

SELECTIVITY AND MECHANISM IN THE SIDE-CHAIN  
HALOGENATION OF METHYLBENZENES PROMOTED PHOTOCHEMICALLY  
AND BY METAL COMPLEXES IN THE PRESENCE OF HALIDE IONS

Enrico Baciocchi\* and Manuela Crescenzi\*\*

Dipartimento di Chimica, Università di Roma "La Sapienza"

P.le A. Moro, 2, 00185 Roma (Italy).

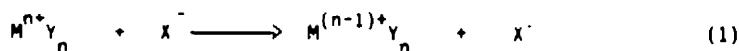
(Received in UK 18 July 1988)

**ABSTRACT:** The intramolecular selectivity in a variety of side-chain halogenations of alkylaromatics has been determined in AcOH by measuring the isomeric distribution in the reactions of 4-t-butyl- and 4-chloro-1,2-dimethylbenzene (1 and 2, respectively) with: Br<sub>2</sub>/hν, CAN/Br<sup>-</sup>, CAN=cerium(IV) ammonium nitrate, cobalt(III) acetate/Br<sup>-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/Br<sup>-</sup>, N-bromosuccinimide (in CCl<sub>4</sub>), Cl<sub>2</sub>/hν, CAN/Cl<sup>-</sup>, cobalt(III) acetate/Cl<sup>-</sup>. In the bromination reactions selectivity is independent of the reaction conditions, thus suggesting that in all brominating systems Br· is the actual reacting species. Very surprisingly, with 1 as the substrate, Cl<sub>2</sub>/hν is a more selective system than Br<sub>2</sub>/hν. With 2 the two systems display similar selectivity. It has been suggested that in AcOH the transition state for photochlorination has an electron transfer character which increases as the substrate becomes more electron rich. The idea of a "variable" transition state for the photochlorination in AcOH is supported by data of relative reactivity of substituted toluenes indicating that the effect on the rate increases as the substituent becomes more electron donor. AcOH must have an essential role in this respect since in CCl<sub>4</sub> situation returns to be "normal" with chlorination less selective than bromination. Selectivity of CAN/Cl<sup>-</sup> is very similar to that of Cl<sub>2</sub>/hν, whereas significant differences are observed with cobalt(III) acetate/Cl<sup>-</sup>. Probably Cl· and a cobalt(III) chloride complex are the reacting species in CAN/Cl<sup>-</sup> and cobalt(III) acetate/Cl<sup>-</sup>, respectively.

The halogenation of alkanes and of the side-chain of alkylaromatic compounds is certainly one of the most important reactions in organic chemistry and, therefore, it has been the subject of intensive investigations ever since. The free radical nature of the process has been recognized long ago,<sup>1</sup> even though, in special cases (electron rich polysubstituted methylaromatics), an electrophilic nuclear process leading to side-chain halogenated products can take place<sup>2</sup>.

In spite of the continuous research there are still unsettled problems which especially concern the exact nature of the halogenating species in the photochlorination<sup>3</sup> and in those halogenations where the actual reactant is formed in the one electron oxidation of halide ions by metal complexes<sup>4</sup>.

In the latter processes the main question is whether the active species is: (a) the halogen atom X· formed (eq. 1) by the reaction of the metal complex M<sup>n+</sup>Y<sub>n</sub> (Y = ligand of the metal) with the halide X<sup>-</sup>; (b) a new complex where one or more halide ions have replaced a corresponding



number of Y ligands (eq. 2) or (c) the anion radical X<sub>2</sub><sup>-</sup> formed in the reaction of X<sup>-</sup> with X·.

\*\* and Centro di Studio C.N.R. sui Meccanismi di Reazione, Roma.



The brominations promoted either by CAN or cobalt(III) acetate in the presence of bromide ions (oxidant:  $\text{Br}^-$ : substrate = 2:1:1) turned out to be a very efficient process, leading to 65-90% of side-chain brominated products in 1-3 h<sup>7</sup>. The higher yields were observed with 1 and the reaction rate was much greater than that observed when the same oxidants are used in the absence of bromide ions. In the latter case the products were benzyl acetates with cobalt(III) acetate and a mixture of benzyl acetates and benzyl nitrates with CAN.<sup>9</sup>

It is remarkable that the reactivity of CAN/ $\text{Br}^-$  and cobalt(III) acetate/ $\text{Br}^-$  in AcOH is significantly higher than that exhibited by the more common brominating system, NBS in  $\text{CCl}_4$  in the presence of azobisisobutyronitrile (AIBN), which, at 60°, with 1, afforded only 50% of side-chain brominated products after 20 h.

With  $\text{S}_2\text{O}_8^{2-}/\text{Br}^-$ , bromides were used in catalytic amounts<sup>10</sup>. In this case, as expected, benzyl acetates were obtained.

In the reaction of 1 and 2 with CAN in the presence of chloride ions (CAN: $\text{Cl}^-$ : substrate = 2:1:1) the rate was greater than that observed in the absence of chloride ions. However, only with 1 substantial amounts (overall yield: 80%) of side-chain substituted products (a mixture of benzyl chloride, benzyl nitrate and benzyl acetate in a 2.8:1.0:1.8 ratio) were obtained. With 2 benzyl derivatives accounted for one third of the reaction product, the main process being ring chlorination. The use of  $\text{Cl}^-$  in excess with respect to CAN led to a very complex mixture of products.

In the reaction of cobalt(III) acetate, in the presence of chloride ions an excess of  $\text{Cl}^-$  with respect to the oxidant,  $\text{Cl}^-$ : cobalt(III) acetate = 10:1, appeared necessary in order to obtain an efficient side-chain chlorination. With 1, the yield in benzyl chlorides was 85% after 3 h. With  $\text{Cl}^-$ : cobalt(III) acetate 1:1, the reaction was much slower and the major products were benzyl acetates.

Photochemical bromination and chlorination of 1 and 2 were carried out by using an immersion high pressure mercury lamp. In both cases, the halogen: substrate molar ratio was 1:2 and the concentration of the substrate was 0.08M. As expected, benzyl halides were the major products, together with small amounts of benzyl acetates (certainly coming from acetolysis of the formers) and ring halogenated products.

The distribution of the two isomeric benzyl derivatives 3 and 4 under the reaction conditions described above was determined by GLC analysis. Since in several cases the formation of benzyl halides was accompanied by that of other benzyl derivatives (see above) the crude reaction product was reacted with AcONA in AcOH (for compound 1) and with  $\text{Ag}_2\text{O}$  in  $\text{H}_2\text{O}$  (for compound 2) to convert all benzyl derivatives into the corresponding benzyl acetates and benzyl alcohols, respectively, which were quantitatively determined by GLC. The different procedure was made necessary by the difficulty experienced in the GLC separation of the isomeric benzyl acetates coming from 2.

For comparison purposes the isomeric distribution has also been determined in the photochemical chlorination in  $\text{CCl}_4$ , in the reactions with NBS in  $\text{CCl}_4$ , and with CAN and

cobalt(III) acetate, in AcOH, in the absence of halide ions. All results are reported in Table 1.

Table 1: Ratio of Isomeric Products ( $\frac{3}{4}$ ) in a Variety of Benzylic Halogenations of 4-Z-1,2-Dimethylbenzenes at 60° (eq. 3)

Halogenating System	solvent	$\frac{3}{4}$ <sup>a</sup>	
		Z = C(CH <sub>3</sub> ) <sub>3</sub>	Z = Cl
1. CAN/Br <sup>-b</sup>	AcOH	1.8	2.6
2. Co(OAc) <sub>3</sub> /Br <sup>-b</sup>	AcOH	1.8	2.7
3. Br <sub>2</sub> /hν	AcOH	1.6	
4. NBS <sup>c</sup>	CCl <sub>4</sub>	1.6	3.0
5. Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /Br <sup>-d</sup>	AcOH	1.6	3.1
6. Cl <sub>2</sub> /hν	AcOH	3.6	3.3
7. Cl <sub>2</sub> /hν	CCl <sub>4</sub>	1.2	2.0
8. CAN/Cl <sup>-</sup>	AcOH	4.2	3.2
9. Co(OAc) <sub>3</sub> /Cl <sup>-e</sup>	AcOH	2.5	2.4
10. CAN <sup>f</sup>	AcOH	6.0	13.0
11. Co(OAc) <sub>3</sub> <sup>f</sup>	AcOH	2.6	2.4

(a) Molar ratio. Average error ± 10%; (b) oxidant: halide molar ratio 2:1; (c) in the presence of AIBN; (d) at 115 °C; (e) oxidant: chloride molar ratio 1:10; (f) reactions in the absence of halides carried out for comparison purposes. For the products see text.

In the case of photochemical chlorination data of intramolecular selectivity have also been complemented by relative reactivity values for a number of substituted toluenes by using the competitive technique. The results are in Table 2.

Table 2: Relative Reactivities in the Photochlorination of Substituted Toluenes in Acetic Acid at 60 °C

Substrate	Relative Reactivity <sup>a</sup>
p-Xylene	4.14
Toluene	1
p-Chlorotoluene	0.70
m-Chlorotoluene	0.48

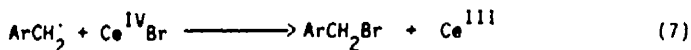
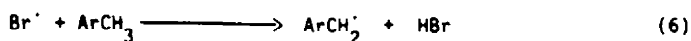
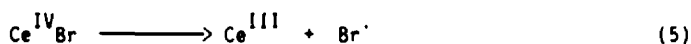
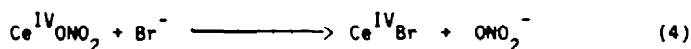
(a) Determined by the competitive technique (triplicate experiments) Average error ± 5%.

## DISCUSSION

Bromination Reactions. Data of Table 1 indicate that CAN is a much more selective reactant in the absence than in the presence of bromide ions (entries 1 and 10), the difference being particularly remarkable with 2. Certainly, different reacting species are involved, which probably react by a different mechanism. In the absence of  $\text{Br}^-$ , CAN is the effective reactant and previous study has shown that this species is involved in an electron transfer mechanism<sup>11</sup>. The strong effect of substituents on the intramolecular selectivity has already been noted and ascribed to the operation of this mechanism<sup>6</sup>.

In the presence of  $\text{Br}^-$  the attacking species is mostly probably the bromine atom formed in the reaction between CAN and  $\text{Br}^-$ . This suggestion is supported by the observation that, with both 1 and 2, the intramolecular selectivity exhibited by the  $\text{CAN}/\text{Br}^-$  system (entry 1) is very similar to that found in the corresponding photochemical and NBS-promoted brominations (entries 3 and 4, respectively) which are "bona fide" examples of reactions induced by bromine atoms<sup>5</sup>.

It seems therefore possible to exclude that the reacting species is  $\text{Br}_2^-$  or a cerium(IV) bromide complex where  $\text{Br}^-$  has replaced one or more nitrate ligands (eq 2,  $X = \text{Br}$ ,  $Y = \text{NO}_3$ ). It is however possible that this complex forms since the oxidation of  $\text{Br}^-$  by CAN might take place by an inner sphere mechanism in view of the significantly larger  $E^\circ$  value for the  $\text{Br}/\text{Br}^-$  couple than for the  $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$  couple<sup>12</sup>. Moreover, such a complex would allow us to suggest that benzyl bromides form by an oxidative ligand transfer of bromide ions from this complex to a benzyl radical, in line with the observation that benzyl bromides are the nearly exclusive reaction products in  $\text{AcOH}$ . The complete mechanistic scheme might be the following (eqs 4-7).



With cobalt (III) acetate/ $\text{Br}^-$  the selectivity, with both 1 and 2, is very similar to that observed with  $\text{CAN}/\text{Br}^-$  and the other brominating systems.  $\text{Br}^\cdot$  should therefore be the active species in the reaction promoted by cobalt(III) acetate

in the presence of  $\text{Br}^-$ . Probably a cobalt(III) bromide complex is first formed also in this case for the same reasons discussed above for the  $\text{CAN}/\text{Br}^-$  system.

It can be observed that cobalt(III) acetate/ $\text{Br}^-$  exhibits a selectivity which is not much different from that observed for the reaction of cobalt(III) acetate alone (entries 2 and 11). This is due to the fact that probably cobalt(III) acetate reacts by a H-atom transfer mechanism<sup>6,15</sup>, so as  $\text{Br}^-$  does.

Finally, the selectivity data (entry 5) support the suggestion, based on measurements of intermolecular selectivity<sup>10</sup>, that  $\text{Br}^-$  is involved in the side-chain bromination promoted by  $\text{S}_2\text{O}_8^{=}$  in the presence of  $\text{Br}^-$ .

In view of previous observations indicating that  $\text{Br}^-$  is the active reactant also in the  $\text{Mn}(\text{OAc})_3/\text{Br}^-$  system<sup>16</sup>, it seems possible to conclude that this outcome seems to be a general behavior of the side-chain reactions promoted by one electron oxidants and  $\text{Br}^-$ .

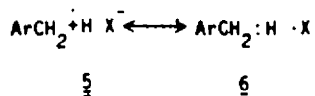
Chlorination Reactions. A first observation is that photochemical chlorination of 1 in  $\text{AcOH}$  is a significantly more selective reaction than the corresponding photochemical bromination (Table 1, entries 3 and 6). Control experiments have shown that no side-chain reaction takes place in the dark. With 2 the situation is slightly different since chlorination and bromination exhibit similar selectivity. Both results, however, are surprising since bromination is expected to be a more selective reaction than chlorination<sup>17</sup>.

Very interestingly, when the solvent is changed from  $\text{AcOH}$  to  $\text{CCl}_4$  situation returns to be "normal": with both substrates chlorination is less selective than bromination.

This latter finding, together with the previously noted different behaviors of 1 and 2, indicates that selectivity of photochlorination in  $\text{AcOH}$  can significantly be altered by the combined effects of solvent and substrate structure.

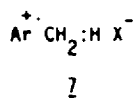
It is unlikely that this phenomenon is due to the well known capability of aromatic systems to complex  $\text{Cl}^-$  giving a more selective chlorinating species<sup>18</sup>, since a very small concentration of the aromatic substrate (0.08 M) has been used in our experiments. More reasonably, an explanation may be found by an extension of the current analysis of the polar effects in the free radical side-chain reactions of alkylaromatics<sup>5</sup>.

According to this analysis, the electronic effect of substituents on the reaction rate depends on the contribution of the polar structure 5 to the transition state.



Thus, to explain that  $\text{Br}^\cdot$  is generally more selective than  $\text{Cl}^\cdot$ , it has been suggested that the contribution of 5 to the transition state is less important when X is Cl than when it is Br. This because chlorination is a more exothermic reaction than bromination and therefore it should possess a transition state with a smaller degree of C-H bond breaking, and consequently, with less positive charge density at the benzylic carbon.

We feel however that in addition to that of structures 5 and 6, the analysis should also consider the contribution to the transition state of the electron transfer structure 7, where the electron is transferred from the



aromatic system to X. As 7 does not involve any nuclear motion, its contribution might be more important in chlorination than in bromination since, as already noted, the former reaction exhibits a transition state where C-H bond rupture has occurred to a very small extent, and moreover  $\text{Cl}^\cdot$  is a significantly stronger oxidant than  $\text{Br}^\cdot$ <sup>19</sup>. In most cases, the contribution of 7 to the transition state of the chlorination reaction is not high since this reaction is generally less sensitive to electronic effects than bromination where, instead, the structure 5 plays a significant role, as already mentioned.

However, changes in the substrate and solvent structure could significantly modify the situation. Thus, with a substrate as electron rich as 1 and a solvent like AcOH, capable of strong interactions, via H-bonding, with  $\text{Cl}^\cdot$ , the contribution of 7 to the transition state might become so important as to make photochlorination more selective than photobromination. With 2, which is less electron rich than 1, the contribution of 7 should certainly be smaller and accordingly chlorination and bromination display similar selectivity. The role of 7 is probably negligible

in  $\text{CCl}_4$  (very scarce interaction of the solvent with  $\text{Cl}^-$ ) so that in this case we find the "normal" result that bromination is more selective than chlorination.

If these reasonings are correct, the transition state for the photochlorination of alkylaromatics would be "variable", the actual structure depending on the ionization potential of  $\text{ArCH}_3$  and the strength of the interactions of the solvent with  $\text{Cl}^-$  (which also modify the oxidizing power of the  $\text{Cl}^\cdot/\text{Cl}^-$  couple), both these factors influencing the contribution of  $\underline{I}$  to the transition state itself.

Interestingly, some support to this suggestion is found in the relative reactivity values for the photochlorination in  $\text{AcOH}$  of substituted toluenes, reported in Table 2. No correlation exists between these data and the  $\sigma^+$  or  $\sigma$  values of the substituent (Fig. 1), in contrast to what observed in  $\text{CCl}_4$  or other solvents<sup>20</sup>, but the effect on the rate becomes greater the more electron donor is the substituent, in line with the previous hypothesis.

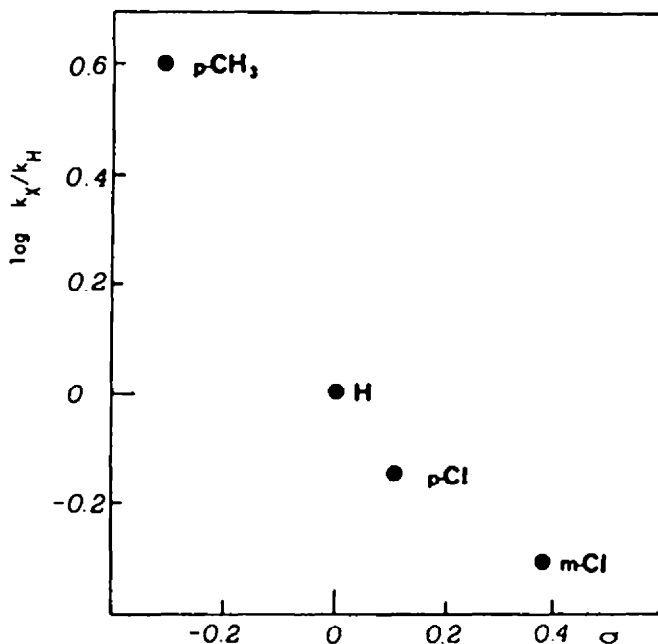


Figure. Logarithms of the relative reactivities of photochlorination of X substituted toluenes ( $k_X/k_H$ ) vs  $\sigma_p$  and  $\sigma_m$  values of the substituents

In principle, a mechanistic changeover, from a hydrogen atom transfer to an electron transfer mechanism, should be possible as the ionization potential of the substrate becomes progressively lower. With the data available, we cannot say whether this point has been reached in the case under study. On the other hand, the use of substrates more electron rich than  $\underline{I}$  presents the problem of the competing electrophilic processes, including those leading to side-chain substituted products.



In the reaction promoted by CAN and  $\text{Cl}^-$  in AcOH intramolecular selectivity is similar to that observed in the photochemical chlorination (compare entries 6 and 8). The small difference observed with  $\frac{1}{2}$  can be due to the incursion, in the CAN/ $\text{Cl}^-$  system, of a direct reaction of CAN (which accordingly exhibits a higher selectivity, entry 10). In line with this observation we have found substantial amounts of benzyl nitrates in the reaction product (see above).

The mechanism could be very similar to that proposed in eqs 4-7 for the side-chain bromination; oxidation of  $\text{Cl}^-$  is more difficult than that of  $\text{Br}^-$  and therefore an inner sphere mechanism of oxidation is very probable also in this case.

More complicated is the interpretation of the selectivity data concerning the  $\text{Co}(\text{OAc})_3/\text{Cl}^-$  system. In the reaction where  $\text{Cl}^-$  is in strong excess with respect to  $\text{Co}(\text{OAc})_3$ , the selectivity is significantly different than that observed in the photochemical chlorination (compare entries 6 and 9), with both  $\frac{1}{2}$  and  $\frac{2}{3}$ . Nearly certainly  $\text{Cl}^-$  is not involved in these reactions and this conclusion is in agreement with that reached by Helba et al. who studied the intermolecular selectivity of the same reaction<sup>25</sup>. These authors have also suggested that a cobalt(III) chloride complex is the actual reacting species and that an one electron transfer mechanism is operating. However we feel that the latter hypothesis is unlikely as the intramolecular selectivity is low and is practically unaffected by the nature of the substituent. In view of our previous observations<sup>6</sup>, a H-atom transfer mechanism seems more probable.

It has also to be noted that the intramolecular selectivity of the  $\text{Co}(\text{OAc})_3/\text{Cl}^-$  system is very similar to that observed with  $\text{Co}(\text{OAc})_3$  alone (compare entries 9 and 11), whereas the two systems appear to exhibit quite different intermolecular selectivity<sup>25</sup>. At present we have no reasonable hypothesis to explain this discrepancy.

#### EXPERIMENTAL SECTION

<sup>1</sup>H NMR were taken in the FT mode at 80.13 MHz on a Bruker WP80SY spectrometer. GLC analyses were performed on a VARIAN Vista 6000 gas chromatograph connected with a HP 3390 A integrator using a 50m fused silica CPSil 19 CB capillary column. GC-MS analyses were performed on a HP 5890 gas chromatograph equipped with a 12m x 0.2mm silica capillary column coated with methyl silicone gum, and coupled with a HP 5970 MSD.

**Materials.** Ceric ammonium nitrate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (Fluka, 99% pure) was dried at 85 °C for 1h. Sodium bromide (Fluka, 99% pure) was dried at 100 °C under vacuum. Solutions of cobaltic acetate in acetic acid were prepared by oxidation of cobalt(II) acetate with ozone<sup>26</sup>. The conversion of Co(II) into Co(III) was determined by iodometric titration to be  $99 \pm 1\%$ . Acetic acid (ErbaRP, 99.8% pure) was thoroughly purged with pure argon before use. N-Bromosuccinimide (Erba, 99%) and 2,2'-azobisisobutyronitrile were recrystallized from hot-water and 50%  $\text{H}_2\text{O}$ -EtOH, respectively. Toluene (Erba R.P).

p-chlorotoluene (Erba, 99% pure), m-chlorotoluene (Erba, 99% pure), p-xylene (Erba, 99% pure), 4-chloro-1,2-dimethylbenzene (Aldrich, 98% pure), lithium chloride (Fluka, puriss) were commercial samples and were used as received. 4-t-Butyl-1,2-dimethylbenzene was synthesized according to a literature method<sup>27</sup>.

Reaction products. Authentic specimens were prepared as follows.

2-Methyl-5-t-butylbenzyl alcohol (8) was prepared by the reaction of the Grignard reagent of 2-bromo-4-t-butyltoluene<sup>28</sup> with formaldehyde. Mass spectrum (70 eV), m/z (relative intensity) 178 (23), 163 (100), 105 (36), 91 (27), 77 (20). <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ: 7.20-7.05 (m, 3H), 4.71 (s, 2H), 2.35 (s, 3H), 1.63 (s, 1H), 1.33 (s, 9H).

2-Methyl-4-t-butylbenzyl alcohol (9) was isolated by silica gel column chromatography (light petroleum ether and ethyl acetate in a 6:1 ratio) from the mixture of 8 and 9 obtained by oxidation of 1 with CAN followed by H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O hydrolysis. Mass spectrum (70 eV), m/z (relative intensity) 178 (23), 163 (100), 105 (34), 91 (30), 77 (20). <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ 7.4-7.1 (m, 3H), 4.69 (s, 2H), 2.39 (s, 3H), 1.63 (s, 1H), 1.33 (s, 9H).

For the synthesis of 2-Methyl-5-chlorobenzyl alcohol (10) 2-bromo-4-nitrotoluene<sup>29</sup> was reduced to 3-bromo-4-methylaniline (11) by Sn/HCl according to a general procedure<sup>30</sup>. 11 was converted to the corresponding diazonium salt which was subjected to the Sandmeyer reaction to give 2-bromo-4-chlorotoluene (12). The Grignard reagent of 12 was then reacted with formaldehyde to form 10. Mass spectrum (70 eV), m/z (relative intensity) 156 (24), 138 (100), 91 (55), 77 (59).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.4-7.0 (m, 3H), 4.67 (s, 2H), 2.33 (s, 3H), 1.91 (s, 1H).

2-Methyl-4-chlorobenzyl alcohol (13) was obtained from the reaction of CAN with 2. The crude product was hydrolysed (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O 5% v/v) and eluted on a silica gel column, as in the case of 9, to give 13. Mass spectrum (70 eV) m/z (relative intensity) 156 (41), 138 (67), 91 (100), 77 (95). <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ: 7.4-7.1 (m, 3H), 4.63 (s, 2H), 2.31 (s, 3H), 2.18 (s, 1H).

In all the reactions performed in the present work, the various benzyl derivatives (acetates, nitrates, bromides and chlorides) were identified by converting them into the corresponding benzyl alcohols which were compared (GLC and GC-MS analyses) with the authentic samples.

Oxidation reactions: general procedure.

The reactions were all conducted at 60 °C under argon atmosphere and magnetical stirring.

Oxidation with CAN. The aromatic hydrocarbon (2.5 mmol) and CAN (5.0 mmol) were added to 60 mL of Acetic acid. The red orange colour of the mixture faded after 2h with 1 but it was still present after 28h (when the reaction was quenched) with 2 as the substrate. The reaction mixture was cooled, poured into water and extracted for several times (light petroleum ether). The organic extract was washed with water and with a saturated aqueous solution of NaHCO<sub>3</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. GLC and GC-MS analyses indicated that the reaction product was a mixture of benzyl acetates and benzyl nitrates.

Oxidation with cobalt(III) acetate. The aromatic substrate (2.5 mmol) was added to 25 mL of a 0.2M solution of cobaltic acetate. After being cooled to room temperature, the reaction mixture was worked up and analysed as above. Benzyl acetates were the only products present.

Halogenation with CAN and Br<sup>-</sup> or Cl<sup>-</sup>. The substituted o-xylene (2.5 mmol), CAN (5.0 mmol) and NaBr (2.5 mmol) or LiCl (2.5 mmol) were mixed in acetic acid (10 mL). When the red orange colour faded the mixture was cooled and worked up as usual. GLC and GC-MS analyses showed that in the reaction of CAN/Br<sup>-</sup> with both 1 and 2 benzyl bromides were the only products formed. From the reaction of 1 with CAN/Cl<sup>-</sup> a mixture of benzyl chlorides, benzyl nitrates and benzyl acetates was obtained, while with 2 benzyl derivatives were only 1/3 of the reaction products, the main reaction being ring chlorination.

Halogenation with cobalt(III) acetate and Br<sup>-</sup> or Cl<sup>-</sup>. A mixture of the aromatic hydrocarbon and the halide 1:1 molar ratio in the case of NaBr and 1:10 in the case of LiCl) were added to a 0.2M solution of cobalt(III) acetate (substrate to oxidant ratio, 1:2). The reaction mixtures were worked up analyzed as before and the products shown to be benzyl bromides and benzyl chlorides, respectively.

Bromination with N-bromosuccinimide (NBS). The aromatic hydrocarbon (2.5 mmol) was reacted with NBS (0.6 mmol) in anhydrous CCl<sub>4</sub> (2 mL). The reaction was stopped after 20h in the case of 1 and after 30h with 2. Work up was as previously reported<sup>3</sup>.

Photochemical halogenations. A solution of the aromatic hydrocarbon (8 mmol) in 80 mL of acetic acid, was irradiated with a 125 W high pressure mercury lamp whose emission was filtered through pyrex. During 1-3 h, 20 ml of a 0.2M solution of Cl<sub>2</sub> or 5 mL of a 0.8M solution of Br<sub>2</sub> in acetic acid was added from a dropping funnel. The reaction mixture was cooled and worked up as usual. GLC analysis showed that benzyl halides were the only products present.

Determination of isomeric distributions. The crude materials coming from oxidation or halogenation of 1 were added to 20 mL of a 3 M solution of CH<sub>3</sub>COONa in acetic acid and refluxed overnight. Before cooling, the mixture was diluted with 30 mL of acetic acid and worked up as usual. GC-MS analyses indicated the complete conversion of the mixture of benzyl halides or nitrates into the corresponding acetates which were analysed by GLC. The reaction mixture of the benzyl halides of 2 was reacted with 10 mL of H<sub>2</sub>O, 1 mL of diethylenedioxiide and a few mg of Ag<sub>2</sub>O under reflux (reaction time was 6 and 12h for the bromides and chlorides, respectively). The mixture was cooled, extracted with light petroleum ether and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. GC-MS analyses confirmed complete conversion of benzyl halides into the benzyl alcohols which were analysed by VPC.

The mixture of the benzyl nitrates and acetates coming from oxidation of 2 with CAN was refluxed overnight in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O 5% v/v in order to obtain a quantitative conversion into the corresponding alcohols which were analysed as above.

Competitive photochlorinations. A mixture of toluene and substituted toluene (whose ratio ranged from 1:1 to 1:3 depending on the relative reactivity) was irradiated the as above and a 0.2M solution of Cl<sub>2</sub> in acetic acid was added from a dropping funnel (the moles of Cl<sub>2</sub> added never exceeded 10% of those of the substrate). After cooling an internal standard (cyclododecane) was added, the reaction mixture was worked up as usual and the product analysed by GLC.

The relative reactivity was directly obtained by the ratio of the gas chromatographic areas of the products, relative to that of the internal standard, and corrected for the initial concentrations of the reactants. All reactions were run in triplicate.

Acknowledgments. Thanks are due to the Ministero della Pubblica Istruzione for financial support.

## REFERENCES

1. For a review see M. L. Poutsma in J. K. Kochi Ed. "Free Radicals", Wiley, New York (1973), Vol. II, Chapter 15.
2. E. Baciocchi, A. Ciana, G. Illuminati, C. Pasini, *J. Am. Chem. Soc.*, **87**, 3953 (1965); E. Baciocchi, M. Casula, G. Illuminati, L. Mandolini, *Tetrahedron Lett.*, 1275 (1969); E. Baciocchi, G. Illuminati, *Tetrahedron Lett.*, 2265 (1975).
3. C. Walling, *J. Org. Chem.*, **53**, 305 (1988) and references therein.
4. J. Schlosserová, M. Hronec, V. Vesely, *J. Chem. Soc. Faraday Trans. 1*, **81**, 2095 (1985) and references therein; G. H. Jones, *J. Chem. Res. (S)*, 207 (1982).
5. G. A. Russell, in J. K. Kochi Ed., "Free Radicals", Wiley, New York (1973), Vol. I, Chapter 7.
6. E. Baciocchi, A. Dalla Cort, L. Ebersson, L. Mandolini, C. Rol, *J. Org. Chem.*, **51**, 4544 (1986).
7. The CAN/Br<sup>-</sup> system has confirmed itself as a very good side-chain bromination system for methylbenzenes in line with previous observation<sup>8</sup>.
8. E. Baciocchi, C. Rol, G. V. Sebastiani, B. Serena, *J. Chem. Res. (S)*, **24** (1984).
9. E. Baciocchi, C. Rol, L. Mandolini, *J. Org. Chem.*, **42**, 3682 (1977).
10. A. Citterio, R. Santi, A. Paganì, *J. Org. Chem.*, **51**, 4925 (1987).
11. E. Baciocchi, C. Rol, L. Mandolini, *J. Am. Chem. Soc.*, **102**, 7597 (1980).
12. Actually a direct comparison can only be made in MeCN, where E for Br<sup>·</sup>/Br<sup>-</sup> is 1.7 V vs. NHE (estimated value)<sup>13</sup> and E for Ce(IV)/Ce(III) is 1.3V vs. NHE<sup>14</sup>.
13. L. Ebersson, *Adv. Phys. Org. Chem.*, **18**, 79 (1982).
14. G. P. Rao, A.R. Murthy, *J. Phys. Chem.*, **68**, 1573 (1964).
15. E. Baciocchi, R. Ruzziconi, *J. Chem. Soc. Chem. Commun.*, 445 (1984).
16. J. M. Mellor, *J. Chem. Soc. Chem. Commun.*, 570 (1970).
17. T. H. Lowry, K. S. Richardson "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 2nd Ed, pp 717-721. See also ref. 5 pp 283-298.
18. Ref. 5, pp 317-321; for more recent discussion on the nature of the reacting species see ref. 3.
19. The estimated values of E for Cl<sup>·</sup>/Cl<sup>-</sup> are 0.3-0.4 V higher than those for Br<sup>·</sup>/Br<sup>-</sup><sup>13</sup>.
20. Ref. 5, p 294; J. Hradil, V. Chvalovsky, *Coll. Czech. Chem. Commun.*, **33**, 2029 (1968).
21. Factors which stabilize  $\ddot{7}$  are felt as perpendicular effects to the reaction coordinate and therefore tend to make the transition state more similar to  $\ddot{7}$  (anti-Hammond effect)<sup>22</sup>. As the substrate becomes more electron rich the mechanism may switch from a concerted one to a stepwise process involving a radical cation intermediate.
22. Perpendicular effects have first been discussed in the context of proton transfer reactions<sup>23</sup>. The same reasonings, however, can be applied as well to reactions where electron transfer is coupled to atom transfer<sup>24</sup>.
23. R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970).
24. C. L. Perrin, *J. Phys. Chem.*, **88**, 3611 (1984); A. Pross, *Acc. Chem. Res.*, **18**, 212 (1985); A. Pross, *Adv. Phys. Org. Chem.*, **21**, 99 (1985).
25. E.I. Heiba and R. M. Dessau, W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 6830 (1969).
26. Y. Kamiya, M. Kashima, *J. Catal.*, **25**, 326 (1972).
27. D. Nightingale, J. R. Janes, *J. Am. Chem. Soc.*, **66**, 154 (1944).
28. L. M. Stock, H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5615 (1959).
29. H. J. Lucas, N. F. Scudder, *J. Am. Chem. Soc.*, **50**, 244 (1928).
30. A. I. Vogel, "Vogel's Textbook of Practical Organic Chemistry", 4th Ed., p 659 (1978).