

Mechanism of Oxidation of Alkylaromatic Compounds by Metal Ions. 3. A Product Study of the Reaction of Some Polymethylbenzenes with Cerium Ammonium Nitrate in Acetic Acid¹

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The oxidation of hexamethylbenzene, isodurene, mesitylene, and hemimellitene promoted by cerium ammonium nitrate (CAN) in acetic acid, in the dark and in the absence of oxygen, has been investigated. The reaction requires 2 mol of CAN for 1 mol of hydrocarbon and leads in each case to the formation of benzylic nitrates and acetates. With mesitylene significant ring acetoxylation was also observed. The nitrate/acetate molar ratio appears to depend on the reaction conditions (homogeneous or heterogeneous reaction) but it is unaffected by the presence of NH_4NO_3 as well as by the structure of the substrate. With isodurene and hemimellitene the isomeric distribution of nitrates and acetates indicates that the side-chain substitution occurs predominantly at the 2- CH_3 group. These results can be accounted for by a mechanism involving the formation of a radical cation and its conversion to a benzylic radical which, in turn, can give the final products through an alkyl- Ce^{IV} species or by a ligand-transfer process.

Oxidation reactions of methylbenzenes by cerium ammonium nitrate (CAN) are long known.² However, very scanty information is available concerning the mechanism of these reactions.

We have recently studied the kinetic aspects and the structural effects on the reaction rate of the oxidation of polymethylbenzenes by CAN in acetic acid and shown that this reaction occurs by a rate-limiting electron-transfer process.¹ In this paper we wish to report a detailed product study of the oxidation by CAN of hexamethylbenzene, isodurene, mesitylene and hemimellitene.

Results

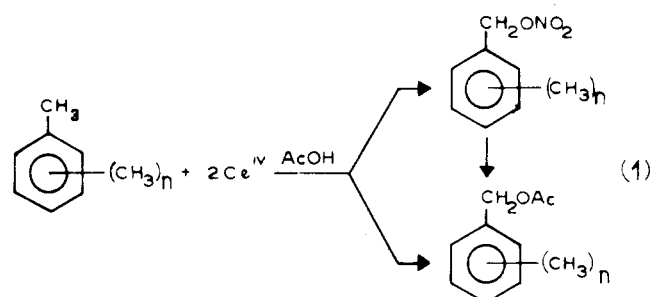
All oxidation reactions were carried out in the dark and under nitrogen atmosphere. Moreover, owing to the low solubility of CAN in acetic acid, ca. 8×10^{-3} M at room temperature, heterogeneous conditions, the only ones suitable for synthetic purposes, were generally used. Some experiments under homogeneous conditions were also brought about for comparison purposes.

The stoichiometry of the reaction was determined using hexamethylbenzene (homogeneous conditions) and isodurene (homogeneous and heterogeneous conditions) as the substrates. In each case it was found that 2 mol of CAN oxidizes 1 mol of hydrocarbon. Interestingly, in the presence of oxygen the stoichiometric ratio CAN/hydrocarbon is significantly less than 2.

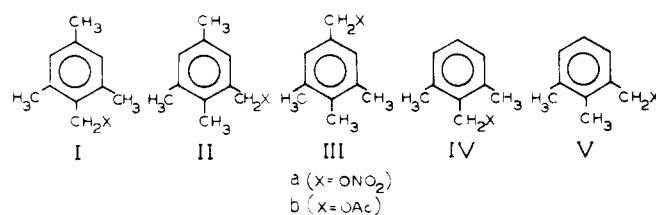
¹H NMR analysis of the reaction product indicated that side-chain oxidation is the only one reaction for hexamethylbenzene, isodurene, and hemimellitene. With mesitylene, also ring acetoxylation was observed. At the first stages of the reaction, 2,4,6-trimethylphenyl acetate accounts for about 50% of the reaction product. This figure, however, decreases to 25% as the reaction is complete.³

The products of the side-chain oxidation were, in each case, benzylic nitrates and acetates. However, since the former solvolyze in the solvent acetic acid, the nitrate/acetate molar ratio in the reaction product depends upon the reaction time and the solvolysis rate of the nitrate, as nicely illustrated in Figure 1 for the specific case of the oxidation of isodurene. According to these results the side-chain oxidation of polymethylbenzenes by CAN in acetic acid, in the dark and in the absence of oxygen, can be described by eq 1.

In order to establish the relative yields of benzylic nitrate and acetate actually obtained in the oxidation, the reaction



mixtures were analyzed at different reaction times and the molar ratio benzylic nitrate/benzylic acetate was extrapolated to zero time. For isodurene and hemimellitene the ratios have been determined for all isomeric derivatives (I-V) which can be formed. The results are reported in Table I.



When the reaction is carried out under heterogeneous conditions, the nitrate/acetate ratio appears to depend upon the amount of solid CAN dispersed in the liquid phase. As the amount of undissolved CAN increases, a significant increase in the nitrate/acetate ratio is observed. Although the error affecting the determination of the nitrate/acetate ratio is rather large because of the low precision of the ¹H NMR technique and of the uncertainty in the extrapolation to zero time, there is no doubt that the observed trend is real. Under homogeneous conditions, the nitrate/acetate ratio was determined only for the reaction of mesitylene where the slow solvolysis of the nitrate allows a quite reliable extrapolation of the data in spite of the very small amounts of products obtained. It seems possible to conclude that the nitrate/acetate ratio determined under homogeneous conditions is lower than that obtained under heterogeneous conditions.

Other interesting observations are: (a) the nitrate/acetate ratio, in a given condition, does not significantly depend on the structure of the substrate; for isodurene and hemimellitene, it is the same for each isomer formed; (b) the nitrate/

Table I. Benzylic Nitrate/Benzylic Acetate Molar Ratio, Extrapolated to Zero Time, in the Reaction of Some Polymethylbenzenes with CAN in Acetic Acid at 50 °C

Substrate, M	Registry no.	CAN, solid phase (mmol) ^a	Benzylic nitrate/benzylic acetate, molar ratio
Mesitylene, 0.0251 ^b	108-67-8		1.5 ± 0.2
0.220 ^b			1.5 ± 0.2
0.119		0.20	3.0 ± 0.5
Isodurene, 0.0252	527-53-7	0.033	2.2 ± 0.2 (Ia/Ib)
			2.1 ± 0.2 (IIa/IIb)
0.0255 ^c		0.033	2.1 ± 0.4 (IIIa/IIIb)
			2.2 ± 0.2 (Ia/Ib)
			2.2 ± 0.2 (IIa/IIb)
			2.1 ± 0.4 (IIIa/IIIb)
0.224 ^c	0.033	0.033	2.1 ± 0.2 (Ia/Ib)
0.112		0.11	2.8 ± 0.4 (Ia/Ib)
			3.2 ± 0.4 (IIa/IIb)
	0.44		3.1 ± 0.6 (IIIa/IIIb)
0.224		0.44	>4 (Ia/Ib)
			5.0 ± 0.8 (IIa/IIb)
Hemimellitene, 0.224	526-73-8	0.44	5.0 ± 1.2 (IIIa/IIIb)
			4.8 ± 1.8 (IVa/IVb)
Hexamethylbenzene, 0.0251	87-85-4	0.042	5.5 ± 1.0 (Va/Vb)
			>1.4

^a Millimoles of undissolved CAN dispersed in 1 mL of liquid phase. ^b [CAN] = 8.05 × 10⁻³ M, homogeneous condition. ^c In the presence of NH₄NO₃, 2.07 × 10⁻² M.

Table II. Distribution of Isomeric Benzylic Acetates and Nitrates, Extrapolated to Zero Time, in the Side-Chain Reaction of Isodurene and Hemimellitene with CAN in Acetic Acid at 50 °C

Substrate	CAN, solid phase ^a (mmol)	Benzylic nitrates, % ^b			Benzylic acetates, % ^b		
		Ia	IIa	IIIa	Ib	IIb	IIIb
Isodurene	0.44	74	16	10	77	14	9
	0.033	72	18	10	72	20	8
	0.033 ^c	71	19	10	74	17	9
Hemimellitene	0.44	IVa	Va		IVb	Vb	
		69	31		69	31	

^a Millimoles of undissolved CAN dispersed in 1 mL of liquid phase. ^b The average error is ±5%. ^c In the presence of NH₄NO₃, 2.07 × 10⁻² M.

acetate ratio is not influenced by the presence of ammonium nitrate in the reaction medium.

The distribution of the isomeric nitrates Ia–Va and acetates Ib–Vb in the oxidation of isodurene and hemimellitene, extrapolated to zero time, appears to be the same for the two side-chain derivatives, as expected by the previously observed independence of the nitrate/acetate ratio on the position of the methyl group (see Table II). No appreciable effect of the temperature was noted in the range 30–80 °C; moreover, the positional selectivity is not significantly influenced by the amounts of undissolved CAN dispersed in the solution.

Even though not high, the positional selectivity appears sufficient to allow some synthetic application of the reaction. Thus, 2,4,6-trimethylbenzyl alcohol can be isolated in 40% yield from the oxidation of isodurene followed by reduction with LiAlH₄ (see Experimental Section).

Discussion

Side-Chain Oxidation. As stated above, the side-chain oxidation of polymethylbenzenes by CAN in acetic acid probably involves an electron-transfer mechanism leading to the formation of radical cations as reaction intermediates.¹ The suggested mechanism, which is similar to that generally accepted⁴ for this type of reaction, is reported in eq 2–4.

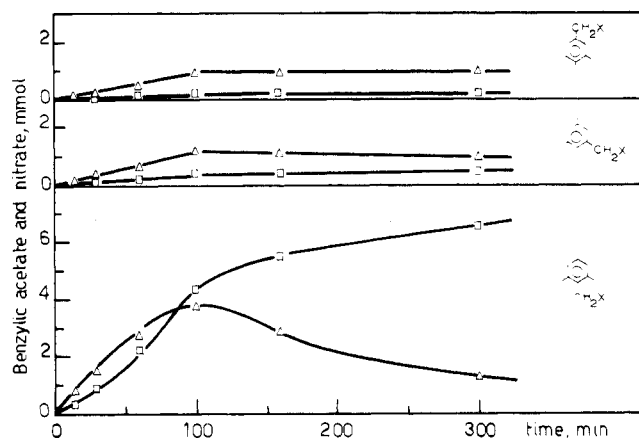
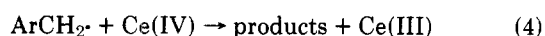
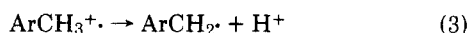
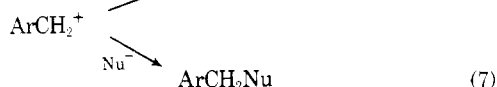


Figure 1. Millimoles of benzylic acetates (□) and nitrates (Δ) as a function of the reaction time obtained in the oxidation of isodurene (11.2 mmol) by CAN (22.4 mmol) in acetic acid.

The results of our product study are in agreement with this mechanism, which indeed predicts the 2:1 stoichiometric ratio CAN/hydrocarbon observed in the oxidation of hexamethylbenzene and isodurene. Moreover, it is also possible to rationalize the observation that the stoichiometric ratio decreases in the presence of oxygen. Accordingly, when oxygen is present it competes with Ce(IV) for the free radical ArCH₂[·], presumably forming carbonyl derivatives (see Experimental Section), and less Ce(IV) is consumed for the oxidation of I

mol of hydrocarbon. Also, the isomeric distribution observed for isodurene and hemimellitene is in agreement with this mechanism.⁵ The fact that with both these hydrocarbons the side-chain substitution mainly involves the 2-methyl group can be explained by considering that in both cases the initially formed radical cation preferentially loses the proton from the 2-methyl group, since in this way the more stable benzylic free radical can be formed. However, also the amount of positive charge at the substituted ring positions of the radical cation can be of importance.⁶ Accordingly, the reactivity order of the three nonequivalent methyl groups of isodurene qualitatively parallels the order of positive charge density calculated⁶ for the substituted ring positions of isodurene radical cation.

With regard to the mechanism by which the benzylic free radicals are converted into the final products, the reaction paths reported in eq 5-7, involving the formation of a free



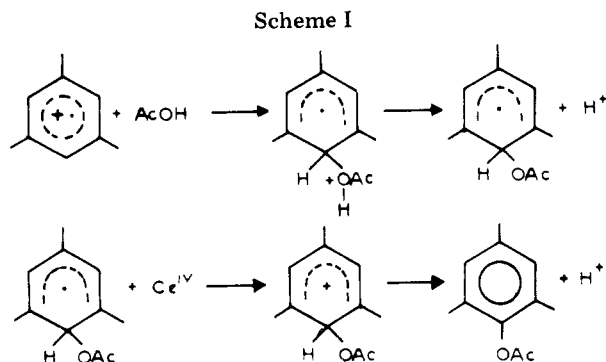
carbocation, appear unlikely, since they do not fit in with the finding that the yield of nitrate is unaffected by the presence of added nitrate ions. A reasonable suggestion could be that, as it has been already proposed for the oxidation of free radicals with Cu^{2+} ,^{7a} the benzylic radical and Ce(IV) form an alkyl- Ce(IV) intermediate^{7b} which subsequently undergoes competitive oxidative solvolysis (leading to acetate) and oxidative displacement (leading to nitrate). The two processes should have similar electronic requirements, thus accounting for the finding that the nitrate/acetate ratio, in a given condition, is substantially independent of the structure of the radical being oxidized. Alternatively, a ligand-transfer mechanism might take place.⁸ In this respect, it has been reported that when CAN is dissolved in acetic acid it undergoes the exchange of two labile nitrate ions with two solvent molecules.⁹ Thus, the ratio of benzyl nitrate to benzyl acetate would be determined by the relative rates of the two ligand-transfer reactions.

The observation that in the reaction carried out under heterogeneous conditions the nitrate/acetate ratio depends on the amount of solid CAN dispersed in the liquid phase suggests that the oxidation of the benzylic radical can also take place at the surface of the undissolved salt. Accordingly, the rate of this oxidation should depend on the surface development of the solid phase which, in turn, should be in some way related to the number of moles of CAN dispersed in the solution. If this interpretation is correct, the observed results indicate also that the reaction occurring at the surface of the undissolved CAN should predominantly lead to the formation of the nitrate, which is quite reasonable since the undissolved Ce(IV) would probably possess nitrate ligands, exclusively.

Finally, the comparison of the results of the oxidation of polymethylbenzenes by CAN in AcOH with those of the oxidation of the same substrates by $\text{Ce(OCOCF}_3)_4$ in CF_3COOH ¹⁰ is of interest. In the latter reaction, biaryls and diarylmethanes are by far the main reaction products, whereas very small amounts of side-chain trifluoroacetates were observed. Probably the difference between the two reactions lies in the minor basicity and nucleophilicity of CF_3COOH as compared to CH_3COOH . Thus, in CF_3COOH , the reaction of the radical cation with another molecule of aromatic compound (formation of biaryl) can compete with the proton loss to give the benzylic radical. Moreover, even when the radical is formed and is oxidized to carbocation (eq 5), the carbocation reacts with another molecule of aromatic substrate, giving

diarylmethanes, rather than with the solvent.

Nuclear Acetoxylation. The formation of 2,4,6-trimethylphenyl acetate in the oxidation of mesitylene is further evidence of the intervention of a radical cation in the oxidation reaction, since such an intermediate can undergo the attack of a nucleophile (in this case the solvent) on the aromatic nucleus, as shown in Scheme I.



With mesitylene radical cation the ring reaction with the solvent competes significantly with the side-chain reaction (eq 3), which is, in contrast, the only one reaction observed with the other investigated hydrocarbons. In other oxidation processes too mesitylene shows a much larger tendency to ring oxidation with respect to other polymethylbenzenes. Thus, in the anodic oxidation of mesitylene and durene ring acetoxylation is observed only with the first substrate;¹¹ moreover, the relative amounts of biaryls (ring substitution) to diarylmethanes (side-chain substitution) are much higher with mesitylene than with durene in the reactions promoted by $\text{Ce(OCOCF}_3)_4$,¹⁰ FeCl_3 ,¹² $\text{Co(OCOCF}_3)_3$,¹³ and $\text{Mn(OCOCF}_3)_3$.¹³ Similar results have been also found in the anodic oxidation in nonnucleophilic media,⁶ and ring acetoxylation appears to be the major reaction observed in the oxidation of mesitylene by Ag(II) .¹⁴

Thus, it clearly appears that in the competition between side-chain and ring reaction the relative position of the methyl groups plays a very important role, the side-chain reactions being clearly favored in the reaction of substrates having methyl groups ortho or para to each other. The phenomenon has been rationalized⁶ by considering that when ortho or para CH_3 groups are present the radical cation carries a much larger amount of positive charge in the methyl-substituted position, thus favoring the loss of a proton in the benzylic position, than when the methyl groups are meta. It is interesting to note in this respect that also in the oxidation of methylnaphthalenes and methoxytoluenes by $\text{Co(OCOCH}_3)_3$ in the presence of KOCOCH_3 or LiCl the extent of side-chain oxidation was found to be directly related to the degree of positive charge adjacent to the methyl group.¹⁵

Another factor which could favor ring acetoxylation in the case of mesitylene is that the three methyl groups are in a position very suitable to stabilize the resulting σ complex. However, the role of this factor seems less important than that previously discussed, since no nuclear acetoxylation is observed in the oxidation of isodurene where a similar stabilization of the σ complex is possible.

Experimental Section

Proton magnetic resonance spectra were taken on a Jeol JNM-C60HL spectrometer, using Me_4Si as the internal standard. Infrared spectra were obtained on a Perkin-Elmer 257 from 2% solutions in CCl_4 . VPC analyses were performed on a GI Fractovap (C. Erba). Elemental analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. All melting points are uncorrected.

Materials. Cerium ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ (Schuchardt, 99.9% pure) was dried at 85°C for 1 h. Acetic acid (ERBA

Table III. ^1H NMR Chemical Shifts in CCl_4 of Some Polymethylbenzyl Nitrates and Acetates^a

Registry no.	Compound	Chemical shift, δ			
		Arom	$-\text{CH}_2-$	$-\text{CH}_3$	$-\text{COCH}_3$
51445-98-8	2,6-Dimethylbenzyl nitrate	7.03	5.49	2.38	
63548-89-0	2,3-Dimethylbenzyl nitrate	7.06	5.36	2.25, 2.22	
62346-87-6	2,6-Dimethylbenzyl acetate	6.97	5.11	2.38	2.00
13651-57-5	2,3-Dimethylbenzyl acetate	6.98	5.00	2.26, 2.19	1.98
63548-90-3	2,4,6-Trimethylbenzyl nitrate	6.77	5.43	2.31 (s, 6 H) 2.22 (s, 3 H)	
63548-91-4	2,3,5-Trimethylbenzyl nitrate	7.01	5.30	2.27 (m, 9 H)	
60367-95-5	3,4,5-Trimethylbenzyl nitrate	7.03	5.20	2.29 (s, 6 H) 2.18 (s, 3 H)	
63548-92-5	2,4,6-Trimethylbenzyl acetate	6.70	4.99	2.30 (s, 6 H) 2.22 (s, 3 H)	1.97
63548-93-6	2,3,5-Trimethylbenzyl acetate	6.75	4.87	2.15 (s, 6 H) 2.06 (s, 3 H)	1.89
39126-12-0	3,4,5-Trimethylbenzyl acetate	6.90	4.82	2.26 (s, 6 H) 2.14 (s, 3 H)	1.99
19405-90-4	Pentamethylbenzyl nitrate		5.50	2.26 (s, 6 H) 2.19 (s, 9 H)	
19936-85-7	Pentamethylbenzyl acetate		5.13	2.24 (s, 6 H) 2.19 (s, 9 H)	1.97

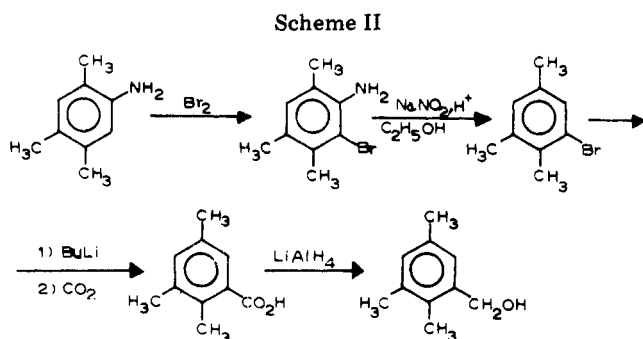
^a Chemical shifts may vary with concentration ($\delta \pm 0.08$), but in case of isomeric substrates the relative order remains unchanged.

RPE) was thoroughly fluxed with pure nitrogen before use. The purity of hexamethylbenzene (Fluka, 99% pure), isodurene (Schuchardt, 98% pure), hemimellitene (Schuchardt, 98% pure), and mesitylene (ERBA, 99.5% pure) was checked by VPC. 2,6-Dimethylbenzoic acid (Fluka, 98% pure), 2,3-dimethylbenzoic acid (Fluka, 97% pure), and pseudocumidine (Fluka) were commercial samples and were used as received. Bromomesitylene (Aldrich) was distilled before use. 3,4,5-Trimethylbenzoic acid was prepared according to a literature method,¹⁶ mp 218–220 °C, lit.¹⁶ mp 218–220 °C.

Pentamethylbenzyl alcohol was available from a previous investigation.¹⁷

2,4,6-Trimethylbenzyl alcohol was prepared by the reaction of the Grignard reagent derived from bromomesitylene¹⁸ with gaseous formaldehyde,¹⁹ mp 88.5–89 °C from hexane, lit.²⁰ mp 88 °C.

2,3,5-Trimethylbenzyl alcohol was synthesized according to the reaction sequence in Scheme II. Any attempt to obtain 6-bromo-



pseudocumene from pseudocumidine according to Smith and Moyle²¹ failed, as well as any modification derived therefrom, involving H_3PO_2 as the reducing agent for the diazo compound. In all cases, 2-bromo-3,4,6-trimethylphenol was obtained as the sole product, mp 31–32 °C, lit.²² mp 32 °C. Better results were achieved following the method of Carpenter and Easter.²³ 6-Bromopseudocumene was obtained as a colorless liquid, n_{D}^{25} 1.5524, lit.²¹ n_{D}^{26} 1.5516. Treatment of the latter compound with *n*-BuLi in dry ether solution, followed by reaction with excess carbon dioxide, afforded 2,3,5-trimethylbenzoic acid, mp 123–127 °C from aqueous ethanol, lit.²⁴ mp 124 °C. Reduction of the acid with LiAlH_4 ²⁵ gave 2,3,5-trimethylbenzyl alcohol in virtually quantitative yield, mp 50–51 °C from hexane.

Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.97; H, 9.40. Found: C, 79.86; H, 9.33.

The other benzyl alcohols were similarly obtained from the corresponding acids.

3,4,5-Trimethylbenzyl alcohol, mp 72–73 °C from hexane, lit.²⁶ mp 72–74 °C. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.97; H, 9.40. Found: C, 79.83; H, 9.51.

2,6-Dimethylbenzyl alcohol, mp 81–82 °C from ligroine, lit.²⁷ mp 82–83 °C.

2,3-Dimethylbenzyl alcohol, mp 66–68 °C from ligroine, lit.²⁸ mp 65–66 °C.

Benzylic Nitrates. These compounds were obtained in 70–90% yield by treatment of the corresponding alcohols with SOCl_2 , followed by reaction with AgNO_3 in CH_3CN . All the compounds showed strong $-\text{ONO}_2$ absorption in the IR spectra at 1635 and 1280 cm^{-1} . The ^1H NMR spectral data are reported in Table III.

Benzylic Acetates. These compounds were prepared in quantitative yield by acetylation of the appropriate alcohol with acetic anhydride. The ^1H NMR spectral data are reported in Table III.

The Oxidation of Polymethylbenzenes with CAN. A mixture of the hydrocarbon (5.0–45 mmol) and CAN (1.6–90 mmol) in 200 mL of acetic acid was stirred at 50 °C in a nitrogen atmosphere in the dark. Aliquots (20–50 mL) were taken at intervals, quenched in cold petroleum ether 30–50 °C, washed with a solution of FeSO_4 , concentrated, and analyzed by ^1H NMR. In all cases, the ^1H NMR signal of the oxidation products was compared with those of authentic samples. These were synthesized by independent routes in the cases of hexamethylbenzene, isodurene, and hemimellitene (see above), and obtained by direct isolation in the case of mesitylene (*vide infra*). In each case the relative amounts of nitrates and acetates present in the reaction product and the isomeric distribution were determined by integration of ^1H NMR peaks due to the CH_2X groups (Table III).

Stoichiometry of the Reaction. The stoichiometry of the reaction was determined under a variety of conditions using hexamethylbenzene and isodurene as the substrates. A solution of hexamethylbenzene (0.202 mmol) and CAN (0.202 mmol) in 80 mL of acetic acid was heated at 40 °C, in the dark and under nitrogen. When all Ce(IV) was consumed, 0.13 mmol of menthol and 0.14 mmol of 4-nitrobiphenyl (internal standards) were added to the cooled reaction mixture. The solution was diluted with pentane and washed with water. After removing most of the solvent, the residue was analyzed by VPC using a 3-mm i.d. glass column (1.8 m) containing 0.1% FFAP on carbon-coated beads²⁹ with nitrogen as carrier gas. The column temperature was 90 °C for the analysis of hexamethylbenzene and 150 °C for the analysis of pentamethylbenzyl acetate. It was observed that 0.099 mmol of hexamethylbenzene had reacted and that 0.096 mmol of pentamethylbenzyl acetate had been produced. When the same experiment was carried out in the presence of air, it was found that, starting from 0.260 mmol of hexamethylbenzene and 0.255 mmol of CAN, 0.216 mmol of hexamethylbenzene had been oxidized. IR analysis of the reaction product indicated the presence of significant amounts of carbonyl derivatives.

Isodurene (11.2 mmol), CAN (22.4 mmol, most undissolved), and 1,4-dibromobenzene (standard, 1.13 mmol) in acetic acid (50 mL) were heated with stirring at 50 °C, in the dark under nitrogen. At the end of the reaction the mixture was cooled and worked up as described before. ^1H NMR analysis showed that 10.9 mmol of benzylic nitrates and acetates had been formed. Performing the same experiment under

homogeneous conditions it was found that 1.60 mmol of isodurene reacts with 0.80 mmol of CAN to give 0.41 mmol of benzylic acetates and nitrates.

Oxidation of Mesitylene. Isolation of the Reaction Products.

A mixture of mesitylene (16.6 mmol) and CAN (33.2 mmol) in acetic acid (200 mL) was treated as above until the red-orange color of CAN faded (45 h). The pale-yellow liquid (2.5 g) obtained after usual workup was chromatographed on silica gel. Elution with CHCl_3 -light petroleum 1:9 gave 3,5-dimethylbenzyl nitrate (0.93 g, 31% yield) as a colorless liquid: n_D^{25} 1.5172 (lit.³⁰ 1.5172); IR 2920 and 1640 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 6.90 (s, 3 H), 5.22 (s, 2 H), 2.27 (s, 6 H). Recovery was not quantitative, since several fractions containing the product in a less pure form were discarded. Elution with pure CHCl_3 gave 0.81 g of a mixture of two products, which were later shown to be 3,5-dimethylbenzyl acetate and 2,4,6-trimethylphenyl acetate. Pure samples of the latter compounds were obtained by resolution of the mixture by preparative VPC, on a 2-m column packed with CWX 20M 10% operating at 140 °C. Structure assignments were based on the following properties. 2,4,6-Trimethylphenyl acetate: IR 2920 and 1760 cm^{-1} ; $^1\text{H NMR}$ (C_6D_6) δ 6.73 (s, 2 H), 2.10 (s, 3 H), 2.05 (s, 6 H), 1.90 (s, 3 H); mass spectrum (70 eV) m/e (rel intensity) 179, M^+ (16), 137 (13), 136 (100), 135 (15), 121 (56), 91 (14), 43 (13). 3,5-Dimethylbenzyl acetate: n_D^{20} 1.5032 (lit.³¹ $n_D^{23.5}$ 1.5028); IR 2920 and 1740 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 6.88 (s, 3 H), 4.94 (s, 2 H), 2.27 (s, 6 H), 2.00 (s, 3 H).

Oxidation of Isodurene. Isolation of 2,4,6-Trimethylbenzyl Alcohol. Isodurene (7.5 mmol) was made to react with CAN (15.0 mmol) in acetic acid at 80 °C for 10 min, and the crude reaction product was reduced with LiAlH_4 . The mixture of alcohols was recrystallized from hexane, and 2,4,6-trimethylbenzyl alcohol, mp 83–85 °C, was obtained in 40% yield.

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Registry No.—CAN, 16774-21-3; acetic acid, 64-19-7; 3,5-dimethylbenzyl nitrate, 15285-43-5; acetate, 19082-49-6; 2,4,6-trimethylbenzyl alcohol, 4170-90-5; 3,4,5-trimethylbenzyl alcohol, 39126-11-9; 2,6-dimethylbenzyl alcohol, 62285-58-9; 2,3-dimethylbenzyl alcohol, 13651-14-4.

References and Notes

- (1) Part 2: E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Lett.*, 3343 (1976).
- (2) (a) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966); (b) L. Syper, *Tetrahedron Lett.*, 4493 (1966); (c) L. A. Dust and E. W. Gill, *J. Chem. Soc. C*, 1630 (1970).
- (3) An easier oxidability of the ring acetoxyated product with respect to the other reaction products and the starting material can be reasonably suggested, since it is known that nuclear monoacetates are often much less resistant to oxidation than the parent compound. See L. Ebersson, *J. Am. Chem. Soc.*, **89**, 4669 (1967).
- (4) D. Benson, "Mechanisms of Oxidation by Metal Ions", Elsevier, New York, N.Y., 1976, p 2, and references cited therein.
- (5) It is interesting to note that the isomeric distribution of nitrates and acetates obtained from the reaction of isodurene compares well with the "overall" isomeric distribution determined after conversion of both nitrates and acetates to the corresponding alcohols and VPC analysis. See E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Lett.*, 3787 (1973).
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A Study of the Mode of Decomposition of Some Carboxylic *tert*-Alkylcarbonic Anhydrides^{1a}

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Three hindered carboxylic carbonic anhydrides—pivalic *tert*-butylcarbonic anhydride, pivalic *tert*-butylthiolcarbonic anhydride, and 2,2-dimethylbutyric *tert*-amylthiolcarbonic anhydride—have been prepared and studied with respect to their mode of decomposition and reactivity with a primary amine. While the products from the decomposition of pivalic *tert*-butylcarbonic anhydride are consistent with an ionic chain mechanism, the products from the decomposition of the two pure thiolcarbonic anhydrides are more consistent with an intramolecular decomposition. In addition, results from the decomposition of a mixture of the two thiolcarbonic anhydrides argue strongly against an ionic chain mechanism. Other considerations are discussed briefly.

There have been numerous reports² dealing with the synthesis, reactions, and mode of decomposition of carboxylic carbonic anhydrides **1**. In general, this type of compound is thermally unstable, particularly in solution or in the liquid state. Two sets of decomposition products are possible,^{3,4} as shown by eq 1 and 2. Usually, mixed anhydrides from alcohols ($\text{X} = \text{O}$) tend to give varying ratios of the possible products,^{5,6}

while anhydrides from thiols ($\text{X} = \text{S}$) give primarily thiol ester and carbon dioxide.⁷ Although both systems have exhibited first-order or pseudo-first-order decomposition kinetics, the kinetic measurements for thiol-mixed anhydrides were consistent and reproducible, while those for alcohol-mixed anhydrides were erratic and apparently quite susceptible to the influences of trace impurities. It has been proposed that mixed