Positional Reactivity of Acylpolymethylbenzenes in Electrophilic Substitution

Kazunori MATSUURA,# Yasuo KIMURA, Hisakazu TAKAHASHI, Toshio MORITA, Ichiro TAKAHASHI, Hidehiko KITAJIMA,* and Takashi KEUMI##

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910

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Friedel–Crafts acylation, bromination, deuteration, and nitration of acetylpentamethylbenzene (APMB), 1-acetyl-2,3,4,6-tetramethylbenzene (ATMB), and 1-benzoyl-2,3,4,6-tetramethylbenzene (BTMB) and the resulting product distributions were investigated. Friedel–Crafts acylation, bromination, and deuteration of APMB and Friedel–Crafts acylation of ATMB gave deacetylation-substitution products. On the other hand, bromination and deuteration of ATMB (or BTMB) and Friedel–Crafts acylation of BTMB gave 5-substituted products. In both cases, the positional reactivities were in accordance with the relative σ-complex stability. Conversely, except for Friedel–Crafts-type nitration, the positional reactivities in the nitration of these substrates were strikingly different from those of the above three reactions. Thus, side-chain functionalization at the 6-methyl group occurred in nitration with fuming nitric acid, depending on the solvents in use. The MNDO calculations and the reaction of APMB with single-electron transfer reagents such as tetranitromethane-$h\nu$ or cerium(IV) ammonium nitrate suggest that the product distribution in nitration can be explained in terms of a single-electron transfer mechanism.

Considerable controversy still exists concerning substrate and positional selectivities in electrophilic aromatic substitution reactions. It has been generally thought that this accords with the relative stability of the intermediate σ-complexes.[1] However, in electrophilic aromatic nitration, where selectivities deviate from Brown's selectivity rule,[1] the proposed mechanism was by way of the formation of a rate determining "early" intermediate (a π-complex,[2] encounter pair[3] or ion-radical pair, which are based on a single electron transfer (SET) mechanism[4]) prior to the formation of the σ-complex.[4a,5] This is attributed to the character of NO_2^+ as a strong ET oxidant (E°+1.57 V),[6] which would involve ET processes when reacted with aromatic compounds (E°+1.6—2.9 V).[7] Such an early transition state mechanism in aromatic nitration, however, has not yet been widely accepted. This is because the positional reactivities expected from this mechanism would be much the same as those from the classical σ-complex (late transition state) mechanism, for the substrates hitherto investigated (i.e. toluene, anisole, naphthalene, etc.). Consequently, it would be difficult to differentiate the mechanistic alternatives out of the observed product distributions.

Recently, we have found that dibenzofuran is a substrate for which the mechanistic alternatives can be easily differentiated.[8] Thus, Friedel–Crafts acylation occurs at the 2-position leading to the most stable σ-complex, whereas nitration with nitric acid occurs at the 3-position. In the latter, reactive sites are either those with the highest HOMO electron density of dibenzofuran or those with the highest spin density of dibenzofuran radical cation.

In connection with this, we have reported that nitration of polysubstituted acylbenzenes (bearing at least three methyl groups at the 2-, 4-, and 5-positions) with fuming nitric acid preferentially occurs at the 2-position on the side chain.[9—12] MNDO calculations of 1-acryloyl-2,3,4,6-tetramethylbenzene[10] and 1-acetyl-2,4,5-trimethybenzene[11] suggest that the positional reactivities in nitration are in accordance with the HOMO electron density, rather than the stability of the σ-complex.

In this paper, we wish to report the product distribution of three types of acylpolymethylbenzenes: acetylpentamethylbenzene (APMB), 1-acetyl-2,3,4,6-tetramethylbenzene (ATMB), and 1-benzoyl-2,3,4,6-tetramethylbenzene (BTMB) in Friedel–Crafts acylation, bromination, deuteration, and nitration. Also, the positional reactivities of the acylpolymethylbenzenes are examined by MNDO calculations.

Results and Discussion

Friedel–Crafts Acylation of Acylpolymethylbenzenes. The acylation of acylpolymethylbenzenes was carried out under usual Friedel–Crafts conditions using 1—2 equiv of acid chlorides and 2—3 equiv of aluminum chloride (Scheme 1). The results are summarized in Table 1.

Acylation of APMB gave acyl-exchanged products at the 1-position as the sole products (Entries 1—5). For example, benzoylation of APMB with benzoyl chloride and aluminum chloride at 30 °C for 5 h gave benzoylpentamethylbenzene **1a** as the sole product in a 94% yield (Entry 1). Similarly, acyl-exchanges at the 1-position preferentially took place in the acylation of ATMB (Entries 6—9). Although the propionylation of ATMB at a reaction time shorter than 7 h afforded only propionyl-2,3,4,6-tetramethylbenzene **1f** (as in Entry 8), prolonged reaction time gave rise to 1,5-diacetyl- **2a**, 1-acetyl-5-propionyl- **2b**, and 1,5-dipropionyl-2,3,4,6-

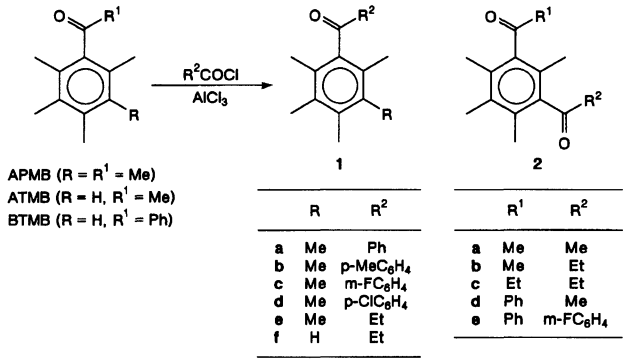
#Present address: Department of Biomolecular Engineering, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227.

##Deceased in December 25, 1991.

Table 1. Friedel–Crafts Acylation of Acylpolymethylbenzenes

Entry	Substrate	R^2	Solvent	Temp/°C	Time/h	Conv./%	Product (yield/%)[a]
1	APMB	Ph	CH_2Cl_2	30	5	94	**1a** (94)
2		p-MeC_6H_4	o-$Cl_2C_6H_4$	30	5	59	**1b** (58)
3		m-FC_6H_4	o-$Cl_2C_6H_4$	30	5	82	**1c** (82)
4		p-ClC_6H_4	o-$Cl_2C_6H_4$	30	5	45	**1d** (45)
5		C_2H_5	CH_2Cl_2	30	5	58	**1e** (58)
6	ATMB	Ph	CH_3NO_2	50	24	78	BTMB (72), **2d** (trace)
7		CH_3	CH_2Cl_2	Reflux	24	95	**2a** (91)
8		C_2H_5	CH_2Cl_2	Reflux	7	39	**1f** (39)
9		C_2H_5	CH_2Cl_2	Reflux	24	99	**2a** (18), **2b** (41), **2c** (39)
10	BTMB	CH_3	CH_2Cl_2	Reflux	5	90	**2d** (80), ATMB (6)
11		m-FC_6H_4	CH_2Cl_2	Reflux	24	87	**2e** (87)

a) Determined by GLC analyses.



Scheme 1.

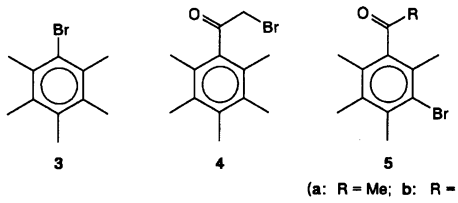


Chart 1.

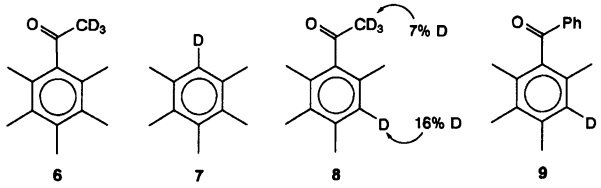


Chart 2.

tetramethylbenzene **2c** (Entry 9). On the other hand, acylations of BTMB predominantly occurred at the unsubstituted aromatic nuclei (the 5-position); acylation-debenzoylation products were determined in only trace amounts by GLC analyses (Entries 10 and 11).

Bromination of Acylpolymethylbenzenes. Results of the bromination of the acylpolymethylbenzenes are shown in Chart 1 and Table 2.

In the bromination of APMB, electrophilic bromination gave only the bromination-deacetylation product, i.e. bromopentamethylbenzene **3**, which agrees with the positional reactivity of the acylation of APMB (Entries 1 and 4). In contrast, when a homolytic bromination reagent or an enolization-promoting solvent was used, the reaction preferentially occurred at the α-position of the acetyl group (Entries 2 and 3). Electrophilic bromination of ATMB or BTMB took place at the 5-position similar to the acylation of BTMB, and neither bromination-deacetylation product **3**, nor α-bromo-substituted product **4** were detected by GLC analyses (Entries 5 and 6).

Deuteration of Acylpolymethylbenzenes. ^1H NMR spectral measurements (Chart 2) showed that the deuteration of APMB with trifluoroacetic acid-*d* under mild reaction conditions (room temperature, 72 h) occurred first at the α-position of the acetyl group (**6**). Addition of a small amount of deuterium oxide to the reaction mixture promoted deuteration on the aromatic ring, which in turn afforded the deuteration-deacetylation product, i.e. 1-deuterio-pentamethylbenzene **7**, in an 80% yield (based on GLC and ^1H NMR spectral measurements), when the reaction was carried out under reflux for 1 h. The ^1H NMR spectrum of the reaction mixture revealed that no deuteration occurred at the side-chain methyl group. On the other hand, when ATMB was reacted with trifluoroacetic acid-*d* at room temperature for 5 h, ATMB deuterated 7% on the α-proton and 16% on the 5-position ring proton was obtained (**8**). Elongation of the reaction time and elevation of the reaction temperature (reflux) led to deacetylation. In the case of BTMB, only the 5-position ring proton completely underwent deuteration in the reaction with trifluoroacetic acid-*d* under reflux for 20 h (**9**).

Nitration of Acylpolymethylbenzenes. As we have previously reported, nitration of APMB,[9] ATMB,[9] and BTMB[11] with fuming nitric acid in acetic anhydride at 0 to 5 °C results predominantly in side-chain nitration on the methyl group at the 6-position (Scheme 2). The results of extensive studies on the nitration of acylpolymethylbenzenes with fuming nitric acid are summarized in Table 3.

Analogous to the results of Suzuki et al.,[13] the reaction of APMB with fuming nitric acid in dichloro-

Table 2. Bromination of Acylpolymethylbenzenes

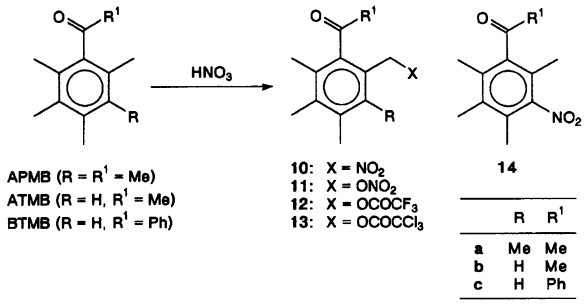
Entry	Substrate	Brominating reagent	Solvent	Temp/°C	Time/h	Conv./%	Product (yield/%)[a]
1	APMB	$Br_2/AlBr_3$	CH_2Cl_2	RT	2	71	**3** (71)
2[b]		Br_2	AcOH	RT	1	92	**3** (6), **4** (86)
3		NBS	CCl_4	Reflux	5	49	**4** (48)
4		$Br_2/AgNO_3$ /HNO_3	AcOH/H_2O /dioxane[c]	30	16	98	**3** (90), **4** (8)
5[d]	ATMB	$Br_2/AlBr_3$	CH_2Cl_2	RT	12	99	**5a** (97)
6[d]	BTMB	$Br_2/AlBr_3$	CH_2Cl_2	RT	8	92	**5b** (85)

a) Determined by GLC analyses. b) See Ref. 10. c) 4/2/1 (v/v/v). d) Bromination-deacylation product was not detected.

Table 3. Nitration of Acylpolymethylbenzenes with Fuming Nitric Acid

Entry	Substrate	Solvent	Temp/°C	Time/h	Conv./%	Product (yield/%)[a]
1[b]	APMB	Ac_2O	0—5	2	98	**10a** (91), **11a** (2)
2[c]		CH_2Cl_2	0—5	10	87	**10a** (trace), **11a** (80)
3		CH_3NO_2	0—5	5	40	**10a** (4), **11a** (29)
4		$(CF_3CO)_2O$	0—5	0.5	99	**10a** (25), **12a** (55)
5		$(CCl_3CO)_2O$	5—10	2	98	**10a** (7), **11a** (16), **13a** (35)[e]
6		CH_3CN	RT	10	70—80	**15a** (42)[e]
7		AcOH	RT	24	30—40	**15a** (20)[e]
8[b]	ATMB	Ac_2O	0—5	2	90	**10b** (72), **14b** (27)
9		CH_2Cl_2	0—5	4	92	**11b** (35), **14b** (51)
10		CH_3CN	RT	10	70—80	**15b** (47),[e] **14b** (trace)
11[d]	BTMB	Ac_2O	0—5	5	99	**10c** (65), **11c** (4), **14c** (25)
12		CH_2Cl_2	25	20	89	**10c** (3), **11c** (35), **14c** (39)
13		$(CF_3CO)_2O$	0—5	2.5	82	**10c** (20), **11c** (2), **12c** (32), **14c** (25)
14		CH_3CN	RT	24	45	**10c** (9), **11c** (11), **14c** (12)

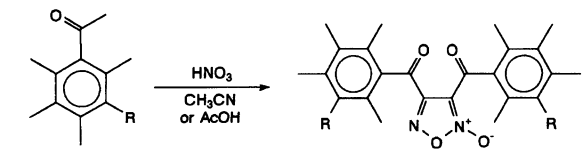
a) Determined by HPLC analyses. b) Data in Ref. 7. c) See also Ref. 11. d) See also Ref. 9. e) Isolated yields.



Scheme 2.

methane at 0 to 5 °C led to side-chain nitrooxylation on the methyl group of the 6-position in an 80% yield (Entry 2). It was also observed in nitromethane that the side-chain nitrooxylation reaction exceeds the nitration reaction on the 6-position methyl group (Entry 3). Similarly, ATMB and BTMB were reacted with fuming nitric acid in dichloromethane to give 6-nitrooxymethyl products **11b** and **11c**, together with 5-position ring nitrated products **14b** and **14c**, respectively (Entries 9 and 12). In these reactions, the selectivities were lower than those in Entries 8 and 11. When **11b** was allowed to stand for a few days at room temperature, it underwent oxidation and was converted into 1-acetyl-2-formyl-4,5,6-trimethylbenzene.[14] Use of trifluoro- or trichloroacetic anhydride as the solvent for nitration with fuming nitric acid gave rise to solvolysis on the methyl group of the 6-position as the major path, respectively (Entries 4, 5, and 13).

Unexpectedly, reactions of APMB and ATMB with fuming nitric acid in acetonitrile or acetic acid at room temperature (Scheme 3) yielded the corresponding bis-(polymethylbenzoyl)furazan 2-oxides **15a** and **15b**, respectively, as the sole isolated products (Entries 6, 7, and 10). Only trace amounts of the corresponding 6-position side-chain functionalized products and ring-nitrated products were observed in HPLC analyses. However, BTMB was reacted with fuming nitric acid in ace-



Scheme 3.

tonitrile under similar reaction conditions to give 6-position side-chain functionalized products (**10c** and **11c**) and a 5-position ring-nitrated product (**14**) in low yields (Entry 14). The structures of the dibenzoylfurazan 2-oxides were determined by typical absorption bands assignable to the furazan 2-oxide skeleton in the IR spectra[15] (see Experimental). Solvents such as acetonitrile promote the enolization of the acetyl group, and therefore, nitration would occur at the α-position of the acetyl group, followed by the formation of bis(polymethylbenzoyl)furazan 2-oxides via α-oxophenylacetonitrile *N*-oxide intermediates.[16]

On the contrary, Friedel–Crafts-type nitration[17] of APMB with 1-cyano-1-methylethyl nitrate (CMN) and aluminum chloride gave nitration-deacetylation products, i.e. nitropentamethylbenzene **16** together with chloropentamethylbenzene **17**, which agrees with the positional reactivity of Friedel–Crafts acylation, bromination, and deuteration of APMB (Scheme 4 and Entry 1 in Table 4). Similarly, ATMB and BTMB were reacted with CMN and aluminum chloride to give 5-position ring-nitrated products exclusively, which agrees with the positional reactivity of Friedel–Crafts acylation, bromination, and deuteration of BTMB (Entries 2 and 3).

Factors Controlling the Positional Reactivities of Acylpolymethylbenzenes in Electrophilic Substitution Reactions. As described above, it was found that in the electrophilic fuming nitric acid nitration of acylpolymethylbenzenes (APMB, ATMB, and BTMB), anomalous positional reactivities indicated that the side-chains at the 6-position were functionalized. At this point, we carried out MNDO calculations[18] of APMB and ATMB, in order to estimate the positional reactivities of these acylpolymethylbenzenes. The calculations with full geometry optimization were carried out on these reactivity indices: (i) HOMO electron densities of free APMB and ATMB as models for the electrophilic early transition state, (ii) spin densities and net charge of the radical cations of APMB and ATMB as models for the electron transfer early transition state, and (iii) relative stabilities of protonated APMB and ATMB as models for the late transition state. The results are listed in Tables 5 and 6.

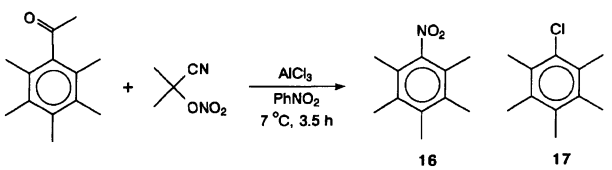
1-Protonated APMB$^+$ was the most stable of the protonated APMB$^+$'s, which agrees with the positional reactivity of the Friedel–Crafts acylation, bromination, deuteration, and Friedel–Crafts-type nitration of APMB. The relative stability of protonated ATMB$^+$ was the largest for 5-protonated APMB$^+$. This structure is energetically favored to a lesser extent than its corresponding 1- and 3-counterparts (0.32 and 0.37 kcal mol^{-1}, respectively), however, this is in accordance with the positional reactivity observed in the bromination, deuteration, and Friedel–Crafts-type nitration of ATMB and BTMB, and the Friedel–Crafts acylation of BTMB (except for the Friedel–Crafts acylation of ATMB). Therefore, the positional reactivities observed in these electrophilic reactions can be explained in terms of the late transition state mechanism (Scheme 5), which agrees with the reaction of dibenzofuran with these electrophiles.

On the other hand, the 6-position side-chain functionalization of acylpolymethylbenzenes could not be interpreted by the late transition state mechanism. MNDO calculations of APMB showed that the HOMO electron density of the 3-(5-)position of APMB was as large as that of the 2-(6-)position. If nitration occurs according to the HOMO electron density of APMB, it would yield a mixture of 5- and 6-position side-chain nitration products. In contrast, the spin density of the 3-position of the APMB radical cation was by far larger than any other position of the aromatic nucleus, whereas the 6-position methyl group was more acidic than any other methyl group (see the net charge of the APMB radical cation in Table 5). Thus, the positional reactivity in the nitration of APMB with fuming nitric acid, giving 6-position side-chain functionalization, might favorably be interpreted by the following single-electron transfer mechanism suggested by Kochi et al.[4b,19] and Suzuki et al.[13b] (Scheme 6).

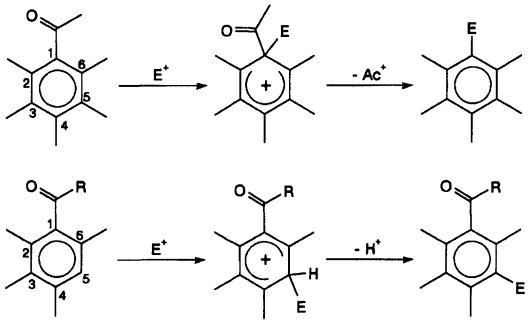
It is recognized that the nitrating agent in the fuming nitric acid/acetic anhydride system is acetyl nitrate (Eq. 1).[17]

$$HNO_3 + Ac_2O = AcONO_2 + AcOH \quad (1)$$

Similarly, the nitrating agent in the fuming nitric acid/trifluoroacetic anhydride system is assumed to be trifluoroacetyl nitrate (Eq. 2).



Scheme 4.



Scheme 5.

Table 4. Nitration of Acylpolymethylbenzenes with CMN

Entry	Substrate	Solvent	Temp/°C	Time/h	Conv./%	Product (yield/%)[a]
1	APMB	$PhNO_2$	7	3.5	42	**16** (15), **17** (25)[a]
2	ATMB	CH_2Cl_2	0—5	2	100	**14** (99)[b]
3	BTMB	CH_2Cl_2	0—5	2	96	**14** (88)[b]

a) Determined by GLC analyses. b) Determined by HPLC analyses.

Table 5. Positional Reactivity Indices of APMB Caluculated by MNDO Methods

Position of APMB	HOMO electron density	Spin density of $APMB^{\cdot+}$ [a]	Net charge of $APMB^{\cdot+}$ [a]	Total energy of protonated $APMB^+$ / eV	Rel. energy of Protonated $APMB^+$ / kcal mol^{-1}
1	0.00000	−0.31256	−0.1741	−2245.941806	0.00
2	0.44655	0.35723	0.0970	−2245.675727	6.14
3	0.44519	0.51305	0.0881	−2245.841579	2.31
4	0.00002	−0.33576	−0.1089	−2245.784476	3.63
5	0.44859	0.32551	0.0527		
6	0.45306	0.42545	0.1194		

a) Calculations were performed for the open-shell system of APMB radical cation.

Table 6. Positional Reactivity Indices of ATMB Caluculated by MNDO Methods

Position of APMB	HOMO electron density	Spin density of $APMB^{\cdot+}$ [a]	Net charge of $APMB^{\cdot+}$ [a]	Total energy of protonated $APMB^+$ / eV	Rel. energy of Protonated $ATMB^+$ / kcal mol^{-1}
1	0.05583	−0.29705	−0.1584	−2089.644480	0.37
2	0.28689	0.34737	0.0856	−2089.493571	3.85
3	0.61266	0.52821	0.1114	−2089.646907	0.32
4	0.07501	−0.24600	−0.0989	−2089.388993	6.26
5	0.24285	0.24004	0.0617	−2089.660668	0.00
6	0.54294	0.41812	0.1193	−2089.366439	6.79

a) Calculations were performed for the open-shell system of ATMB radical cation.

$$HNO_3 + (CF_3CO)_2O = CF_3COONO_2 + CF_3CO_2H \quad (2)$$

On the other hand, fuming nitric acid in dichloromethane exists in the following equilibrium (Eq. 3).[13b,17]

$$2HNO_3 = N_2O_5(NO_2^+/NO_3^-) + H_2O \quad (3)$$

The basicity of the nitronium carrier seems to be $AcO^- >> CF_3CO_2^- > NO_3^-$.

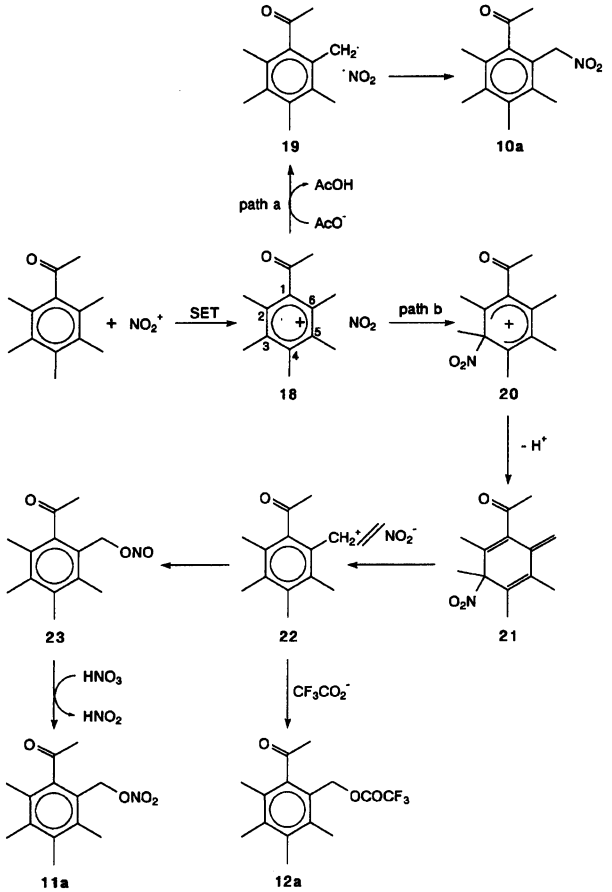
Thus, it seems that in the nitration of APMB in acetic anhydride, acetate ion plays a role as a base to abstract a proton from the most acidic 6-methyl group in the APMB radical cation, which is formed by single-electron transfer from APMB to a nitronium ion, to provide 6-position benzyl radical-nitrogen dioxide pair **19** (path a in Scheme 6). Decay of radical pair **19** would give 6-position side-chain nitrated product **10a**. In contrast, due to the weaker basicity of the nitronium carrier, nitration in trifluoroacetic anhydride or dichloromethane might proceed by way of decay of APMB radical cation-nitrogen dioxide pair **18** on the *ipso*-position of the 3-position of the APMB radical cation, which has the largest spin density (path b in Scheme 6). This is followed by deprotonation *para* to the *ipso*-attacked position,[20] i.e. the 6-position methyl group, to give methylcyclohexadiene **21**,[21] and heterolytic dissociation into benzyl cation–nitrite ion pair **22**.[22] The hard acid–hard base interaction of benzyl cation and nitrite ion (an ambident nucleophile) gives 6-position benzyl nitrite compound **23**. Oxidation of **23** with nitric acid affords 6-position benzyl nitrate product **11a**.[23] Nucleophilic attack of trifluoroacetate ion on the 6-position benzyl cation would provide 6-position side-chain trifluoroacetoxylated product **12a**.

According to the MNDO calculations of the ATMB radical cation, it has the largest spin density on the 3-position and the cationic center on the 6-position, which are similar to the APMB radical cation. Thus, nitration of ATMB and BTMB with fuming nitric acid, giving 6-position side-chain functionalized products, also could be interpreted by the single-electron transfer mechanism as described above.

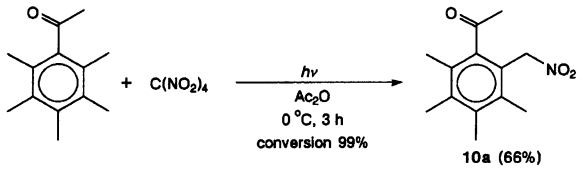
In order to confirm the idea of an electron transfer mechanism in the nitration of acylpolymethylbenzenes, we undertook the nitration of APMB with tetranitromethane in acetic anhydride under irradiation using a high-pressure mercury lamp, which was suggested

by Kochi et al.[4b,19] to occur via an electron transfer mechanism. This photonitration of APMB afforded **4a** as the only product in a 66% isolated yield, which agrees with thermal nitration with fuming nitric acid in acetic anhydride (Scheme 7). However, nitration with tetranitromethane did not proceed without irradiation. Moreover, single-electron oxidation[24] of APMB with cerium(IV) ammonium nitrate (CAN) gave **4a** and **4b** in 13% and 14 % isolated yields (as major products together with minor two unidentified products), respectively (Scheme 8).

These results led us to emphasize that the nitration of acylpolymethylbenzenes with fuming nitric acid proceeds by way of an electron transfer mechanism. In conclusion, our present investigation in terms of the product distribution showed that electrophilic nitration with fuming nitric acid is clearly distinct from any other electrophilic reaction including Friedel–Crafts-type nitration via the late transition state.



Scheme 6.



Scheme 7.

Experimental

Measurements. All melting and boiling points are uncorrected. IR spectra were recorded on a JASCO FT/IR-8000 Fourier transform infrared spectrometer as KBr pellets (unless otherwise stated). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX200 Fourier transform NMR spectrometer (270 MHz) as chloroform-*d* solutions. All signals are expressed as ppm downfield from tetramethylsilane (TMS) used as an internal standard (δ value). The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Mass spectra (EI mode) were taken with a JEOL JMS-DX300 mass spectrometer. GLC analyses were carried out on a Hitachi GC Model 163 gas chromatograph equipped with a hydrogen flame ionization detector and a stainless-steel column (l=3 m, ϕ=3 mm) packed with 3% Dexil 300 GC on Chromosorb W. HPLC analyses were carried out on a JASCO-TRI ROTAR-IV high performance liquid chromatograph using a Megapak SIL column (l=30 cm, ϕ=7.2 mm) and hexane/ethyl acetate (8/2 v/v) as the eluent. Product distributions based on HPLC were calculated from the relative peak area with respect to the internal standard (naphthalene or dibenzofuran) on a System Instruments Chromatocorder 11 instrument after calibration for each authentic sample. Column chromatography and thin layer chromatography (TLC) were all performed using silica gel as an adsorbent.

Materials. APMB (mp 84—85 °C; lit,[25] mp 84 °C), ATMB (bp 147 °C/22 mmHg; lit,[26] bp 135—137 °C/10 mmHg), and BTMB (mp 61—62 °C; lit,[27] mp 62—63 °C) were prepared from the corresponding polymethylbenzenes and acid chlorides (1 mmHg=133.322 Pa). CMN (bp 72 °C/25 mmHg; lit,[28] bp 62—65 °C/10 mmHg) was prepared according to Freeman's procedure. CAN was purchased from Wako Pure Chemicals Co., Ltd., and was dried at 100°C for 20 h prior to use. Acetonitrile was distilled from calcium hydride prior to use. Other reagents were obtained from commercial sources and used without further purification.

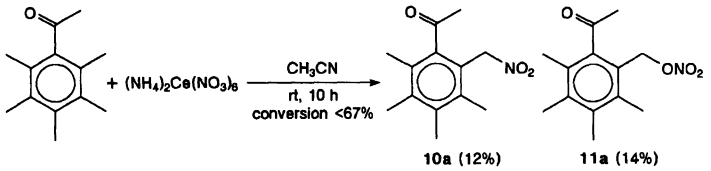
General Procedure for Friedel–Crafts Acylation of Acylpolymethylbenzenes. Benzoylation of APMB. To a solution of APMB (0.50 g, 2.6 mmol) in dichloromethane (4 mL) was added a solution of benzoyl chloride (0.74 g, 5.2 mmol) and aluminum chloride (1.05 g, 7.8 mmol) in dichloromethane (4 mL) over 10 min at 0—5 °C. After stirring for 5 h at 30 °C, the reaction mixture was quenched with 1 M hydrochloric acid and was extracted with dichloromethane (1 M=1 mol dm^{-3}). The combined organic extracts were washed with water and then dried over anhydrous sodium sulfate. After the evaporation of solvent, the resulting residue was analyzed by GLC and HPLC.

Acylation reactions of APMB, ATMB, and BTMB were also carried out by procedures similar to that described above. The physical data of the products are as follows.

Benzoylpentamethylbenzene (1a). Mp 136—137 °C (from EtOH; lit,[29] mp 135—136 °C).

(*p*-Methylbenzoyl)pentamethylbenzene (1b). Mp 138—139 °C (from EtOH; lit,[30] mp 138—139 °C).

(*m*-Fluorobenzoyl)pentamethylbenzene (1c). Mp 135—136 °C (from EtOH). ^{1}H NMR δ=1.96 (s, 6H), 2.18 (s, 6H), 2.23 (s, 3H) and 7.08—7.50 (m, 4H). IR ν 1674 and 1237 cm^{-1}. MS (EI) m/z 270 (M$^+$). Anal. Calcd for



Scheme 8.

$C_{18}H_{19}OF$: C, 79.97; H, 7.08%. Found: C, 80.14; H, 7.31%.

(*p*-Chlorobenzoyl)pentamethylbenzene (1d). Mp 144—145 °C (from EtOH; lit,[31] mp 144—145 °C).

Propionylpentamethylbenzene (1e). Mp 84—85 °C (from MeOH; lit,[31] mp 84—85 °C).

1-Propionyl-2,3,4,6-tetramethylbenzene (1f). Mp 54—55 °C (from 80% EtOH; lit,[12] mp 54—55 °C).

1,5-Diacetyl-2,3,4,6-tetramethylbenzene (2a). Mp 125—126 °C (from hexane; lit,[13a] mp 126—128 °C).

1-Propionyl-5-acetyl-2,3,4,6-tetramethylbenzene (2b). Mp 82—83 °C (from 80% EtOH). ^{1}H NMR δ=1.19 (t, 3H, J=7 Hz), 2.02 (s, 3H), 2.11 (s, 3H), 2.15 (s, 6H), 2.44 (s, 3H), and 2.68 (q, 2H, J=7 Hz). IR ν 1698 cm^{-1}. MS (EI) m/z 232 (M^+). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Found: C, 77.59; H, 8.41%.

1,5-Dipropionyl-2,3,4,6-tetramethylbenzene (2c). Mp 97—98 °C (from 80% EtOH; lit,[32] mp 99—100 °C).

1-Acetyl-5-benzoyl-2,3,4,6-tetramethylbenzene (2d). Mp 111—112 °C (from 90% EtOH). ^{1}H NMR δ=1.95 (s, 3H), 2.04(s, 3H), 2.19 (s, 3H), 2.21 (s, 3H), 2.47 (s, 3H), 7.44 (t, 2H, J=7 Hz), 7.59 (t, 1H, J=7 Hz), and 7.81 (d, 2H, J=7 Hz). IR ν 1698 and 1663 cm^{-1}. MS (EI) m/z 280 (M^+). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%. Found: C, 81.73; H, 7.38%.

1-Benzoyl-5-(*m*-fluorobenzoyl)-2,3,4,6-tetramethylbenzene (2e). Mp 120—121 °C (from hexane). ^{1}H NMR δ=1.83 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.23 (s, 3H), 7.26—7.32 (m, 1H), 7.39—7.49 (m, 3H), 7.57—7.62 (m, 3H), and 7.84 (d, 2H, J=7 Hz). IR ν 1674 and 1254 cm^{-1}. MS (EI) m/z 361 (M^++1). Anal. Calcd for $C_{24}H_{21}O_2F$: C, 79.98; H, 5.87%. Found: C, 79.90; H, 5.62%.

General Procedure for Bromination of Acylpolymethylbenzenes. Bromination of APMB. To a solution of APMB (0.50 g, 2.6 mmol) in dichloromethane (4 mL) was added a solution of bromine (0.42 g, 2.6 mmol) and aluminum bromide (0.70 g, 2.6 mmol) in dichloromethane (4 mL) over 5 min at room temperature in the dark. After stirring for 2 h, the reaction mixture was quenched with 1 M hydrochloric acid and was extracted with dichloromethane. The combined organic extracts were washed with water and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the resulting residue was analyzed by GLC and HPLC.

Bromination reactions of ATMB and BTMB were carried out by procedures similar to that described above. The physical data of the products are as follows.

Bromopentamethylbenzene (3). Mp 159—160 °C (from MeOH; lit,[33] mp 159—160 °C).

(α-Bromoacetyl)pentamethylbenzene (4). Mp 106—107 °C (from MeOH; lit,[12] mp 106—107 °C).

1-Acetyl-5-bromo-2,3,4,6-tetramethylbenzene (5a). Mp 96—97 °C (from 80% MeOH). ^{1}H NMR δ=2.11 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), and 2.45 (s, 6H). IR ν 1694 cm^{-1}. MS (EI) m/z 256 (M^++2), 254 (M^+). Anal. Calcd for $C_{12}H_{15}OBr$: C, 56.49; H, 5.93%. Found: C, 56.24; H, 5.74%.

1-Benzoyl-5-bromo-2,3,4,6-tetramethylbenzene (5b). Mp 132—133 °C (from 80% MeOH). ^{1}H NMR δ=2.01 (s, 3H), 2.17(s, 3H), 2.27 (s, 3H), 2.50 (s, 3H), 7.45 (t, 2H, J=7 Hz), 7.59 (t, 1H, J=7 Hz), and 7.81 (d, 2H, J=7 Hz). IR ν 1674 cm^{-1}. MS (EI) m/z 318 (M^++2), 316 (M^+). Anal. Calcd for $C_{17}H_{17}OBr$: C, 64.37; H, 5.40%. Found: C, 63.99; H, 5.69%.

General Procedure for Deuteration of Acylpolymethylbenzenes. Acylpolymethylbenzene (0.50 g) was dissolved in trifluoroacetic acid-*d* (10 mL) with (or without) deuterium oxide (1.8 mL) and the solution was stirred at room temperature (or under reflux) for several hours. The reaction mixture was then quenched with ice-water and extracted with ether. The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the resulting residue was analyzed by GLC and ^{1}H NMR.

General Procedure for the Reaction of Acylpolymethylbenzenes with $HNO_3/(CX_3CO)_2O$ (X=F or Cl). Reaction of APMB. To a solution of APMB (1.00 g, 5.3 mmol) in trifluoroacetic anhydride (10 mL) was added a solution of 99% nitric acid (0.33 g, 5.3 mmol) in trifluoroacetic anhydride (10 mL) at 0—5 °C over 10 min. The black reaction mixture turned yellow after being stirred for 30 min. The solution was then poured into ice-water and extracted with ether. The combined organic extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. After measurement by HPLC, the reaction mixture was chromatographed on silica gel using benzene as the eluent to isolate **10a** (0.25 g, 22%) and **12a** (0.70 g, 47%).

Reactions of BTMB with $HNO_3/(CF_3CO)_2O$ and APMB with $HNO_3/(CCl_3CO)_2O$ were carried out by procedures similar to that described above. The physical data of the products are as follows.

1-Acetyl-2-(nitromethyl)-3,4,5,6-tetramethylbenzene (10a). Mp 120—121 °C (from 80% MeOH; lit,[10] mp 120—121 °C).

1-Acetyl-2-(trifluoroacetoxymethyl)-3,4,5,6-tetramethylbenzene (12a). Mp 111—112 °C (from 80% MeOH). ^{1}H NMR δ=2.18 (s, 3H), 2.24 (s, 3H), 2.26 (s, 6H), 2.50 (s, 3H), and 5.31 (s, 2H). IR ν 1782, 1690, 1226 and 1145 cm^{-1}. MS (EI) m/z 302 (M^+). Anal. Calcd for $C_{15}H_{17}O_3F_3$: C, 59.90; H, 5.67%. Found: C, 59.60; H, 5.81%.

1-Benzoyl-2-(trifluoroacetoxymethyl)-4,5,6-trimethylbenzene (12c). Mp 57—58 °C (from hexane). ^{1}H NMR δ=2.05 (s, 3H), 2.23 (s, 3H), 2.37 (s, 3H), 5.14 (s, 2H), 7.14 (s, 1H), 7.43 (t, 2H, J=7 Hz), 7.58 (t, 1H, J=7 Hz), and 7.78 (t, 2H, J=7 Hz). IR ν 1782, 1669, 1271, 1219, and 1171 cm^{-1}. MS (EI) m/z 350 (M^+). Anal. Calcd for $C_{15}H_{17}O_3Cl_3$: C, 51.23; H, 4.87%. Found: C, 50.97; H,

4.71%.

1-Acetyl-2-(trichloroacetoxymethyl)-3,4,5,6-tetramethylbenzene (13a). Mp 119—121 °C (from MeOH). ^{1}H NMR δ=1.18 (s, 3H), 2.24 (s, 3H), 2.26 (s, 3H), 2.29 (s, 3H), 2.53 (s, 3H), and 5.29 (s, 2H). IR ν 1763, 1696, 1237, and 1219 cm^{-1}. MS (EI) m/z 350 (M^+). Anal. Calcd for $C_{19}H_{17}O_3F_3$: C, 65.14; H, 4.89%. Found: C, 65.22; H, 5.03%.

1-Acetyl-3-nitro-2,4,5,6-tetramethylbenzene (14b). Mp 111—112 °C (from EtOH; lit,[9] mp 111—112 °C).

1- Benzoyl- 3- nitro- 2, 4, 5, 6- tetramethylbenzene (14c). Mp 158—159 °C (from hexane/ethyl acetate=8/2 v/v); lit,[11] mp 152—153 °C).

Reaction of Acylpolymethylbenzenes with HNO_3/CH_2Cl_2. Reactions were carried out using the procedure reported by Suzuki et al.[13a] The physical data of the products are as follows. Due to the difficulties in dealing with 11b and its corresponding aldehyde, only **11c** was analytically identified. The first two compounds were identified through spectral comparison (**11b** vs. **11c**) and derivatization (see text).

1-Acetyl-2-(nitrooxymethyl)-4,5,6-trimethylbenzene (11b). Mp 53—63 °C ^{1}H NMR δ=2.20 (s, 3H), 2.21 (s, 3H), 2.31 (s, 3H), 2.54 (s, 3H), 5.31 (s, 2H), and 7.07 (s, 1H). IR ν 1699, 1634, 1279, and 857 cm^{-1}. MS (EI) m/z 237 (M^+).

1-Acetyl-2-formyl-4,5,6-trimethylbenzene. Oil. ^{1}H NMR δ=2.19 (s, 3H), 2.27 (s, 3H), 2.39 (s, 3H), 2.50 (s, 3H), 7.47 (s, 1H), and 9.85 (s, 1H). IR (neat) ν 1769 and 1698 cm^{-1}. MS (EI) m/z 190 (M^+).

1-Benzoyl-2-(nitrooxymethyl)-4,5,6-trimethylbenzene (11c). Mp 87—88 °C (from 90% EtOH). ^{1}H NMR δ=2.04 (s, 3H), 2.22 (s, 3H), 2.36 (s, 3H), 5.23 (s, 2H), 7.15 (s, 1H), 7.44 (t, 2H, J=7 Hz), 7.59 (t, 1H, J=7 Hz), and 7.78 (d, 2H, J=7 Hz). IR ν 1665, 1647, 1285, and 845 cm^{-1}. MS (EI) m/z 299 (M^+). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72; N, 4.68%. Found: C, 67.93; H, 5.53; N, 4.42%.

Reaction of Acylpolymethylbenzenes with Fuming HNO_3 in Acetonitrile or Acetic Acid. Reaction of APMB in Acetonitrile. To a solution of APMB (1.00 g, 5.3 mmol) in acetonitrile (5 mL) was added a solution of fuming nitric acid (1.66 g, 26.3 mmol) in acetonitrile (3 mL) at 0—5 °C over 10 min. The reaction mixture was stirred for 10 h at room temperature, then poured into ice-water, extracted with dichloromethane, washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. After measurement by HPLC, 3,4-bis(pentamethylbenzoyl)furazan 2-oxide **15a** (0.48 g, 42% yield) was isolated by washing the residue with hexane/ethyl acetate (8/2 v/v).

The reactions of ATMB with fuming nitric acid in acetonitrile were also carried out by procedures similar to that described above. The physical data are as follows.

3,4-Bis(pentamethylbenzoyl)furazan 2-Oxide (15a). Mp 225—226 °C (from ethyl acetate). ^{1}H NMR δ=2.10 (s, 6H), 2.20 (s, 18H), and 2.25 (s, 6H). ^{13}C NMR δ=16.01, 16.05, 17.02, 17.05, 17.38, 17.47, 112.25, 129.99, 130.35, 133.39, 134.68, 135.16, 138.06, 138.13, 154.97, 186.75, and 189.86. IR ν 1696, 1680, 1615, 1464, 1441, and 1318 cm^{-1}. MS (EI) m/z 434 (M^+). Anal. Calcd for $C_{26}H_{30}N_2O_4$: C, 71.87; H, 6.96; N, 6.45%. Found: C, 72.23; H, 7.01; N, 6.52%.

3,4-Bis(2,3,4,6-tetramethylbenzoyl)furazan 2-Oxide (15b). Mp 154—155 °C (from EtOH). ^{1}H NMR δ=2.14 (s, 3H), 2.16 (s, 6H), 2.21 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), 2.29 (s, 3H), and 6.91 (s, 2H). ^{13}C NMR δ=14.98, 15.03, 17.11, 17.52, 19.13, 19.22, 20.83, 20.88, 112.20, 129.89, 130.07, 132.23, 132.55, 133.44, 133.51, 133.64, 133.95, 134.21, 134.70, 139.65, 139.85, 154.97, 185.66, and 188.95 IR ν 1698, 1682, 1615, 1462, 1443, and 1312 cm^{-1}. MS (EI) m/z 406 (M^+). Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89%. Found: C, 71.37; H, 6.31; N, 6.89%.

General Procedure for Friedel-Crafts-Type Nitration of Acylpolymethylbenzenes with CMN. Nitration of APMB. To a solution of APMB (1.00 g, 5.3 mmol) and CMN (0.75 g, 5.8 mmol) in nitrobenzene (4 mL) was added a solution of aluminum chloride (1.61 g, 12.1 mmol) in nitrobenzene (4 mL) at 0—5 °C over 10 min. The mixture was stirred for 3.5 h at room temperature, and then quenched with 1 M hydrochloric acid. The reaction mixture was extracted with ether. The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the resulting residue was analyzed by GLC and HPLC.

The nitration reactions of ATMB and BTMB with CMN were also carried out by procedures similar to that described above. The physical data of the products are as follows.

Nitropentamethylbenzene (16). Mp 153—155 °C (from EtOH; lit,[34] 158—159 °C).

Chloropentamethylbenzene (17). Mp 152—154 °C (from EtOH; lit,[35] 155—156 °C).

Photoreaction of APMB with Tetranitromethane. A solution of APMB (0.50 g, 2.6 mmol) and tetranitromethane (4.12 g, 21.0 mmol) in acetic anhydride (50 mL) was irradiated with a 100 W high-pressure mercury lamp fitted through a Pyrex glass at 0 °C for 3 h under a nitrogen stream. The reaction mixture was then poured into ice-water and extracted with ether. The combined organic extracts were washed successively with aqueous sodium hydroxide and water, dried over anhydrous sodium sulfate, then evaporated under reduced pressure. After measurement by HPLC, the residue (tetranitromethane remained) was chromatographed on silica gel using benzene as the eluent to isolate **4a** (0.40 g, 66%).

Reaction of APMB with CAN. A solution of APMB (0.5 g, 2.6 mmol) and CAN (2.88 g, 5.3 mmol) in acetonitrile (5 mL) was stirred for 10 h at room temperature under nitrogen in the dark. During the reaction, the color of the solution changed from red to yellow and a precipitate formed. The reaction mixture was quenched with water, then extracted with ether, dried over anhydrous sodium sulfate, and evaporated in vacuo. After analysis by HPLC, the residue was chromatographed on silica gel using hexane/ethyl acetate (8/2 v/v) as the eluent to isolate **4a** (84 mg, 13%) and **4b** (84 mg, 14%).

MNDO Calculations. The MNDO calculations of APMB, ATMB, their corresponding protonated σ-complexes, and radical cations were made using the AMPAC-MNDO program by Dewar and collaborators.[18] All geometric parameters (bond lengths, bond angles, and dihedral angles) were optimized without any specific assumptions. The calculations of the spin densities and net charges were performed for open-shell systems of these radical cations.

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