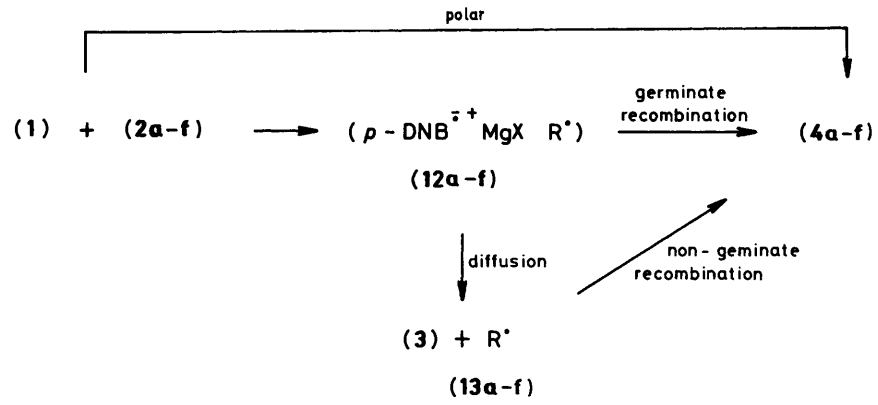
Similar stereocontrol[16] exerted by an axial group in an *aci*-nitrocyclohexadiene system has already been observed for electrophilic attack at the *aci*-nitro function. For example, in 2-alkyl-4-methoxy-1,2-dihydro-1-*aci*-nitronaphthalene, solvated proton[13] and sodium hypobromite[17] showed, respectively, 80 and 99% preference for axial attack. Therefore, it is not surprising to observe in the present system in which a bulky negative charged species is involved an almost absolute degree of stereoselectivity.

E.s.r. Experiments.—The reaction was performed under dry and deaerated conditions in an e.s.r. sample tube; the presence of the 1,4-dinitrobenzene radical anion (**3**) was thus demonstrated. In contrast with literature reports,[18] the e.s.r. spectrum of (**3**) shows the non-equivalence[19] of the spin distribution on the two nitrogen atoms: therefore we have radical anion (**3**) [a_N 1.02, $a_{N'}$ 0.105, a_{H^m}(2H) 0.105, a_{H^o}(2H) 0.34 mT, g 2.0051 ± 0.0001] paired with the Grignard cation. To identify this radical anion, different and independent methods were followed. The first was to produce the radical species by direct electron transfer from a magnesium mirror to dinitrobenzene (**1**) in the presence of 1,2-dibromoethane, or by electron transfer from 4-chloronitrobenzene radical anion to (**1**) as reported in Scheme 4. In both cases the radical species obtained has the hyperfine splitting constants reported above. An indirect proof of non-equivalent spin distribution in (**3**), *i.e.* the presence, in THF, of an ion pair, was obtained using hexamethylphosphoramide as the solvent. This solvent is known to favour the formation of radical anions free from ion pairing.[20] Actually, the reaction between MeMgX and (**1**) in this medium leads to a radical anion with a totally





Scheme 4.



$$R^{\bullet} + R^{\bullet} \longrightarrow R{-}R$$

$$R^{\bullet} + SolvH \longrightarrow RH + Solv^{\bullet}$$

Scheme 5.

symmetric spin distribution ($a_N^{2N} = a_H^{4H} = 0.116$ mT, g 2.0051 ± 0.0001).[21] Another experiment to confirm the correct identification of radical anion (**3**) was to produce the same intermediate using a different reagent such as MeLi. In this case, radical anion (**3**) still shows an e.s.r. spectrum with a non-equivalent spin distribution on the two nitrogen atoms [a_N 0.69, $a_{N'}$ 0.06, a_{H^m}(2H) 0.06 mT, a_{H^o}(2H) mT, g 2.0052 ± 0.0001].

Finally, it is noteworthy that by mixing the reactants at low temperatures (−40 to −50 °C), the e.s.r. signal is quite poor and a positive dependence of its intensity on the temperature was observed. Most likely, this fact can be attributed to slow exchange in the ion pair and/or the low solubility of radical anion (**3**) at low temperatures and/or dimer ion-pair formation.[22]

Discussion

The introduction of a second nitro group in the *para* position of a nitrobenzene ring results in a dramatic enhancement of the redox process. In the reaction of 4-chloronitrobenzene with a primary alkyl Grignard reagent[23] in THF at −30 °C, no evidence of the formation of 4-chloronitrobenzene radical anion was found, while, under the same experimental conditions as the present system, the redox process accounts for 59% of the reaction with MeMgX.

Recently several theoretical[24,25] and experimental[22,26] studies have been performed to determine whether, in the reaction of high electron-affinity substrates with strong basic carbanions, the redox and the addition (or substitution) products arise from either a unique or two separate initial interactions. On the basis of previous mechanistic studies,[3,6,7,23] we suggest a single electron transfer (SET) pathway as the most complete and reasonable mechanism (Scheme 5).

According to this hypothesis, the probability that the free nitroarene radical anion can scavenge all the free alkyl radicals is very low when most of the radical pairs escape geminate recombination.[3,23] Therefore, all the factors delaying radical-pair collapse will favour the formation of the redox product. Since dinitrobenzene radical anion (**3**) is much more stable than 4-chloronitrobenzene radical anion (**10**), as demonstrated by the complete formation of (**3**) starting from (**10**) (see Scheme 4), a low tendency of (**3**) to undergo geminate recombination can be expected. In consequence, a dramatic increase in the redox process must be observed.

There are other aspects of the reactivity of (**1**) which can easily be explained in terms of an SET pathway such as the effect of reaction temperature (Table, entries 3–5) and steric hindrance of the alkyl framework of the Grignard reagent (Table, entries 3, 8, 9, and 13) on the distribution of reaction product.

Furthermore, assuming an SET pathway, the low polarity of

the solvent should decrease the ionic character of the radical anion and make it similar to a neutral nitroxide radical. It is well known that the collapse of alkyl and nitroxide radicals occurs close to the diffusion-controlled rate.[28] On this basis, the increase in the yield of addition product observed on going from THF to the less polar Et_2O can be easily accounted for (Table, entries 4 and 6). Moreover, high viscosity in the medium delays the diffusion of the radical pair. Therefore, it is not surprising that the maximum addition product yield is obtained when a weakly polar and highly viscous solvent such as t-butylbenzene–benzene is employed (Table, entries 7 and 14).

In conclusion, the formation of addition product is enhanced by all the factors which favour the in-cage reaction.[29] Therefore, these results provide strong support for the SET pathway. Nevertheless, since in a 'full in-cage' reaction it is very difficult to distinguish between polar and SET pathways this problem can be resolved by assuming the existence of a continuous spectrum from 'full polar' to 'full SET' mechanisms.[25]

1,4-Dinitrobenzene has been commonly employed as a 'radical-anion scavenger'[30] to 'short circuit' SET reactions between Grignard reagents and ketones.[31] The present results show that dinitrobenzene quickly and irreversibly reacts with Grignard reagents. Therefore, it seems unlikely that dinitrobenzene can survive unaffected at room temperature for long periods of time in the presence of an excess of Grignard reagent. In our opinion, the actual 'scavenger' is a different species. We hypothesize that dinitrobenzene radical anion is this species, since it could remove the electron from free ketyl radical anions giving the corresponding dianion and regenerating the starting ketone. Nevertheless, this idea needs further experimental investigation.

Finally, the present reaction may be synthetically useful. Although the yields are low in many cases, the 'unreacted' starting material can be easily and inexpensively recovered by procedure B: for instance, the conversion of dinitrobenzene into the corresponding dimethylcyclohexadiene derivative is 81%.

Experimental

^1H N.m.r. spectra were recorded with Varian EM360L and Bruker CXP-300 instruments with Me_4Si as an internal standard. E.s.r. spectra were recorded with a Varian E-104 spectrometer. Quantitative g.l.c. analyses were performed using the internal standard procedure, with an HP-5890 gas chromatograph equipped with a methyl silicone wide-bore capillary column and f.i.d.-integration. All compounds were identified by comparison of retention times with those of authentic samples. M.p.s were uncorrected and were determined with a Buchi apparatus. THF and diethyl ether were dried by being refluxed over sodium wires until the blue colour of diphenyl ketyl persisted and then distilled into a dry receiver under nitrogen. Benzene and t-butylbenzene were dried by being refluxed over sodium and distilled into a dry receiver under nitrogen. Commercial 1,4-dinitrobenzene was re-crystallized before use. Grignard reagents were prepared by standard methods (alkyl halides and magnesium turnings) and titrated before use.[32]

Preparation of 5,6-*Dialkyl*-1,4-*dinitrocyclohexa*-1,3-*dienes* (**6a–f**) *from* 1,4-*Dinitrobenzene* (**1**) *and Grignard Reagents* (**2a–f**).—*General procedure.* A THF solution of Grignard reagents (**2a–f**) or MeLi (10 mmol) was added to a THF-stirred solution (30 cm^3) of (**1**) (5 mmol) in the same solvent at the appropriate temperature (Table) under nitrogen. After 10 min the mixture was treated as follows.

Procedure A. A THF solution (20 cm^3) of DDQ (12 mmol) was added and stirring was continued at −10 °C for 60 min. The mixture was poured into 5% acetic acid (40 cm^3), extracted with dichloromethane, washed with saturated aqueous $NaHCO_3$ and with water, dried (Na_2SO_4), evaporated under reduced pressure, and submitted to chromatographic separation on silica gel [light petroleum (b.p. 40–60 °C)–diethyl ether (9:1) as eluant]. T.l.c. analysis of the mixture containing compounds (**1**) and (**6a**) showed no separation of products. Partial separation was observed on eluting with benzene–hexane (1:1).

Procedure B. The mixture was poured into saturated aqueous ammonium chloride (50 cm^3) previously bubbled with oxygen, extracted with ether, and filtered on a short silica gel column [light petroleum (b.p. 40–60 °C)–diethyl ether (9:1) as eluant] to give pure compound (**1**). The aqueous layer was treated with 8% NaOCl (17 cm^3) in a separating funnel. The solution was shaken and then neutralized by dropwise addition of 10% sulphuric acid. Extraction with dichloromethane, evaporation under reduced pressure, and crystallization from hexane led to pure compounds (**6**). This procedure was not applied to the synthesis of compound (**6e**) to avoid oxidation of the double bond in the side chain.

Yields of compounds (**6a–e**) and recovered starting material are reported in the table. Physical data follow: (**6a**), m.p. 127–129 °C, $\delta_H(CDCl_3)$ 1.23 (d, 6 H, Me, *J* 8.0 Hz), 3.23 (q, 2 H, H-5 and -6), 7.50 (s, 2 H, H-2 and -3) (Found: C, 48.5; H, 5.0; N, 14.1. $C_8H_{10}N_2O_4$ requires C, 48.5; H, 5.05; N, 14.1%); (**6b**), m.p. 60–62 °C, $\delta_H(CDCl_3)$ 0.77–1.16 (m, 6 H, Me), 1.30–1.83 (m, 4 H, CH_2), 3.10–3.43 (m, 2 H, H-5 and -6), and 7.43 (s, 2 H, H-2 and -3) (Found: C, 53.0; H, 6.2; N, 12.35. $C_{10}H_{14}N_2O_4$ requires C, 53.1; H, 6.2; N, 12.4%); (**6c**), m.p. 115–117 °C, $\delta_H(CDCl_3)$ 2.63 (AB system, 4 H, CH_2); 3.50 (dd, 2 H, H-5 and -6, $J_{5,A}$ 2.2, $J_{5,B}$ 4.8 Hz), and 6.80–7.57 (m, 12 H, Ar) (Found: C, 68.5; H, 5.15; N, 8.0. $C_{20}H_{18}N_2O_4$ requires C, 68.6; H, 5.1; N, 8.0%); (**6d**), m.p. 69–71 °C, $\delta_H(CDCl_3)$ 1.53–2.07 and 2.43–2.83 (m, 8 H, CH_2CH_2), 3.23–3.60 (m, 2 H, H-5 and -6), and 7.03–7.53 (m, 12 H, Ar) (Found: C, 69.9; H, 5.8; N, 7.4. $C_{22}H_{22}N_2O_4$ requires C, 69.8; N, 5.8; N, 7.4%); (**6e**), oil, $\delta_H(CDCl_3)$ 1.43–2.47 (m, 8 H, CH_2CH_2), 3.47 (t, 2 H, H-5 and -6, *J* 6.0 Hz, 4.87–5.37 (m, 4 H, $=CH_2$), 5.53–6.27 (m, 2 H, CH=), and 7.50 (s, 2 H, H-2 and -3) (Found: C, 58.35; H, 6.25; N, 9.7. $C_{14}H_{18}N_2O_4$ requires C, 58.3; H, 6.25; N, 9.7%); (**6f**), m.p. 120–121 °C, $\delta_H(CDCl_3)$ 0.10 (s, 18 H, Me_3Si), 0.80 (d, 4 H, CH_2Si, *J* 7.0 Hz), 3.30 (t, 2 H, H-5 and -6), and 7.37 (s, 2 H, H-2 and -3) (Found: C, 53.2; H, 8.3; N, 8.9. $C_{14}H_{26}N_2O_4Si_2$ requires C, 53.5, H, 8.3; N, 8.9%).

Reaction of (**1**) *with* (**2a**) *or Methyl-lithium in Stoicheiometric Amounts.*—The reaction was carried out by adding (**2a**) or MeLi (1 mmol) to a stirred THF solution of (**1**) (1 mmol) at −70 °C under nitrogen and then following procedure A. A sample was submitted to quantitative g.l.c. analysis (4-chloronitrobenzene as internal standard). The results are reported in the Table, entries 1 and 15.

Preparation of a Solution of Grignard Reagent in t-Butylbenzene.—A diethyl ether solution of Grignard reagent was placed in a two-necked flask connected to a vacuum distillation apparatus and equipped with a septum inlet. The solvent was distilled into a cooled receiver and the apparatus was saturated with nitrogen, then dry t-butylbenzene was added with a syringe through the septum. The new solution of Grignard reagent was then titrated before use.

Reaction of (**1**) *with Grignard Reagents in t-Butylbenzene and Diethyl Ether.*—A benzene solution (40 cm^3) of (**1**) (5 mmol) was added to a stirred solution of Grignard reagent (10 mmol) in t-butylbenzene at −30 °C under nitrogen. After 10 min the mixture was treated as described in procedure B. Yields of products (**1**) and (**6a,f**) are reported in the Table, entries 7 and 14. A solution of (40 cm^3) of (**1**) (5 mmol) in diethyl ether was added to a stirred solution of Grignard reagent (10 mmol) in the same solvent at −50 °C under nitrogen. After 10 min the

mixture was treated as described in procedure B. Yields of products (**1**) and (**6a**) are reported in the Table, entry 6.

Preparation of 2-*Chloro*-1,4-*dinitrobenzene* (**8**).—In a beaker, commercial 3-chloro-4-nitroaniline (10.75 g) was dissolved in commercial fluoroboric acid (27.5 cm^3). The mixture was cooled in an ice-bath and vigorously stirred, then a pre-cooled solution of $NaNO_2$ (4.25 g) in water (8.5 cm^3) was added dropwise. Stirring was continued for 10 min and the mixture was filtered. The solid was washed with fluoroboric acid, ethanol, and diethyl ether. A suspension of the diazonium fluoroborate in water (100 cm^3) was then added dropwise to a stirred slurry of $NaNO_2$ (5.0 g), copper bronze (10 g), and water (100 cm^3). The product was filtered and washed with water, dilute NaOH, and water. Recrystallization from methanol gave 2-chloro-1,4-dinitrobenzene (**8**) (7.5 g, 60%), m.p. 61–63 °C (lit.,[33] 64 °C).

Reaction of (**8**) *with* (**2a**).—A THF solution of (**2a**) (10 mmol) was added to a stirred solution (30 cm^3) of (**8**) (5 mmol) in the same solvent at −70 °C under nitrogen. After 10 min the mixture was treated as described in procedure A. 2-*Chloro*-5,6-*dimethyl*-1,4-*dinitrocyclohexa*-1,3-*diene* (**9**) was obtained in 25% yield, m.p. 103–104 °C; δ (300 MHz; C_6D_6) 0.59 (d, 6 H, Me, *J* 7.0 Hz), 2.53 (m, 1 H, H-6, $J_{5,6}$ 1.3 Hz), 2.48 (m, 1 H, H-5), and 6.68 (s, 1 H, H-3) (Found: C, 41.2; H, 3.95; N, 12.1. $C_8H_9ClN_2O_4$ requires C, 41.3; H, 3.9; N, 12.0%).

E.s.r. Samples.—A solution of (**1**) in THF or HMPA was introduced in a proper e.s.r. sample tube equipped with a septum inlet. The solution was degassed by the freeze–pump–thaw technique and the tube sealed off. A MeMgX or MeLi solution under nitrogen was added with a microsyringe through the septum, the two reagents were mixed at different temperatures, and the mixture analysed at the e.s.r. spectrometer.

The experiment in which 1,4-dinitrobenzene radical anion (**3**) was generated by reaction of (**1**) with Mg in the presence of 1,2-dibromoethane was carried out in an appropriate sample tube, preparing a magnesium mirror and a deaerated solution of (**1**) and dibromoethane initially kept separate. The tube was sealed off and the solution was allowed to react with the Mg mirror at various temperatures and then analysed in the spectrometer.

Finally, 4-chloronitrobenzene radical anion was generated by the technique described above; the solution containing this radical anion was allowed to react with an oxygen-free solution of (**1**) in THF, initially kept separate, and then analysed in the spectrometer at room temperature.

The hyperfine splitting constants and *g* values of radical anion (**3**) are reported in the text.

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References

1 (*a*) G. A. Russel, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, 1964, **86**, 1807; (*b*) G. A. Russel and W. C. Danen, *ibid.*, 1968, **90**, 347; (*c*) E. Buncel and B. C. Menon, *ibid.*, 1980, **102**, 3499; (*d*) R. D. Guthrie and D. E. Nutter, *ibid.*, 1982, **104**, 7478; (*e*) R. D. Guthrie and N. S. Cho, *ibid.*, 1979, **101**, 4698; (*f*) R. D. Guthrie, D. P. Wesley, G. W. Pendygraft, and A. T. Young, *ibid.*, 1976, **98**, 5870; (*g*) R. D. Guthrie, in 'Comprehensive Carbanion Chemistry,' eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, pp. 197–269.
2 G. Bartoli, *Acc. Chem. Res.*, 1984, **17**, 109.
3 G. Bartoli, R. Dalpozzo, L. Grossi, and P. E. Todesco, *Tetrahedron*, 1986, **42**, 2563.
4 R. D. Guthrie, C. Hartmann, R. Neill, and D. E. Nutter, *J. Org. Chem.*, 1987, **52**, 736.
5 W. H. Baarschers and T. L. Loh, *Tetrahedron Lett.*, 1971, 3483.
6 G. Bartoli, M. Bosco, R. Dalpozzo, and F. Ciminale, *J. Org. Chem.*, 1982, **47**, 5227.
7 G. Bartoli, M. Bosco, G. Cantagalli, R. Dalpozzo, and F. Ciminale, *J. Chem. Soc., Perkin Trans. 2*, 1985, 773.
8 For other methods complementary to the Friedel–Crafts reaction see for example (*a*) M. Makosza and J. Winiarsky, *Acc. Chem. Res.*, 1987, **20**, 282; (*b*) T. V. Rajan Babu, G. S. Reddy, and T. Fukunaga, *J. Am. Chem. Soc.*, 1985, **107**, 5473; (*c*) F. Minisci, A. Citterio, E. Vismara, and C. Giordano, *Tetrahedron*, 1985, **41**, 4157.
9 (*a*) F. Kienzle, *Helv. Chim. Acta*, 1978, **61**, 449; (*b*) G. Bartoli, M. Bosco, and R. Dalpozzo, *Tetrahedron Lett.*, 1985, **26**, 115.
10 (*a*) G. A. Russel and A. G. Bemis, *Inorg. Chem.*, 1967, **6**, 403; (*b*) D. Behar and P. Neta, *J. Phys. Chem.*, 1981, **85**, 690.
11 (*a*) T. Severin and R. Schmitz, *Chem. Ber.*, 1963, **96**, 3081; (*b*) T. Severin and M. Adam, *ibid.*, 1964, **97**, 106.
12 N. Armillotta, G. Bartoli, M. Bosco, and R. Dalpozzo, *Synthesis*, 1982, 836.
13 G. Bartoli, G. Baccolini, and M. Bosco, *J. Org. Chem.*, **45**, 2649.
14 M. J. Cook, A. R. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc. B*, 1969, 523.
15 S. K. Malhotra and F. J. Johnson, *J. Am. Chem. Soc.*, 1965, **87**, 5492, 5493.
16 (*a*) H. E. Zimmermann and T. W. Cutshall, *J. Am. Chem. Soc.*, 1959, **81**, 4365; (*b*) H. E. Zimmermann, *J. Org. Chem.*, 1955, **20**, 449; (*c*) H. E. Zimmermann and H. J. Giallombardo, *J. Am. Chem. Soc.*, 1956, **78**, 6259; (*d*) H. E. Zimmermann, *ibid.*, 1957, **79**, 6554.
17 G. Bartoli, M. Bosco, E. Foresti, and G. Pradella, *J. Org. Chem.*, 1981, **46**, 3109.
18 (*a*) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609; (*b*) T. Abe and Y. Ikegami, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 196; (*c*) V. Jagannadham and S. Steenken, *J. Am. Chem. Soc.*, 1984, **106**, 6542.
19 M. Branca, A. Gamba, and C. Oliva, *J. Magn. Reson.*, 1983, **54**, 216.
20 G. R. Stevenson, R. Concepcion, and I. Ocasio, *J. Phys. Chem.*, 1976, **80**, 861.
21 (*a*) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, 1973, **77**, 2339; (*b*) G. R. Stevenson, Y. Fraticelli, and R. Concepcion, *J. Am. Chem. Soc.*, 1976, **98**, 3410.
22 K. Maruyama and T. Katagiri, *J. Am. Chem. Soc.*, 1986, **108**, 6263.
23 G. Bartoli, M. Bosco, R. Dalpozzo, and L. Grossi, in 'Paramagnetic Organometallic Species in Activation, Selectivity, Catalysis,' NATO ASI Series C, Riedel, Dordrecht.
24 L. Eberson 'Electron Transfer Reactions in Organic Chemistry,' Springer-Verlag, Berlin, 1987.
25 A. Pross, *Acc. Chem. Res.*, 1985, **18**, 212.
26 (*a*) M. Newcomb and M. T. Burchill, *J. Am. Chem. Soc.*, 1984, **106**, 8276; (*b*) M. Dagonneau, *Bull. Soc. Chim. Fr.*, 1982, 269; (*c*) E. C. Ashby and J. R. Bowers Jr., *J. Am. Chem. Soc.*, 1981, **103**, 2242; (*d*) T. Holm, *Acta Chem. Scand., Ser. B*, 1983, **37**, 567; (*e*) W. F. Bailey, R. P. Gagnier, and J. J. Patricia, *J. Org. Chem.*, 1984, **49**, 2098; C. Berti, L. Greci, and L. Marchetti, (*f*) *J. Chem. Soc., Perkin Trans. 2*, 1977, 1032; (*g*) 1979, 233; (*h*) L. Eberson and L. Greci, *J. Org. Chem.*, 1984, **49**, 2135; (*i*) M. Okubo, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3108.
27 J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, 1976, **98**, 1520.
28 M. J. Perkins, in 'Advances in Physical Organic Chemistry,' eds. V. Gold and D. Bethel, Academic Press, London, 1980, vol. 17, p. 34.
29 J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.*, 1976, **98**, 1526.
30 N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 734.
31 (*a*) E. C. Ashby and J. R. Bowers, Jr., *J. Am. Chem. Soc.*, 1977, **99**, 8504; (*b*) E. C. Ashby and T. L. Wiesemann, *ibid.*, 1978, **100**, 189.
32 D. E. Bergbreiter and E. Pendergrass, *J. Org. Chem.*, 1981, **46**, 219.
33 'Dictionary of Organic Compounds,' Eyre and Spottiswood, London, 1961, vol. 1, p. 496.

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