The reactions were followed by analytical GC using biphenyl as an internal standard.

Substituent Effects on Intramolecular Selectivity and Free Energy Relationships in Anodic and Metal Ion Oxidations of 5-X-1,2,3-trimethylbenzenes

Enrico Baciocchi,*[1a] Antonella Dalla Cort,[1b] Lennart Eberson,*[1c] Luigi Mandolini,[1b] and Cesare Rol[1a]

Dipartimento di Chimica, Università di Perugia, 06100, Perugia, Italy, Centro di Studio C.N.R. sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Università di Roma, La Sapienza, 00185 Roma, Italy, and Division of Organic Chemistry 3, Chemical Center, University of Lund, S-221 00, Lund, Sweden
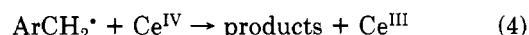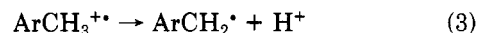
Side-chain oxidations, promoted electrochemically or chemically, by cerium(IV) ammonium nitrate (CAN) or cobalt(III) acetate, of 5-substituted-1,2,3-trimethylbenzenes have been investigated, and the relative reactivity of the 2- and 1-methyl group (k_2/k_1) has been determined. In CAN-promoted and electrochemical reactions, very similar substituent effects on the k_2/k_1 ratio are observed and a strictly linear relationship, extending to electron-withdrawing substituents such as the CO₂Me group, exists between the log k_2/k_1 values of the two processes, which should therefore occur by the same mechanism, i.e., with the formation of an alkylaromatic radical cation which is then deprotonated to benzyl radicals in the selectivity determining step. With +R substituents large k_2/k_1 ratios are observed, which indicates that in the deprotonation of the radical cation the effect of the substituent on the rate exceeds that on the equilibrium, a situation which closely resembles the "nitroalkane anomaly". A plot of log k_2/k_1 vs. $\sigma^+_p - \sigma_m$ values of substituent is also linear. In reactions of Co(OAc)₃ k_2/k_1 values are much less sensitive to the nature of the substituents than in the above reactions and are very close to those which, for comparison purpose, have been determined for the side-chain bromination of the same substrates by N-bromosuccinimide (NBS). The only exception is the result for 5-methoxyhemimellitene which with Co(OAc)₃ exhibits a k_2/k_1 ratio much larger than that with NBS and comparable to those determined in the anodic and CAN-promoted oxidations. It is suggested that the presence of the methoxy group induces an electron-transfer mechanism also in the reaction of Co(OAc)₃.

In a recent paper some of us have determined the intramolecular selectivity of the side-chain acetoxylation of hemimellitene, isodurene, and 5-*tert*-butylhemimellitene (eq 1, X = H, Me, *t*-Bu) promoted either anodically or by one-electron oxidants such as cerium(IV) ammonium nitrate (CAN) and Co(OAc)₃.[2]

$$\text{(1)}$$
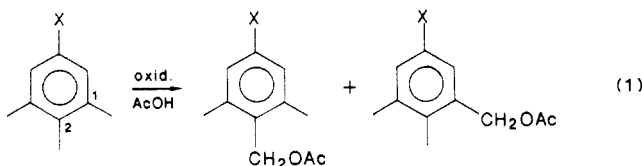
Results of interest with respect to the reaction mechanism have been obtained. Thus, the observation that the effect of the nature of X on the relative reactivity of the 2- and 1-methyl group (k_2/k_1) was very similar for electrochemical and CAN-promoted reactions was considered to support the hypothesis that CAN reactions occur by a one electron transfer mechanism (eq 2-4) equivalent to the ECE mechanism of organic electrochemistry.[3]

$$\text{ArCH}_3 + \text{Ce}^{IV} \rightleftharpoons \text{ArCH}_3^{+\bullet} + \text{Ce}^{III} \qquad (2)$$

$$\text{ArCH}_3^{+\bullet} \rightarrow \text{ArCH}_2^\bullet + \text{H}^+ \qquad (3)$$

$$\text{ArCH}_2^\bullet + \text{Ce}^{IV} \rightarrow \text{products} + \text{Ce}^{III} \qquad (4)$$

Conversely, the finding that the selectivity of Co(OAc)₃-promoted reactions was much lower than that of anodic oxidations led us to suggest that an electron-transfer mechanism might not hold for the reactions of this complex. Interestingly, this suggestion was fully supported by later work.[4]

We felt it worthwhile to expand the study of the intramolecular selectivity of reaction 1 by investigating additional substituents X for the following two reasons:

First, in the previous investigation only two and very similar (Me and *t*-Bu) substituents were considered. It is therefore of interest to check whether the observed correlation between the selectivity of anodic and CAN-promoted oxidations extend also to substituents which span a much larger range of electronic effects. A breakdown in such a correlation might be indicative of a change in the reaction mechanism induced by a change of the substituent.

Second, in side-chain oxidations which take place by an electron-transfer mechanism, intramolecular selectivity is

(1) (a) Università di Perugia. (b) Università di Roma. (c) University of Lund.
(2) Baciocchi, E.; Eberson, L.; Rol, C. *J. Org. Chem.* **1982**, *47*, 5106-5110.
(3) Yoshida, K. *Electrooxidatin in Organic Chemistry*; Wiley-Interscience: New York, 1984; Chapter 5.
(4) Baciocchi, E.; Ruzziconi, R. *J. Chem. Soc., Chem. Commun.* **1984**, 445-446.

Table I. Reactivity Ratios of Nonequivalent α-Hydrogen Atoms in Some Metal Ion and Anode (Pt) Oxidations of 5-X-1,2,3-trimethylbenzenes in Acetic Acid at 60 °C

	$k_2/k_1{}^a$, X =						
oxidant	COOCH$_3$	H^b	C(CH$_3$)$_3{}^b$	Br	CH$_3{}^b$	OAc	OCH$_3$
CAN	2.0^c	3.4	24	42	55	110	>200
anode, Bu$_4$NBF$_4{}^d$	1.5^{e,f}	3.0	16	31^e	37	59	
Co(OAc)$_3$	1.0	1.6	4.9	4.3	4.7	5.4	>200
NBS^g	4.6	3.1	6.3	4.6	5.4	8.2	11^h

^{a} The error is ±5%. ^{b} See ref 2. ^{c} At 80 °C. ^{d} Conversion 1.8 F mol^{-1}, current density 5 mA cm^{-2}. ^{e} In the presence of methanesulfonic acid (0.8% v/v). ^{f} Conversion 1.2 F mol^{-1}, current density 0.5 mA cm^{-2}. ^{g} In CCl$_4$ in the presence of AIBN. ^{h} At 80 °C. Also 4-bromo-5-methoxy-1,2,3-trimethylbenzene (70%) was present in the crude.

determined in the deprotonation step (eq 3).[5] Thus, selectivity data for reaction 1 should also give important information with respect to the nature of the deprotonation process and to the way the substituent X influences charge and (or) spin distribution in the ring positions of the radical cation. To have such kind of information for a wide range of substituents is important in view of the great and current interest on the chemistry of radical ions.[6]

In this paper we report a study of product distributions in the side-chain oxidation of some 5-X-1,2,3-trimethylbenzenes (X = OAc, Br, CO$_2$CH$_3$, OCH$_3$) induced anodically or by CAN in acetic acid. Reactions of the same substrates with Co(OAc)$_3$ and N-bromosuccinimide (NBS) were also studied for comparison purposes.

Results

The reactions with CAN and Co(OAc)$_3$ were carried out at 60 °C in AcOH using a 2:1 oxidant/substrate molar ratio. For 5-carbomethoxyhemimellitene and CAN, however, the reaction temperature was 80 °C since at 60 °C the rate of conversion into products was exceedingly slow.[7] In the Co(OAc)$_3$-induced reactions only benzyl acetates were formed, whereas as expected both benzyl acetates and benzyl nitrates form in the oxidation promoted by CAN.[9] The only exception was 5-methoxyhemimellitene which gave benzyl acetate exclusively also with CAN, probably owing to fast acetolysis of the corresponding benzyl nitrate, possibly formed.

Reactions with NBS, carried out in CCl$_4$, in the presence of azobis(isobutyronitrile) (AIBN) at 60 °C, led to the formation of side-chain brominated products, with the exception of 5-methoxyhemimellitene for which only ring bromination was observed. With this substrate it was necessary to run the reaction at 80 °C[10] to get appreciable amounts of side-chain brominated products.

Anodic oxidations were carried out in AcOH at 60 °C and 5 mA cm^{-2} on a Pt anode up to a conversion of 1.8 F mol^{-1} by using Bu$_4$NBF$_4$ as the supporting electrolyte. Under these conditions, however, some side products were observed in the case of 5-bromohemimellitene. Such inconvenience disappeared by using lower current density (0.5 mA cm^{-2}) and conversion (1.2 F mol^{-1}). Moreover, with this substrate and 5-carbomethoxyhemimellitene side-chain acetoxylated products were observed only in the

presence of a small amount of methanesulfonic acid (0.8% v/v).[12] Experiments with 5-acetoxyhemimellitene showed that the presence of this acid does not affect the product distribution.

In each case the relative reactivity of the 1- and 2-methyl groups was determined by GLC analysis of isomeric benzylic acetates which either directly form in the oxidation process (Co(OAc)$_3$ and anodic oxidation) or are obtained by reacting the crude reaction product with AcOK in AcOH when it contains benzyl nitrates (CAN) or benzyl bromides (NBS). Details are given in the Experimental Section.

The isomeric distribution of the various substrates and the statistically corrected relative reactivity ratios (k_2/k_1) derived therefrom are reported in Table I.

Anodic and CAN-Promoted Oxidations. We first consider these reactions since there is little doubt that both occur by an electron-transfer mechanism.[3] Thus, results can be discussed together as the conclusion should be the same for the two processes.

The data reported in Table I indicate that in either anodic and CAN-induced reactions selectivity is very high with substituents which have a conjugative electron releasing effect (+R effect): Br, Me, OAc, CH$_3$, t-Bu, OMe. With the methoxy group selectivity is so high that only the product of attack at the 2-methyl group has been observed. Therefore for this substituent only a minimum value (>200) of the k_2/k_1 ratio can be given. In contrast with the carbomethoxy substituent, which has an opposite conjugative electronic effect, selectivity is quite low, the 2-methyl group being only twice as reactive as the 1-methyl group.

As previously stated positional selectivity for these electron-transfer reactions is determined in the deprotonation step,[2,5] thus the k_2/k_1 values reported in Table I actually refer to the process shown in eq 5 and should be a measure of the effect of X on the relative deprotonation rate of the 2- and 1-methyl groups to give the benzyl radicals 1 and 2, respectively.

(5)
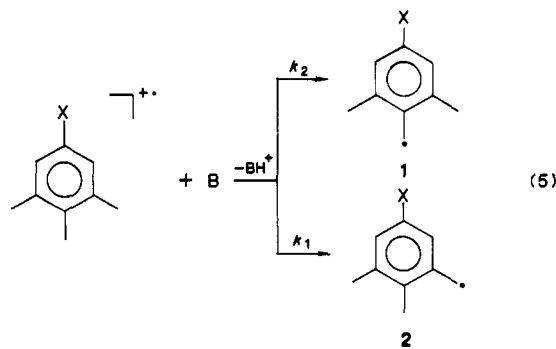
(5) This statement of course is valid only if the deprotonation step (ArCH$_3$·$^+$ → ArCH$_2$· + H$^+$) is irreversible. Evidence that this is the case for the systems studied in this paper is reported in ref 2.

(6) Hammerich, O.; Parker, V. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189.

(7) Temperature has no appreciable effect on the selectivity of CAN-promoted reactions.[8]

(8) Baciocchi, E.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1977**, *42*, 3682–3686.

(9) See ref 8 and references therein.

(10) The temperature increase should not substantially modify the selectivity of this reaction (with isodurene k_2/k_1 rises from 4.4 at 80 °C[11] to 5.4 at 60 °C[2]).

(11) Baciocchi, E.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1980**, *45*, 3906–3909.

(12) In the absence of acid, little or no reaction (<0.5%) takes place on the substrate, so we assume that the role of the acid is to suppress competing Kolbe oxidation of acetate ion.
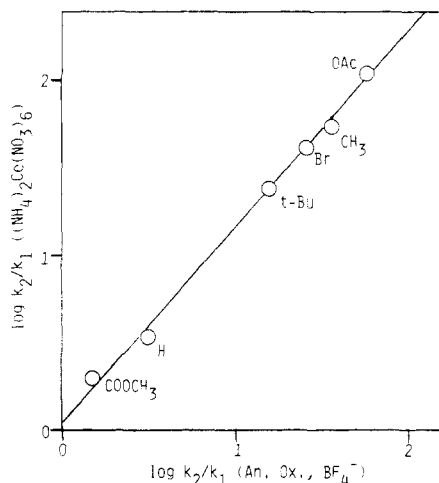
Figure 1. Plot of log k_2/k_1 for the oxidation of 5-substituted-1,2,3-trimethylbenzenes promoted by CAN vs. log k_2/k_1 for the corresponding anodic oxidation.

Figure 2. Plot of log k_2/k_1 for anodic oxidation and CAN-promoted oxidation of 5-substituted-1,2,3-trimethylbenzenes vs. $\sigma^+_p - \sigma_m$ value of the substituent.

The high k_2/k_1 values observed when X is a +R substituent are noteworthy and cannot certainly be explained on the basis of a difference in stability of **1** and **2**, which is expected to be relatively small.[13] This finding indicates that the substituent exerts a much larger influence on the relative stability of the two transition states than on that of the reaction products. In other words, the deprotonation reactions **5** exhibit *substituent effects on rate largely exceeding those on equilibria*, a behavior which closely resembles that observed in the deprotonation of nitroalkanes: "the nitroalkane anomaly".[14]

Clearly, the above finding requires a very reactant-like transition state for reactions **5** and this is in agreement with the observation that side-chain reactivity of an alkylaromatic radical cation strongly depends on the electronic distribution in the radical cation itself, even if there is some discussion about which factor (positive charge density, LUMO electron density, spin density) plays the major role in this respect.[15]

It may be added that a recent investigation has shown that the deprotonation of an alkylaromatic radical cation is characterized by a low Brönsted β value, which also supports the idea of a reactant-like transition state.[16]

A quantitative evaluation of the close similarity between anodic and CAN-promoted reactions is obtained when log k_2/k_1 for the two reactions are plotted against one another (Figure 1). A straight line results, indicating the existence of a very good (slope = 1.1, r = 0.997, s = 0.04) linear correlation between the two reactions. It is remarkable

that also the value for the carbomethoxy group fits the line, which suggests that an electron-transfer mechanism probably still holds even when a very strong electron attracting substituent is present in the hemimellitene moiety.

It was also considered interesting to see whether the relative reactivity of the 2- and 1-methyl groups could be quantitatively related to the different effect of the substituent at the para and meta positions. It turned out that a plot of log k_2/k_1 against the $\sigma^+_p - \sigma_m$ value of the substituent exhibits an excellent linearity for both anodic and CAN-promoted reactions (Figure 2; r = 0.996, s = 0.06 in the former case, r = 0.997, s = 0.06 in the second). Slopes of −4.0 and −4.3 are calculated for the anodic and the CAN-induced reactions, respectively, which give a quantitative assessment of the strong sensitivity of the k_2/k_1 values to the electronic effect of the substituent.

Since the initial state is the same for the two deprotonation reactions, these values measure the substituent effect on the energy difference of the two transition states. Their sign is negative as the energy of the transition state for the para reaction is lower than that for the meta reaction, the difference increasing as the electron-donating power of the substituent increases.

Reactions of Co(OAc)₃ and NBS. Recent studies have shown that, in contrast to the previous hypothesis,[15a,17] side-chain acetoxylation of alkylbenzenes promoted by Co(OAc)₃ does *not* involve an electron abstraction from the π-system. A hydrogen atom transfer from the side chain to the oxidant[4,18] or an electrophilic attack of Co(OAc)₃ at the C–H bond of the alkylaromatic compounds[19] appear to be more plausible mechanisms.

Thus, the observation that the selectivity of Co(OAc)₃ reactions (data in the table for X = CO₂CH₃, H, Br, CH₃, t-Bu) exhibits a much smaller sensitivity to substituent effects than does the selectivity of CAN-promoted and anodic oxidations can be reasonably attributed, as previously suggested,[2] to the different reaction mechanism of Co(OAc)₃.[20]

(13) Dust, S. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221–1227. In this paper the effects of para and meta substituents on the stability of benzylic free radicals are expressed through the σ_α⁺ constants. For the *p*- and *m*-methyl groups the σ_α⁺ values are 0.015 and −0.001, respectively. For chloro the corresponding values are 0.017 and −0.001. A private communication by Professor Arnold has also provided us with the corresponding values for *p*- and *m*-methoxy groups which are 0.018 and 0.001, respectively. On the basis of these values small effects of these groups on the stability of benzylic free radicals can be predicted, certainly much smaller than those observed on the k_2/k_1 ratios reported in this paper.

(14) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99–196.

(15) (a) Heiba, E. I.; Dessau, R. M.; Koehl, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 6830–6837.   (b) Nyberg, K. *Acta Chem. Scand.* **1971**, *25*, 2499–2506. (c) Baciocchi, E.; Rol, C.; Sebastiani, G. V. *Gazz. Chim. Ital.* **1982**, *112*, 513–517. (d) Yoshida, K. *Electrooxidation in Organic Chemistry*; John Wiley & Sons: New York, 1983; pp 121–125. (e) Dolson, M. G.; Swenton, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 2361–2371. (f) Baciocchi, E.; Gabrielli, R.; Giancaspro, C.; Rol, C.; Sebastiani, G. V.; Speranza, M. *Tetrahedron Lett.* **1985**, *26*, 4269–4272.

(16) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472–7482.
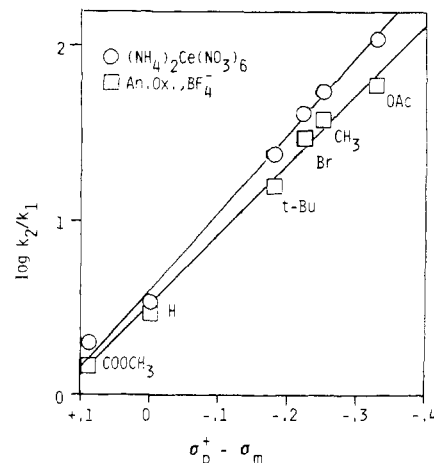
(17) Onopchenko, A.; Schulz, J. G. D.; Seekircher, R. *J. Org. Chem.* **1972**, *37*, 1414–1417.

(18) Hanotier, J.; Hanotier-Bridoux, M. *J. Chem. Soc., Perkin Trans.* 2 **1973**, 1035–1039. Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79–185.

(19) Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic Press: New York, 1978; p 89.
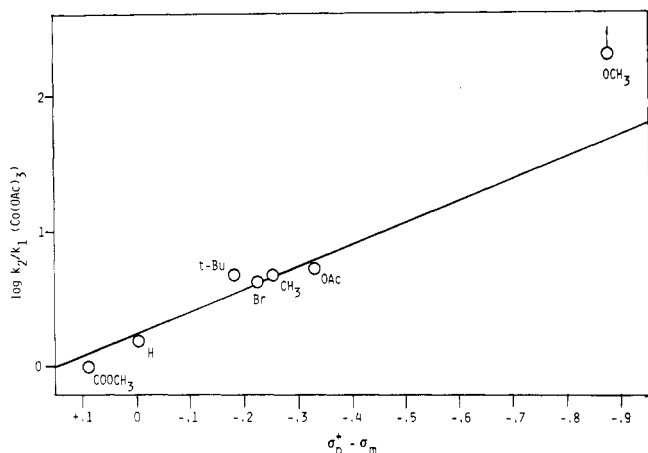
Figure 3. Plot of log k_2/k_1 for Co(OAc)$_3$-promoted oxidations of 5-substituted-1,2,3-trimethylbenzenes vs. $\sigma^+_p - \sigma_m$ value of the substituent.

This hypothesis is further supported by the result that when X = OCH$_3$ also the reaction of Co(OAc)$_3$, as that of CAN or the anodic oxidation, exhibits a k_2/k_1 ratio too large to be measured. This finding suggests a mechanistic change in the reaction of Co(OAc)$_3$ induced by the presence of the methoxy substituent.

Probably, the methoxy group exerts a strong favorable effect on the formation of the radical cation and the reaction of the methoxy-substituted compound takes place by an electron-transfer mechanism.

A quantitative evaluation of the different behavior of the MeO group as compared to the other substituents in the Co(OAc)$_3$ acetoxylation also comes from the plot of log k_2/k_1 vs. $\sigma^+_p - \sigma_m$ values of the substituent for this reaction (Figure 3). Even as a minimum value the point for the MeO group falls well above the line fitted by the other substituents.

Finally, the data in the table show that there is a strong similarity between Co(OAc)$_3$ and NBS (a species which certainly reacts by hydrogen atom transfer) in so far as both reactants exhibit k_2/k_1 values which are low and not very sensitive to the nature of the 5-substituent. However, in line with the above reasonings this similarity drastically disappears with the 5-methoxy group, the k_2/k_1 ratio for the reaction of Co(OAc)$_3$ being in this case much higher than that observed in the reaction of NBS.

Experimental Section

^{1}H NMR spectra were taken at 90 MHz on a Varian EM390 spectrometer. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were obtained on a Varian MAT 311A spectrometer. VPC analyses were carried out on a HP 5880A or Carlo Erba HRGC 5160 gas chromatograph using an SE-30 or CWX capillary column at 50–200 °C. All melting points are uncorrected.

Materials. Reagents have been described previously.[2]

5-Bromo-1,2,3-trimethylbenzene. 3,4,5-Trimethylaniline [mp 77–78 °C (lit.[21] mp 78.5–79 °C); ^{1}H NMR (CDCl$_3$) δ 6.4 (s, 2 H), 3.35 (s, 2 H), 2.2 (s, 6 H), 2.15 (s, 3 H)] prepared as previously described,[21] was converted into 1-bromo-3,4,5-trimethylbenzene by diazotization in hydrobromic acid and treatment with copper.[22] The product was purified by distillation: bp 120 °C (20 mmHg);[23] ^{1}H NMR (CDCl$_3$) δ 7.05 (s, 2 H), 2.2 (s, 6 H), 2.05 (s, 3 H); MS (70 eV), m/z (relative intensity) 200 (37), 198 (39), 185 (13), 183 (15), 119 (100), 91 (37), 77 (25).

5-Methoxy-1,2,3-trimethylbenzene. CH$_3$I (10 mmol) was added to 3,4,5-trimethylphenol (10 mmol) [mp 105–106 °C (lit.[24] mp 108 °C); ^{1}H NMR (CDCl$_3$) δ 6.44 (s, 2 H), 5.58 (s, 1 H), 2.18 (s, 6 H), 2.03 (s, 3 H)], prepared from the diazonium salt of 3,4,5-trimethylaniline according to a standard procedure, and KOH (10 mmol) in 20 mL of absolute EtOH. The distillation of the crude gave the expected product: bp 120 °C (22 mmHg);[25] ^{1}H NMR (CDCl$_3$) δ 6.6 (s, 2 H), 3.6 (s, 3 H), 2.15 (s, 6 H), 2.0 (s, 3 H); MS (70 eV), m/z (relative intensity) 150 (69), 135 (100), 105 (20), 91 (45), 77 (19).

5-Carbomethoxy-1,2,3-trimethylbenzene. Carbonation of the Grignard reagent from 1-bromo-3,4,5-trimethylbenzene gave 3,4,5-trimethylbenzoic acid: mp 216–217 °C (lit.[21] mp 218–219 °C); ^{1}H NMR (CDCl$_3$) δ 9.2 (s, 1 H), 7.6 (s, 2 H), 2.33 (s, 6 H), 2.25 (s, 3 H). The acid, refluxed in absolute methanol containing H$_2$SO$_4$, gave the methyl ester: mp 36–40 °C (lit.[26] mp 40.5–41.5 °C); ^{1}H NMR (CDCl$_3$) δ 7.67 (s, 2 H), 3.89 (s, 3 H), 2.32 (s, 6 H), 2.22 (s, 3 H); MS (70 eV), m/z (relative intensity) 178 (95), 148 (100), 147 (90), 119 (74), 91 (52), 77 (38).

5-Acetoxy-1,2,3-trimethylbenzene; by esterification of 3,4,5-trimethylphenol in acetic anhydride and pyridine; mp 60–61 °C (lit.[27] mp 58.5–59 °C); ^{1}H NMR (CDCl$_3$) δ 6.8 (s, 2 H), 2.30 (s, 9 H), 2.17 (s, 3 H); MS (70 eV), m/z (relative intensity) 178 (13), 136 (99), 121 (100), 91 (32), 77 (19).

Chemical Oxidations. The procedures used for oxidation with CAN and cobaltic acetate have been described.[2] The reaction of 5-carbomethoxyhemimellitene with CAN was performed at 80 °C owing to the complete lack of products operating at 60 °C, even at high Ce(IV) → Ce(III) conversion.

Bromination with NBS. The procedure used has been described.[2] The reaction of 5-methoxyhemimellitene with NBS was performed at 80 °C obtaining, besides a mixture of benzylic bromides, 4-bromo-5-methoxyhemimellitene (70%). The same reaction at 60 °C gave the latter compound as the only product.

Anodic Oxidations. The anodic experiments were performed as described before.[2] 5-Carbomethoxy- and 5-bromohemimellitene gave reaction products only in the presence of methanesulfonic acid (0.8% v/v). To check the influence of the acid on reaction products distribution, 5-acetoxyhemimellitene was made to react both in the presence and in the absence of methanesulfonic acid, and identical results were obtained. With these two compounds lower current density (0.5 mA/cm^2) and conversion (1.2 F/mol) were used to eliminate side products.

Determination of Isomeric Distributions. The isomeric distribution of benzylic acetates obtained from Co(OAc)$_3$ and anodic oxidation was determined by VPC analysis (comparison with authentic samples obtained as described below). On the other hand crude products from CAN oxidation and NBS bromination were refluxed in AcOH/AcO$^-$ for 12 h in order to convert benzylic nitrates and bromides, respectively, into corresponding benzylic acetates before VPC analysis. All isomeric acetates but one, 5-methoxy-2,3-dimethylbenzyl acetate (vide infra), were obtained

(20) One referee has suggested that the observed differences in selectivity between Co(OAc)$_3$ and CAN could simply be due to the different nature of the proton-abstracting base in a common electron-transfer mechanism. Of course this hypothesis is reasonable and should be given careful consideration even though no information in this respect is available in view of the high complexity of the systems which do not allow us to know the exact nature of the bases involved. However, we feel that this hypothesis is unlikely in the light of the evidence reported in ref 4 and 18 which indicate a different reaction mechanism for the two salts. Besides this, we would also like to mention that we have compared selectivities of anodic oxidation in the absence and in the presence of AcOK.[2] Indeed, in the presence of a strong base like AcO$^-$ selectivity is smaller than that measured when the proton-abstracting base is presumably the solvent AcOH. Differences are, however, not large and more significantly the selectivity in the presence of AcO$^-$ is still higher and much more sensitive to substituent effects than that found with Co(OAc)$_3$.

(21) Beringer, F. M.; Ugelow, J. *J. Am. Chem. Soc.* **1953**, *75*, 2635–2639.

(22) *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. I, pp 133–134.

(23) Wright, G. J.; Blacksotck, D. J.; et al. *J. Chem. Soc. B* **1971**, 1212–1213.

(24) Banwell, T.; Morse, C. I.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 3042–3051.

(25) Feldman, K. S.; Myhre, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4768–4769.

(26) Porowska, N. *Rocz. Chem.* **1957** *31*, 677–679.

(27) Doering, W. E.; Beringer, F. M. *J. Am. Chem. Soc.* **1949**, *71*, 2221–2226.

(28) The very high selectivity exhibited by (t-BuO)$_2$-Cu(OAc)$_2$ system toward 1-CH$_3$ hydrogen abstraction from 5-methoxyhemimellitene (k_2/k_1 is ca. 0.1) is a remarkable result worth further investigation.

as pure samples by preparative VPC (4-bromo-2,6-dimethyl-, 5-bromo-2,3-dimethyl-, 4-acetoxy-2,6-dimethyl-, 5-acetoxy-2,3-dimethyl-, and 4-methoxy-2,6-dimethylbenzyl acetate) or by column chromatography (4-carbomethoxy-2,6-dimethyl- and 5-carbomethoxy-2,3-dimethylbenzyl acetate) of the crude products deriving from $Co(OAc)_3$ oxidation and/or NBS bromination (followed by acetoxylation) of the substituted hemimellitene. Structures were assigned on the basis of NMR spectra.

4-Bromo-2,6-dimethylbenzyl acetate: ^{1}H NMR (CDCl$_3$) δ 7.15 (s, 2 H), 5.10 (s, 2 H), 2.30 (s, 6 H), 2.05 (s, 3 H); MS (70 eV), m/z (relative intensity) 258 (2), 256 (2), 198 (100), 196 (95), 117 (63), 91 (44).

5-Bromo-2,3-dimethylbenzyl acetate: ^{1}H NMR (CDCl$_3$) δ 7.20 (s, 2 H), 5.05 (s, 2 H), 2.25 (s, 3 H), 2.10 (s, 3 H), 2.05 (s, 3 H); MS (70 eV), m/z (relative intensity) 198 (100), 196 (95), 117 (20).

4-Acetoxy-2,6-dimethylbenzyl acetate: ^{1}H NMR (CCl$_4$) δ 6.60 (m, 2 H), 5.00 (s, 2 H) 2.40 (s, 6 H), 2.20 (s, 3 H), 2.00 (s, 3 H); MS (35 eV), m/z (relative intensity) 236 (10), 194 (32), 176 (16), 136 (20), 135 (41), 134 (100).

5-Acetoxy-2,3-dimethylbenzyl acetate: ^{1}H NMR (CCl$_4$) δ 6.75 (m, 2 H) 4.95 (s, 2 H), 2.30 (s, 3 H), 2.25 (s, 3 H), 2.20 (s, 3 H), 2.00 (s, 3 H); MS (70 eV), m/z (relative intensity) 194 (5), 176 (13), 134 (100).

4-Methoxy-2,6-dimethylbenzyl acetate: ^{1}H NMR (CDCl$_3$) δ 6.56 (s, 2 H), 5.15 (s, 2 H), 3.70 (s, 3 H), 2.32 (s, 6 H), 1.00 (s, 3 H); MS (70 eV), m/z (relative intensity) 208 (10), 149 (100), 135 (13), 117 (10), 105 (15), 91 (33).

4-Carbomethoxy-2,6-dimethylbenzyl acetate: ^{1}H NMR (CDCl$_3$) δ 7.68 (s, 2 H), 5.20 (s, 2 H) 3.90 (s, 3 H), 2.43 (s, 6 H), 2.07 (s, 3 H); MS (70 eV), m/z (relative intensity) 205 (10), 176 (100), 145 (28), 91 (16), 43 (92).

5-Carbomethoxy-2,3-dimethylbenzyl acetate: ^{1}H NMR (CDCl$_3$) δ 7.78 (s, 2 H), 5.13 (s, 2 H), 3.90 (s, 3 H), 2.35 (s, 3 H), 2.28 (s, 3 H), 2.12 (s, 3 H); MS (70 eV), m/z (relative intensity) 205 (8), 176 (100), 145 (25), 91 (16), 43 (85).

5-Methoxy-2,3-dimethylbenzyl Acetate. 5-Methoxyhemimellitene (5.0 mmol), Cu(OAc)$_2$·H$_2$O (6.4 mmol), and di-*tert*-butyl peroxide (20 mmol) were refluxed for 60 h in AcOH (21 mL) containing Ac$_2$O (9 mL). The reaction mixture was worked up as usual and the desired compound was separated from the unreacted substrate and methylated products[26] by preparative VPC on NPGS at 190 °C: ^{1}H NMR (CDCl$_3$) δ 6.73 (dd, AB system, J = 2.9 Hz, 2 H), 5.10 (s, 2 H), 3.77 (s, 3 H), 2.28 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 3 H); MS (70 eV), m/z (relative intensity) 208 (5), 148 (100), 117 (20), 105 (30), 91 (50).

Reductive Photocarboxylation of Aromatic Hydrocarbons

Shigeo Tazuke,* Shingo Kazama, and Noboru Kitamura

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Photoirradiation of aromatic hydrocarbons such as phenanthrene, anthracene, or pyrene in the presence of an amine and carbon dioxide in dipolar aprotic solvents resulted in reductive carboxylation of the hydrocarbon. The reaction was considered to proceed via the anion radical of the hydrocarbon that reacts with CO$_2$ and then abstracts hydrogen, possibly from the solvent, to yield the corresponding dihydro carboxylic acid of the hydrocarbon. The highest yield was obtained for phenanthrene with *N,N*-dimethyl-*p*-toluidine as reducing agent in dimethyl sulfoxide. A quantum yield of 0.17 for the formation of 9,10-dihydrophenanthrene-9-carboxylic acid with selectivity of 86% based on consumed phenanthrene was achieved. Addition of a hydrogen donor such as cumene, decalin, or others was shown to be effective in increasing the yield.

Carbon dioxide is among the most stable of all carbon compounds. Direct use of carbon dioxide as a reagent for C–C coupling reactions therefore requires a strongly endoergic reaction process unless the reaction partner is highly activated. Since the classical example of salicylic acid synthesis from phenol and CO$_2$, several methods of activating CO$_2$ have been reported, specifically aimed at CO$_2$ fixation.[1] Of particular interest is the use of CO$_2$ as a comonomer for ring-opening polymerization of cyclic ethers. Activation by organometallic compounds is also a fashionable subject.

Carbon dioxide is a linear molecule having a large and negative quadrupole moment. Thus, reaction of CO$_2$ with a carbon-centered nucleophile should provide C–C coupling products, as demonstrated by trapping of carbanions by CO$_2$ to give the corresponding carboxylic acids.

Recent advances in electron-transfer photochemistry gave birth to many examples of photoreactions via ion-radical intermediates or exciplexes.[2] Depending upon solvent polarity, photoinduced electron transfer between donor and acceptor leads to either exciplex formation or ionic dissociation. The detailed mechanism of electron

(1) Inoue, S.; Yamazaki, N. *Organic and Bio-organic chemistry of Carbon Dioxide*; Kodansha, 1981.

(2) *Recent Progress in Organic Photochemistry—Electron Transfer Reactions*, Chemistry Review 33; Chemical Society of Japan: 1982.