Ozone-mediated nitration of bicumene and derivatives with nitrogen dioxide. Preferential mesolytic bond cleavage over nuclear nitration in evidence for the electron transfer nature of the kyodai-nitration of arenes

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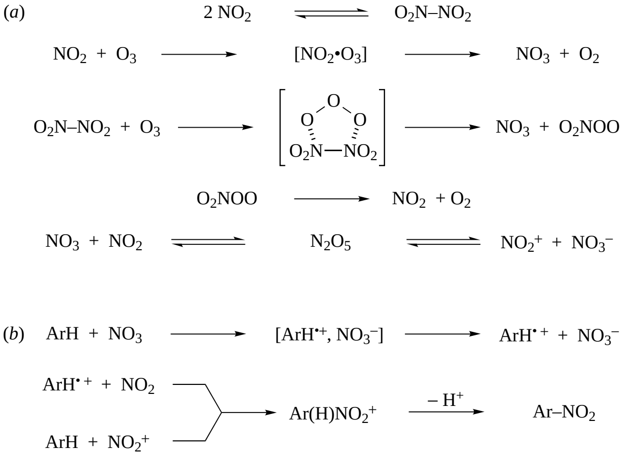
The ozone-mediated reaction of bicumene and some derivatives 1 with nitrogen dioxide in dichloromethane at low temperatures resulted in the facile cleavage of the central C–C bond to give the corresponding benzyl nitrate and its descendants 4–6. Mesolytic bond cleavage occurred almost exclusively over nuclear substitution at temperatures as low as −20 °C, especially at low concentration (2×10^{-3} mol dm^{-3}). This result may be rationalized in terms of initial electron transfer between the aromatic substrate and nitrogen trioxide generated *in situ* to form the aromatic radical cation, which then undergoes C–C bond scission at the benzylic position. In contrast, bibenzyl 2a is simply nitrated on the aromatic ring under similar conditions, giving the expected nitration products 7 and 8a–c along with a small amount of benzaldehyde 9. Results obtained from semi-empirical calculations and cyclic voltammetry are also in accord with the electron transfer nature of the reaction. The C–Si bond fission of benzyltrimethylsilane, C–C bond fragmentation of cyclic acetals of aromatic carbonyl compounds as well as side-chain reactions of toluene and derivatives, have all previously been observed under certain conditions of the kyodai-nitration and can be understood on a similar basis as described above. The possible involvment of electron transfer processes in aromatic nitration with acetyl nitrate has also been suggested.

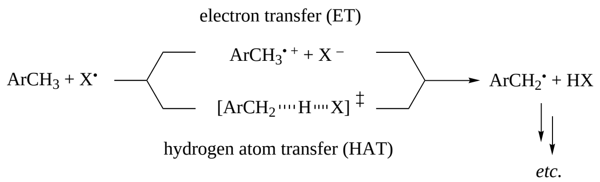
Introduction

In the ozone-mediated nitration of aromatic compounds with nitrogen dioxide (the kyodai-nitration),[1] the reaction proceeds through a dual mode, depending on the oxidation potential of the substrate. Nitrogen dioxide and ozone form dinitrogen pentaoxide through intermediate nitrogen trioxide and the formation of nitrogen trioxide has been established to be rate-determining [Scheme 1(*a*)].[2,3] Deactivated substrates such as aromatic ketones[4] and polyhalogenated arenes[5] are likely to react with dinitrogen pentaoxide in most cases *via* the nitronium ion, but substrates of lower oxidation potential are easily oxidized by nitrogen trioxide to form the corresponding radical cations [Scheme 1(*b*)].[6] Since the complicated nature of this gas–liquid phase reaction invalidates rigid kinetic treatment as well as spectroscopic measurement, a chemical approach such as *via* product analysis is the sole means available at present of inspecting the mechanism of the kyodai-nitration.



Scheme 1

Nitrogen trioxide is highly electron-deficient and therefore can act as a strong electron-transfer (ET) oxidant ($E^0 = 2.3$ V *vs.* normal hydrogen electrode).[7] Although the literature to date contains a few references on the reaction of alkylbenzenes with nitrogen trioxide,[8] no definitive example has yet been reported of the involvement of this radical species in the ring nitration of alkylbenzenes. Baciocchi and co-workers investigated the laser photolysis of cerium(IV) ammonium nitrate (CAN) in acetonitrile in the presence of aromatic substrates and confirmed the electron transfer process in the side-chain substitution of arenes.[9] They suggested the nitrogen trioxide generated from the photolysis of CAN is an effective species for the side-chain oxidation. The reaction was very fast and facilitated by the presence of an electron-donating group on the aromatic ring. Side-chain reactions of alkylaromatic compounds with one-electron oxidants[10] have been shown to involve hydrogen atom transfer (HAT)[11] or an electron transfer[12,13] process (Scheme 2). However, a clear distinction between these two types of process is quite difficult in our case, since the nitrogen trioxide involved is a good hydrogen atom abstractor as well as a strong one-electron oxidant. Over the last three decades, the two-step mechanism (ET process) in which the initial electron transfer step leading to the formation of an aromatic radical cation is followed by deprotonation in the next step has been rather favoured over the single-step mechanism (HAT process), although both mechanisms are still considered by many to operate competitively. This competition should be dependent on the strength of the H–X bond, relative redox potential of



Scheme 2

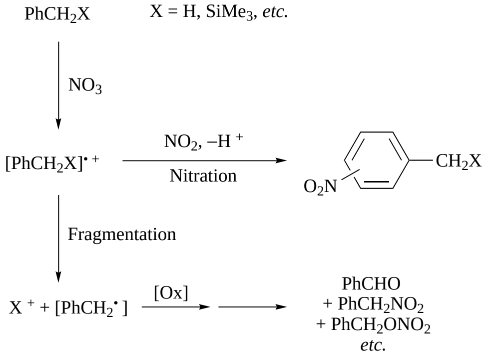
Table 1 Reaction of 2,3-dimethyl-2,3-diphenylbutane (bicumene, **1a**) with several nitrating reagents

[ArH]/mM	[NO$_2$]/mM	Reaction time/min	T/°C	Conversion (%)	Product distributions (%) **3a** (*o*:*m*:*p*):**4a**:**5a**:**6a**
NO$_2$–O$_3$ in CH$_2$Cl$_2$[a]					
2	4	1	0	45	5 (11:23:66):73:14:8
2	4	1	−20	52	ND[c] (—):69:17:14
2	4	1	−20	52[b]	9 (17:15:68):50:24:17
2	40	1	−20	67	8 (6:26:68):47:33:22
100	20	30	0	74	41 (20:15:67):34:17:8
100	20	30	0	62[b]	77 (18:15:67):3:3:17
100	20	30	−20	74	27 (21:14:65):50:16:7
NO$_2$–O$_3$ in ClCH$_2$CH$_2$Cl[a]					
2	4	1	−20	20	1 (2:30:68):48:17:34
100	20	30	−20	75	22 (14:17:69):40:18:20
NO$_2$–O$_3$ in MeCN[a]					
2	4	1	−20	61	4 (1:41:58):14:60:22
NO$_2$–O$_3$ in MeO$_2$[a]					
2	4	1	−20	34	66 (1:33:66):2:25:7
NO$_2^+$BF$_4^-$ in CH$_2$Cl$_2$–sulfolane[d]					
20	—	600	−20	25	99 (7:24:69):1:ND[c]:ND[c]
20	—	300	0	61	100 (8:24:68):trace:ND[c]:ND[c]
AcONO$_2$[e] in CH$_2$Cl$_2$[f]					
10	—	60	−20	47	74 (11:20:69):22:2:2
AcONO$_2$[e] in Ac$_2$O[g]					
7	—	180	−20	27	>99 (2:31:67):<1:—:—

[a] All reactions were carried out in a solvent (50 cm^3) of an appropriate concentration for substrate and nitrogen dioxide. Ozone was introduced at a rate of 0.16 mmol min^{-1}. [b] Methanesulfonic acid (1 equiv. to substrate) was added. [c] Not detected. [d] Nitronium tetrafluoroborate (1.2 equiv.) in sulfolane (10 cm^3) was added dropwise over 30 min to a dichloromethane solution of substrate (40 cm^3). [e] Acetyl nitrate is used here to refer to an equimolar mixture of pure nitric acid and acetic anhydride. [f] Acetyl nitrate (*ca.* 10 equiv.) was added dropwise over 30 min to a dichloromethane solution of substrate (10 cm^3). [g] Acetyl nitrate (*ca.* 100 equiv.) was added dropwise over 30 min to an acetic anhydride solution of substrate (15 cm^3).

$ArCH_3$ and $X^{\bullet}$ systems, and reorganization energy associated with the ET step.

In the ozone-mediated nitration of toluene with nitrogen dioxide, a small but significant amount (2–5%) of benzaldehyde, nitrophenylmethane and benzyl nitrate were detected by ^1H NMR and HPLC analyses, suggesting a possible involvement of the ET process.[14] These products are most likely to have been derived from the benzylic C−H bond scission of a radical cation intermediate (Scheme 3, X = H),[15] although direct hydrogen abstraction by nitrogen trioxide cannot be completely ruled out.[16] Benzyltrimethylsilane is known to be easily oxidized to generate the radical cation,[17] which then releases the trimethylsilyl cation to form the benzyl radical. Thus, the competitive C−H and C−Si bond cleavage of benzyltrimethylsilane has been successfully used to test the mechanistic intricacy between the HAT and the ET reactions.[18] In order to see whether the electron transfer process operates in the kyodai-nitration, the behaviour of this silane toward nitrating agents has been examined under a variety of conditions.[19] The reaction of benzyltrimethylsilane with dinitrogen pentaoxide in dichloromethane at 0 °C for 1 h gave 2- and 4-nitrobenzyltrimethylsilanes (5:2) in 87% yield, with little or no side-chain substitution products being formed. In marked contrast, the ozone-mediated reaction of the same compound with nitrogen dioxide under similar conditions led to extensive C−Si bond cleavage, giving a complex mixture mainly composed of benzyl nitrates, phenylnitromethanes and other nitrated products (Scheme 3, X = SiMe$_3$). Trapping of the benzyl radical by ambident nitrogen dioxide molecules will lead to benzyl nitrite and phenylnitromethane and, in the presence of excess nitrogen dioxide, the former compound easily undergoes NO–NO$_2$ exchange on the side-chain to form benzyl nitrate. With nitrogen dioxide or ozone alone, the silane remained almost intact under the conditions employed. These findings are highly suggestive of the important role of nitrogen trioxide as the effective electrophile in the nitration of electron-rich substrates such as alkylated benzenes and phenolic ethers. With less electron-rich or electron-deficient substrates, however, the oxidative electron transfer would become a less favoured process for arenes, and nitrogen trioxide would tend to react preferentially with nitrogen dioxide to form dinitrogen pentaoxide. Under these circumstances, the aromatic nitration is expected to follow the conventional ionic process well established for dinitrogen pentaoxide.[20]



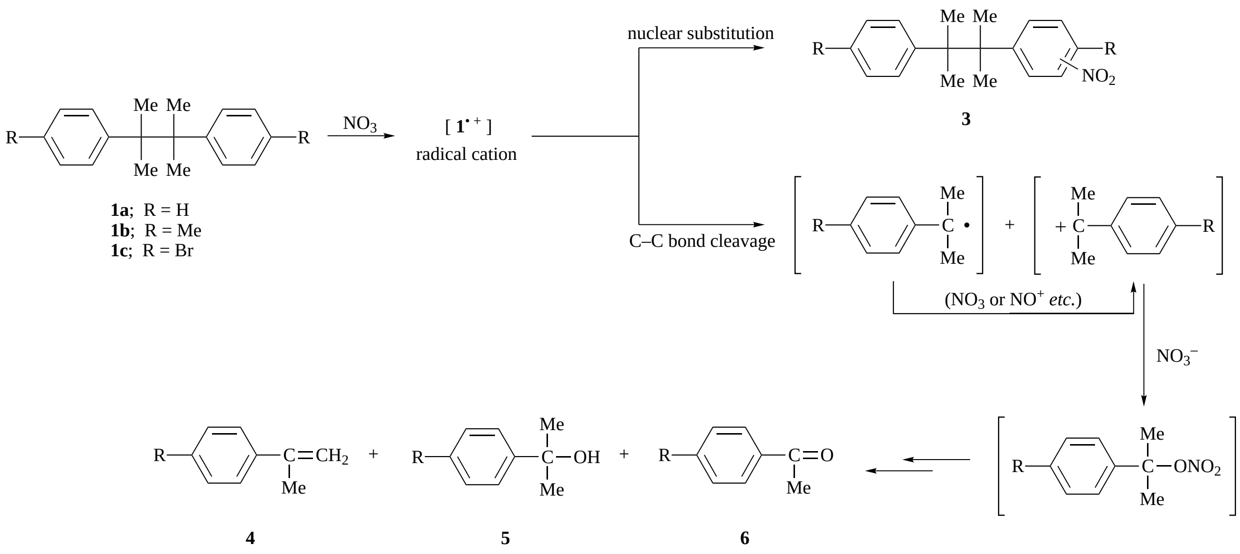
Scheme 3

Recently, the chloranil-sensitized oxidation of benzyltrimethylsilanes has been studied extensively by Baciocchi and his associates in a variety of solvents such as benzene, acetonitrile and dichloromethane.[21] They cautioned against the use of benzyltrimethylsilanes as an ET probe; in a non-polar solvent such as dichloromethane, the charge transfer (CT) complex was found to play a significant role, leading to both C−H and C−Si bond cleaved products. The C−Si bond scission in benzyltrimethylsilane can be associated with the formation of a CT complex; then the silane does not always provide a convincing mechanistic probe to detect the ET process, even if we observe a product arising from C−Si bond cleavage.

Table 2 Ozone-mediated reaction of bibenzyl and related compounds with nitrogen dioxide[a]

Substrate	mmol	Reaction time/min	Conversion (%)	T/°C	Products (%)[b]
1b	1.0	5	78	−20	2-(*p*-Tolyl)propene **4b** (29), 2-(*p*-Tolyl)propan-2-ol **5b** (50), *p*-Methylacetophenone **6b** (27), 2-Nitro-*p*-cresol **12** (45)
1c	1.0	5	19	−20	2-(*p*-Bromophenyl)propene **4c** (160), *p*-Bromoacetophenone **6c** (40)
2a	10.1	30	64	−20	Nitrobibenzyls **7** (80),[c] Benzaldehyde **9** (19)
	5.3	45	86	0	*o*-Nitrobibenzyl *o*-**7** (18), *p*-Nitrobibenzyl *p*-**7** (30), *o,o*′-Dinitrobibenzyl *o,o*′-**8** (6), *o,p*′-Dinitrobibenzyl *o,p*′-**8** (15), *p,p*′-Dinitrobibenzyl *p,p*′-**8** (6),
2a					Benzaldehyde **9** (12)
2b	1.0	5	64	−20	Triphenyl-(*o*-nitrophenyl)ethane *o*-**10** (11), Triphenyl-(*p*-nitrophenyl)ethane *p*-**10** (56), Diphenylmethanol **11** (56)

[a] All reactions were carried out in dichloromethane (30 cm^3). Ozone was introduced at a rate of 0.16 mmol min^{-1}. [b] Isolated yields based on the amount of substrate, not on the number of aromatic rings. [c] Isolated as an isomeric mixture. The isomer ratio was determined by GLC ($o:m:p = 43:5:52$).



Scheme 4

In recent years, bicumenes (2,3-dimethyl-2,3-diphenylbutane and derivatives, **1a–c**) have been widely recognized as excellent probes for ET processes.[22] They are readily oxidized to form radical cations and the scission of the central C–C bond subsequently takes place.[23] 4-Methoxybicumenes, 1,1,2,2-tetraarylethanes and 1,1,2-triarylpropanes have been reported to cleave on irradiation in the presence of an electron acceptor such as naphthalene-1,4-dicarbonitrile.[24] Some compounds containing a bibenzyl framework such as arylpinacols and their silyl ethers are also oxidized to form the corresponding radical cations, which lose a proton or a silyl cation, then undergo indirect fragmentation.[17,25] However, several bibenzyls have been reported in which no fragmentation of the central C–C bond was observed and deprotonation of the benzylic position was followed by the addition to the acceptor radical anion affording an adduct retaining the original framework.[26] Accordingly, we have chosen the bicumene molecule **1** as an alternative chemical probe to confirm the involvement of the ET process in the kyodai-nitration.

Results and discussion

A recent paper reported that on irradiation in dichloromethane, bicumene undergoes homolysis of the central C–C bond to yield two cumyl radicals, whereas in 2,2,2-trifluoroethanol it undergoes biphotonic ionization followed by the C–C fragmentation of the resulting radical cation, leading to one cumyl radical and one cumyl cation.[27] From a clean-cut difference in behaviour in the oxidation of bibenzyl **2a** and bicumene **1a** by cerium(IV) ammonium nitrate (CAN) or cobalt(III) acetate in acetic acid, we can safely conclude that the ET mechanism operates in the former oxidation while the HAT mechanism is important in the latter.[28] The products from the reaction of compound **1a** with CAN were acetophenone, 2-phenylpropane-1,2-diyl diacetate and the corresponding mixed acetate–nitrates, and the rate of this reaction was significantly faster as compared with that of bibenzyl. With these previous findings in mind, we have examined the reaction of bibenzyl **2a** and several derivatives, namely, bicumene **1a**, bi-4-cymene **1b**, bi-4-bromocumene **1c** and 1,1,2,2-tetraphenylethane **2b** with a combined nitrogen dioxide and ozone system and the results are summarized in Tables 1 and 2.

Nitration of bicumene 1a with various nitrating agents

The reactions of 2,3-dimethyl-2,3-diphenylbutane (bicumene, **1a**) with nitrogen dioxide and ozone, nitronium tetrafluoroborate and acetyl nitrate have been carried out under a variety of conditions (Table 1). Bicumene was stable toward nitrogen dioxide in a dilute dichloromethane solution at −20 °C; however, when ozone was introduced into this solution at the same temperature, the hydrocarbon was rapidly cleaved at the central position to produce 2-phenylpropene **4a**, 2-phenylpropan-2-ol (α-cumyl alcohol, **5a**) and acetophenone **6a** (Scheme 4). Little or no nuclear nitration products could be detected even at 50% conversion, although ethyl-, isopropyl-, butyl- and *tert*-butylbenzenes all readily gave the expected nitro derivatives under the same conditions. At a higher temperature (0 °C) or in a more concentrated solution, the formation of nitro derivatives became extensive, but even under these conditions the proportion of the fragmentation products was predominant in the product distribution. In the reactions in 1,2-dichloroethane and acetonitrile, the same trends were observed, but in nitromethane, the nuclear nitration products became important. Thus, in a polar but non-nucleophilic solvent such as nitromethane or in the presence of methanesulfonic acid as catalyst,[29] the nuclear nitration process was preferred, while in acetonitrile, the solvent-supported fragmentation of a radical cation intermediate was preferred, as has been observed in the case of the radical cations from benzyltrimethylsilanes,[21] leading to the preferential cleavage of the C–C bond. In accordance with an observation by Kochi *et al.*,[30] treatment of this hydrocarbon with nitronium tetrafluoroborate in sulfolane–dichloromethane at 0 or −20 °C furnished only nuclear nitration products.

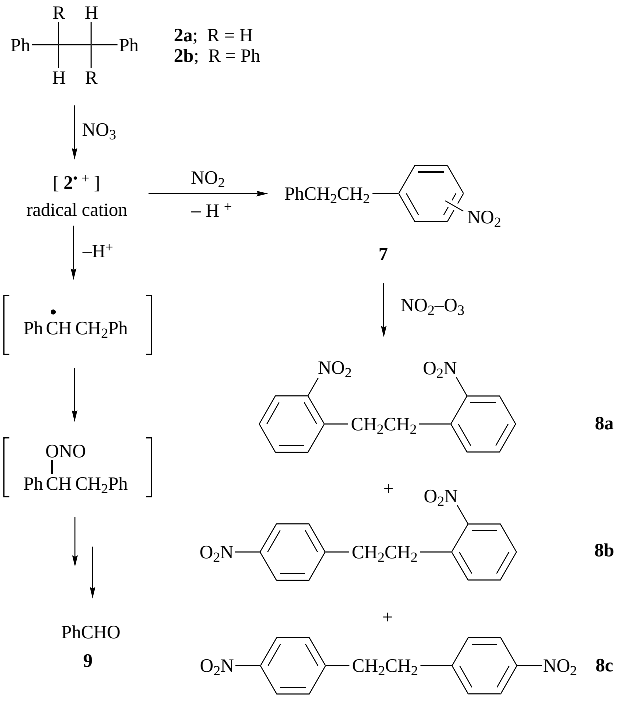
In connection with the present work, the classical aromatic nitration based on acetyl nitrate is worthy of mention. This nitrating agent is known to exist in an equilibrium with dinitrogen pentaoxide (N_2O_5), which has long been accepted as the precursor to the actual nitrating species, NO_2^+. In the gas phase or in a non-polar solution, however, dinitrogen pentaoxide is known to dissociate homolytically to produce nitrogen dioxide and nitrogen trioxide.[2,31] This suggests to us an alternative for the mechanism of nitration with so-called acyl nitrates: that this nitration may occur, at least in part, *via* the ET mechanism [Scheme 1(*b*)]. In fact, the nitration of compound **1a** with acetyl nitrate in dichloromethane was found to produce a significant amount of fragmentation products, along with the expected nitro derivatives (Table 1). Although the Ingold mechanism has been widely accepted as textbook knowledge for aromatic nitration with acetyl nitrate,[20] this mechanistic view needs reevaluation by modern techniques based on advanced instrumentation.†

Kyodai-nitration of bibenzyl 2a

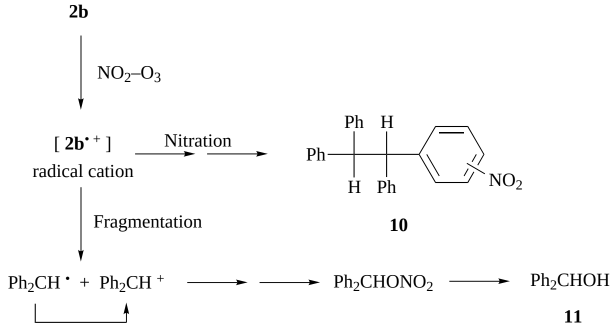
As was the case with simple alkylbenzenes, the ozone-mediated reaction of bibenzyl **2a** with nitrogen dioxide proceeded quite smoothly at low temperature, giving mono-nitro derivatives **7** as the main product. Bis-nitration products **8a–c** were formed when the reaction time was prolonged. Benzaldehyde **9** was the only by-product obtained. The bibenzyl radical cation formed by the oxidation of bibenzyl with nitrogen trioxide is considered to lose a benzylic proton in preference to the central C–C bond fission to form a benzylic radical, which would be trapped by nitrogen dioxide to afford the nitrite, eventually leading to benzaldehyde **9** (Scheme 5).

Kyodai-nitration of 1,1,2,2-tetraphenylethane 2b

The reaction of 1,1,2,2-tetraphenylethane **2b** was similarly carried out in dichloromethane at −25 °C to give the corresponding nitro derivatives **10** together with a significant amount of diphenylmethanol **11** after chromatographic separation on silica gel (Scheme 6). Benzophenone could not be detected by GLC analysis. This result shows that the alcohol **11** was derived from benzylic nitrate or nitrite and not from the direct oxidation of a radical intermediate species by molecular oxygen or ozone.



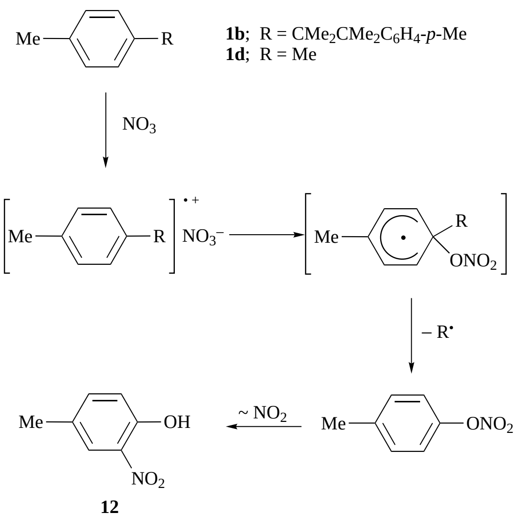
Scheme 5



Scheme 6

Kyodai-nitration of bi-4-cymene 1b

2,3-Dimethyl-2,3-bis-(4-methylphenyl)butane (bi-4-cymene, **1b**) was reacted under similar conditions to afford the expected fragmentation products along with 2-nitro-*p*-cresol **12**. With this substrate **1b**, preferential fragmentation occurred over nuclear nitration. Phenolic product **12** is considered to be formed *via* the coupling of an intermediate radical cation with nitrate anion at the *ipso* position followed by the elimination of the branched alkyl moiety to give the 4-methylphenyl nitrate; migration of the nitro group occurs selectively to the *ortho* position to give nitrophenol **12** (Scheme 7).[32] This nitrophenol was also a major by-product from the nitration of *p*-xylene **1d**.[33]



Scheme 7

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† One referee suggested a possible cleavage of the Wheland intermediate. However, bicumene was simply nitrated on the ring with nitronium tetrafluoroborate under the conditions employed, little mesolytic cleavage being observed (Table 1).

Table 3 Calculated vertical ionization potentials and experimentally determined anodic peak potentials of bibenzyl and related compounds[a]

Substrate	Heat of formation of neutral species/kJ mol^{-1}	Heat of formation of radical cation/kJ mol^{-1}	Vertical ionization potential/eV	ΔG (C–C)[b]/kJ mol^{-1}	ΔG (C–H)[c]/kJ mol^{-1}	Anodic peak potential in CH_2Cl_2, *E*/V *vs.* NHE
1a	135.95	986.35	9.47	−82.57	—	2.37
1b	57.58	881.98	9.20	−57.21	810.36	2.28
1c	200.43	1064.18	9.62	−74.87	—	2.43
2a	154.85	1011.98	9.44	105.35	756.18	2.65
2b	421.85	1268.08	9.38	−24.29 69.87[d]	738.94	2.45 (2.19)[e]
Toluene	59.04	921.74	9.44	—	722.86	2.61 (2.49)[f]
1,3,5-tris-(*tert*-butyl)benzene	−191.92	635.68	9.32	—	—	2.40 (2.20)[f] $E_{\frac{1}{2}} = 2.39$

[a] All calculations were carried out using the PM3 method. [b] The bond dissociation energy for central C–C bond cleavage of the corresponding radical cation. [c] The bond dissociation energy for benzylic C–H bond cleavage of the corresponding radical cation. [d] Calculation using modified MM2 method, from ref. 23(*d*). [e] In acetonitrile, from ref. 44(*a*). [f] In acetonitrile, from ref. 45.

Kyodai-nitration of bi-4-bromocumene 1c

When 2,3-dimethyl-2,3-bis-(4-bromophenyl)butane (bi-4-bromocumene, **1c**) was treated with nitrogen dioxide and ozone at −25 °C, the reaction proceeded markedly more slowly as compared with other bibenzyl derivatives examined. Preferential fragmentation over nuclear substitution was similarly observed and the only products obtained were 2-(4-bromophenyl)propene **4c** and 4-bromoacetophenone **6c**.

Mechanistic considerations

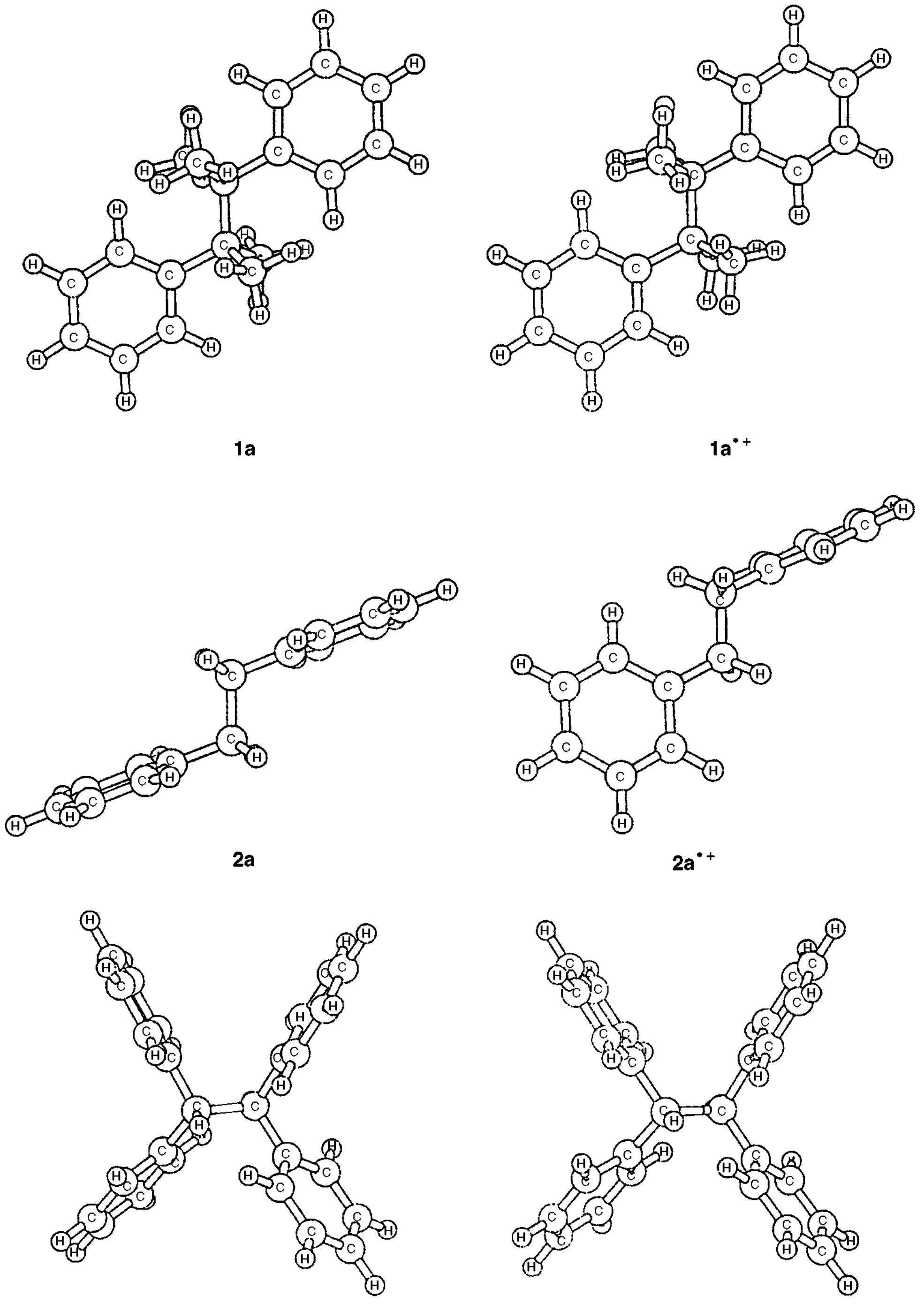
Complete fragmentation observed in the reaction of three bicumene derivatives **1a**–**c**, slight cleavage observed in bibenzyl **2a**, and comparable cleavage and nuclear substitution observed in tetraphenylethane **2b** may all be rationalized in terms of the thermodynamic data shown in Table 3. The energy difference [ΔG(C–C)] for the mesolytic scission of the central C–C bond of the respective radical cations was estimated by the PM3 method as the sum of the heat of formation of the fragment radical and cation minus that of the mother radical cation.[34] The energies needed for the central C–C bond cleavage of the radical cation species from bicumenes **1a**–**c** are all low enough to favour the cleavage process. The ΔG(C–C) value of tetraphenylethane **2b** is also below zero, showing a favoured trend toward fragmentation. However, our calculations were based on the ground state energies rather than the activation energies and the solvent effect was not considered, so it was expected that the actual reaction of these substrates has led to the products arising from both fragmentation and substitution.

The fragmentation barrier of bibenzyl **2a** is quite high and therefore the C–C bond cleavage is considered to take place less readily, especially in the gas phase or in a non-polar solvent system. In contrast, the energy barriers for the benzylic C–H bond scission [ΔG(C–H)] of bibenzyl and tetraphenylethane radical cations are relatively low and roughly comparable to that of the toluene radical cation. Thus, benzaldehyde **9** from the reaction of hydrocarbon **2a** is assumed to be derived from the oxidative degradation of the initially formed benzylic radical species, not from the fission of the central C–C bond in **2a**. The contrasting energy difference between the ΔG(C–C) values for bibenzyl and bicumene radical cations may be attributed to a remarkable conformational change of the optimized structure for the former upon one-electron oxidation of the parent hydrocarbon. The optimized conformation of a radical cation of bibenzyl **2a**, calculated by the PM3 method, showed that one of the phenyl rings undergoes a 90° rotation[35] with respect to the other upon one-electron oxidation to stabilize the radical cation (Fig. 1). For bicumene **1a**, however, such rotation of the aromatic ring is restricted considerably by the presence of four methyl groups in close vicinity. The calculated vertical ionization potentials as well as the anodic peak potentials of relevant bibenzyl derivatives are lower than those of alkylbenzenes and can be considered to be easily oxidized by nitrogen trioxide. Bi-4-bromocumene **1c** possesses a rather high ionization potential and low scission energy and therefore would be of interest as a potential probe for ET process. In fact, the kyodai-nitration of this compound gave solely the fragmentation products in accordance with the low calculated scission energy. Lower conversion rate of this bromo derivative is supposedly due to the high ionization potential. The reversible anodic peak potentials could not be obtained for any of the bibenzyl derivatives examined.

A plausible reaction pathway for the mesolytic fragmentation of bicumene **1** is depicted in Scheme 4. Nitrogen trioxide generated *in situ* oxidizes substrate to the radical cation, which dissociates into the corresponding cumyl cation and the cumyl radical. The cumyl radical can be further oxidized by nitrogen dioxide or other oxides of nitrogen to afford the cumyl cation, since the radical has quite a low oxidation potential, $E^{ox} = 0.16$ V.[36] The cationic species may be trapped by nitrate anion to form *α*-cumyl nitrate, leading to the alcohol **5** after aqueous workup. Loss of nitric acid from the nitrate forms the propene **4**, while oxidative degradation leads to the acetophenone **6**.

Mechanistic considerations for the fragmentation of bicumenes **1a**–**c** can be extended to the fragmentation of aromatic acetals. Aromatic cyclic acetals can be smoothly nitrated with nitrogen dioxide in ice-cooled dichloromethane or acetonitrile in the presence of ozone and magnesium oxide to give the *para*-nitro isomer as the major product in good yield, the acetal protective group remaining almost intact for hindered substrates.[37] Partial fragmentation observed in the reaction of 2-benzyl-2-phenyl-1,3-dioxolane **13** under similar conditions may also be understood in the context described above. Thus, the kyodai-nitration of dioxolane **13** first produces the corresponding radical cation **14**, which undergoes fragmentation into 2-phenyl-1,3-dioxolan-2-ium cation **15** and benzylic radical as shown in Scheme 8.[38] The latter radical is oxidized to form benzaldehyde or trapped by nitrogen dioxide to form nitrophenylmethane and benzyl nitrite. The cation **15** is attacked by nitrate anion to open the 1,3-dioxolane ring to produce the 2-benzoyloxyethyl nitrate ester **16**. The last type of reaction of the 1,3-dioxolan-2-ium cation has many precedents.[39] Photoinduced electron transfer reaction of 2,2-dialkyldioxolanes and some open-chain ketals has been shown to provide a mild route to the generation of alkyl radical species.[40]

In summary, the ET nature of the ozone-mediated nitration of arenes with nitrogen dioxide (the kyodai-nitration) has been confirmed using bicumene and derivatives **1a**–**c** as a chemical probe. These compounds suffer facile cleavage of the central C–C bond, affording the fragmentation products such as *α*-methylstyrenes **4**, 2-arylpropan-2-ols **5** and acetophenones **6**. This result can reasonably be interpreted in terms of an electron transfer process, in which the substrate **1** is first oxidized by



1a **1a$^{\bullet+}$**

2a **2a$^{\bullet+}$**

2b **2b$^{\bullet+}$**

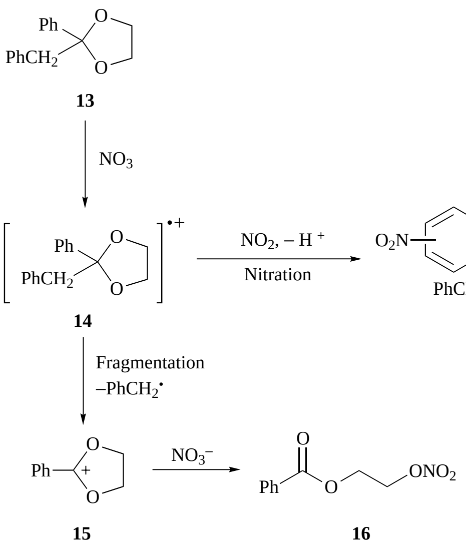
Fig. 1 Optimized conformations for hydrocarbons **1a** and **2a**,**b** and their radical cations **1a**$^{\bullet+}$ and **2a**,**b**$^{\bullet+}$

nitrogen trioxide, generated *in situ* from nitrogen dioxide and ozone, to form a radical cation species, which subsequently undergoes fragmentation eventually leading to the observed degradation products **4**–**6**.

Experimental

Instrumentation

Experimental details were given in a previous paper.[41] ^{1}H and ^{13}C NMR spectra were obtained with a Varian Gemini-200 spectrometer for ($CDCl_3$) solutions with tetramethylsilane as an internal standard. *J* values are given in Hz. Electron impact (EI) mass spectra were recorded on a Shimadzu GCMS QP-2000A mass spectrometer at an ionization potential of 70 eV. Fast atom bombardment (FAB) mass spectra were obtained with a JEOL JMS-HX110 Mass Spectrometer. IR spectra were recorded on a Shimadzu FT-IR DR-8000S/8100S IR spectrophotometer for liquid films or KBr pellets. Merck precoated silica gel sheets 60 F_{254} were used for TLC. Silica gel column chromatography was performed on Wakogel 200 (100–200 mesh) using hexane–ethyl acetate (5–50 : 1) as eluent. Recycling preparative HPLC (LC-908, Japan Analytical Industry, Co., Ltd.) fitted with a gel permeation column using chloroform as the eluent as well as preparative liquid chromatograph Shimadzu LC-8A fitted with a Shimadzu SHIM-PACK PRC-ODS column (250 × 20 mm i.d.) were employed for the isolation of the respective products. All melting points were determined on a Yanaco MP-S3 hot-stage apparatus and are not corrected. Equipment from Nippon Ozone Co. Ltd., type ON-1-2, was used for the generation of ozone. The machine produced ozone at a rate of 10 mmol h^{-1} under the conditions of an oxygen flow rate 10 dm^{3} h^{-1} and an applied voltage 80 V. Calibration of the



Scheme 8

ozone generator was made by iodometric titration. An ice-cooled bath, ice–salt bath or solid carbon dioxide–acetone bath was used for external cooling of the reaction mixture for preparative purposes. A cooling bath (EYELA COOL ECS-1 with two thermocontrollers THS-40 and THD-50) was used for experiments which required constant reaction temperature. GLC analyses were performed on a Shimadzu GC-17A gas chromatograph fitted with a fused silica capillary column (J&W Scientific, DB-5-30N-STD, 30 m × 0.25 mm i.d., 5% phenylmethylsilicone, $\delta\varphi = 0.25$ μm) and a flame ionization detector. Peak areas were determined using a Shimadzu C-R7A plus chromatopac computing integrator. Cyclic voltammetry was performed on a BAS-CV-50W Electrochemical Analyzer. Anodic peak potentials in irreversible cyclic voltammograms were measured with a platinum electrode for 10 mmol dm^{-3} dichloromethane solutions containing 0.1 mol dm^{-1} tetrabutylammonium hexafluorophosphate at a sweep rate of 100 mV s^{-1}. The Ag/AgNO$_3$ reference electrode of 6.0 mm in diameter was used in acetonitrile containing tetrabutylammonium perchlorate and the values obtained were converted to V *vs.* NHE values by the equation: $E(\text{NHE}) = E(\text{Ag/AgNO}_3) + 0.49$ V. All semiempirical molecular orbital calculations were carried out with the MOPAC[34] (version 6.10) program using the PM3 Hamiltonian, implemented on a Sony Tektronix CAChe system (version 3.6). Unrestricted Hartree–Fock wave functions were employed for the calculations of the radical cations and the calculations were carried out by full optimization using an extra keyword PRECISE. Bond dissociation energies were calculated as a difference between the heat of formation for a given radical cation and the sum of the corresponding values for two molecular fragments, *i.e.* a radical and a cation species.

Reagents and solvents

All reagents and solvents used were reagent-grade commercial samples. Dichloromethane was first dried with calcium chloride, then distilled from calcium hydride, and used immediately after distillation. All other solvents, nitromethane, acetonitrile and 1,2-dichloroethane, were distilled from calcium hydride before use and stored over molecular sieves (4 Å) under argon. Commercial 1,2-diphenylethane (bibenzyl) was used after recrystallization from methanol. 2,3-Dimethyl-2,3-diphenylbutane (bicumene)[42] and the 4-methyl derivative[43] as well as 1,1,2,2-tetraphenylethane[44] were prepared from cumene, *p*-cymene and chlorodiphenylmethane, respectively, by the reported procedures. Methanesulfonic acid, fuming nitric acid and acetic anhydride were used as received. Cyclododecane used as an internal standard for GLC analyses was recrystallized from ethanol. Nitrogen dioxide (99% pure) was purchased from Sumitomo Seika Co. Ltd. in a cylinder and used after transfer distillation. Oxygen gas was obtained from Kyoto Teisan Co. Ltd. and used after passage over a NaOH–Drierite tube.

2,3-Bis(4-bromophenyl)-2,3-dimethylbutane (bi-4-bromocumene, 1c). To a solution of bicumene (2.43 g, 10 mmol) in dry chloroform (50 cm^3) was added dropwise bromine (1.06 cm^3, 21 mmol) over 1 h in the presence of iron powder as catalyst. The resulting mixture was refluxed for 15 h to give the crude bromination product (3.3 g, *ca.* 80%), which was recrystallized from dichloromethane to give the pure product (2.39 g, 59%) as white crystals, mp 178–179 °C; ν_{max}(KBr)/cm^{-1} 2980, 1470, 1400, 1090, 1010, 830, 600 and 540; δ_{H}(200 MHz, CDCl$_3$) 1.27 (12 H, s), 6.88 (4 H, d, *J* 8.8) and 7.30 (4 H, d, *J* 8.8); *m*/*z* 199 (M$^+$/2, 97%), 198 (13), 197 (M$^+$/2, 100), 171 (13), 169 (14), 118 (20) and 117 (15) (Found: C, 54.38; H, 5.02. $C_{18}H_{20}Br_2$ requires C, 54.57; H, 5.09%).

Ozone-mediated reaction of bibenzyl derivatives with nitrogen dioxide. Typical procedure

1,1,2,2-Tetraphenylethane (334 mg, 1 mmol) was dissolved in a mixture of dichloromethane (30 cm^3) and nitrogen dioxide (1.0 cm^3, *ca.* 160 mmol) and placed in a two-necked flask. The ozonized oxygen was fed slowly into this solution at −20 °C for 5 min, then iced water was added to quench the reaction. The resulting mixture was worked up as usual to give a crude product (392 mg), which was chromatographed on silica gel with a 10:1 mixture of hexane and ethyl acetate as the eluent. The first eluate was unchanged starting material (119 mg, 36%) and the second eluate was an isomeric mixture of nitrotetraphenylethanes, which was further separated by GPC to afford *p*-nitro (137 mg, 36%) and *o*-nitro (28 mg, 7%) isomers. The third eluate was diphenylmethanol (67 mg, 36%). The residue (84 mg) on the column top was not investigated further.

The product distributions in the nitration of bicumene and derivatives **1a**–**c** were determined by GLC. 2-Phenylpropan-2-ol was found to lose a water molecule partially at the GLC injection port and in a capillary column to afford *α*-methylstyrene. The extent of such conversion was experimentally estimated using an authentic sample to be *ca.* 25–35% under the GLC conditions employed; the yield of the olefinic product **4** was corrected by reducing by 30% the peak area on gas chromatograms. The major nitration product obtained was always the *p*-nitro derivative.

1,2,2-Triphenyl-1-(4-nitrophenyl)ethane. Pale-yellow crystals, mp 200–201 °C; ν_{max}(KBr)/cm^{-1} 3060, 3030, 1600, 1510, 1450, 1350, 820, 750, 700, 610 and 580; δ_{H}(200 MHz, CDCl$_3$) 4.83 (2 H, dd, *J* 16.2, 11.5), 7.0–7.4 (17 H, m) and 7.97 (2 H, d, *J* 8.8); *m*/*z* 212 (M$^+$ − 167, 1%), 168 (14), 167 (100), 165 (26) and 152 (14) (Found: C, 82.37; H, 5.52; N, 3.74. $C_{26}H_{21}NO_2$ requires C, 82.30; H, 5.58; N, 3.69%).

1,2,2-Triphenyl-1-(2-nitrophenyl)ethane. The *ortho* isomer was identified by ^{1}H NMR and GC–MS analyses because of our failure to obtain it in isomer-free form. δ_{H}(200 MHz, CDCl$_3$) 4.73 (1 H, d, *J* 12.3), 5.75 (1 H, d, *J* 12.3) and 7.0–7.7 (19 H, m); *m*/*z*(GC–MS) 212 (M$^+$ − 167, 3%), 168 (15), 167 (100), 165 (22) and 152 (14).

2-Phenyl-1-(2-nitrophenyl)ethane. Pale-yellow crystals, mp 62–63 °C; ν_{max}(KBr)/cm^{-1} 1530, 1350, 910, 860, 790, 750, 700 and 530; δ_{H}(200 MHz, CDCl$_3$) 2.9–3.0 (2 H, m), 3.1–3.3 (2 H, m), 7.1–7.6 (8 H, m) and 7.92 (1 H, dd, *J* 8.0, 1.4); *m*/*z* 210 (M$^+$ − 17, 10%), 132 (17), 92 (10) and 91 (100) (Found: C, 74.03; H, 5.72; N, 6.16. $C_{14}H_{13}NO_2$ requires C, 73.99; H, 5.77; N, 6.16%).

2-Phenyl-1-(4-nitrophenyl)ethane. Pale-yellow crystals, mp 65–66 °C; ν_{max}(KBr)/cm^{-1} 1600, 1510, 1340, 870, 860, 830, 750 and 700; δ_{H}(200 MHz, CDCl$_3$) 2.9–3.0 (4 H, m), 7.1–7.4 (7 H, m) and 8.13 (2H, d, *J* 8.8); *m*/*z* 227 (M$^+$, 9%), 92 (12) and 91 (100) (Found: C, 73.72; H, 5.78; N, 6.02. $C_{14}H_{13}NO_2$ requires C, 73.99; H, 5.77; N, 6.16%).

1,2-Bis(2-nitrophenyl)ethane. Brownish crystals, mp 120–121 °C; $\nu_{\max}$(KBr)/cm^{-1} 1520, 1350, 860, 790, 750, 700 and 530; δ_{H}(200 MHz, CDCl$_3$) 3.26 (4 H, s), 7.3–7.4 (4 H, m), 7.5–7.6 (2 H, m) and 7.97 (2 H, dd, *J* 8.3, 1.4); *m*/*z* 272 (M$^+$, 1%), 136 (88), 106 (34), 105 (55), 92 (41), 91 (100), 89 (40), 78 (92) and 77 (63) (Found: C, 61.69; H, 4.42; N, 10.29. $C_{14}H_{12}N_2O_4$ requires C, 61.76; H, 4.44; N, 10.29%).

1-(2-Nitrophenyl)-2-(4-nitrophenyl)ethane. Yellow crystals, mp 91–92 °C; $\nu_{\max}$(KBr)/cm^{-1} 1610, 1520, 1340, 850, 790, 750, 700 and 520; δ_{H}(200 MHz, CDCl$_3$) 3.15 (4 H, m), 7.2–7.6 (5 H, m), 7.97 (1 H, d, *J* 8.0) and 8.15 (1 H, d, *J* 8.8); *m*/*z* 272 (M$^+$, 1%), 255 (49), 136 (24), 90 (26), 89 (41) and 78 (100) (Found: C, 61.57; H, 4.44; N, 10.23. $C_{14}H_{12}N_2O_4$ requires C, 61.76; H, 4.44; N, 10.29%).

1,2-Bis(4-nitrophenyl)ethane. Yellow crystals, mp 182–183 °C; $\nu_{\max}$(KBr)/cm^{-1} 1600, 1510, 1340, 1110, 850, 750, 700 and 520; δ_{H}(200 MHz, CDCl$_3$) 3.08 (4 H, s), 7.28 (4 H, d, *J* 7.3) and 8.14 (4 H, d, *J* 7.3); *m*/*z* 272 (M$^+$, 27%), 136 (100), 106 (35), 90 (29), 89 (30) and 78 (43) (Found: C, 61.77; H, 4.44; N, 10.21. $C_{14}H_{12}N_2O_4$ requires C, 61.76; H, 4.44; N, 10.29%).

2,3-Dimethyl-3-phenyl-2-(4-nitrophenyl)butane. Yellow crystals, mp 120–121 °C; $\nu_{\max}$(KBr)/cm^{-1} 2980, 1600, 11 510, 1350, 11 090, 850, 760, 700, 690 and 530; δ_{H}(200 MHz, CDCl$_3$) 1.34 (6 H, s), 1.36 (6 H, s), 7.0–7.1 (2 H, m) 7.12 (1 H, s) 7.1–7.2 (4 H, m) and 8.0–8.1 (2 H, d, *J* 9.1); *m*/*z* (FAB) 284 (M$^+$ + 1); *m*/*z* (EI) 165 (M$^+$ − 118, 26%), 134 (6), 120 (11), 119 (100) and 91 (53) (Found: C, 76.41; H, 7.52; N, 4.96. $C_{18}H_{21}NO_2$ requires C, 76,29; H, 7.47; N, 4.94%).

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