

ORIENTATION AND POSITIONAL SELECTIVITY IN THE REACTIONS OF CERIVM (IV)
AND N-BROMOSUCCINIMIDE WITH ISODURENE AND 5-t-BUTYLHEMIMELLITENE.
COMPARISON WITH THE SIDE-CHAIN ELECTROPHILIC REACTIONS.

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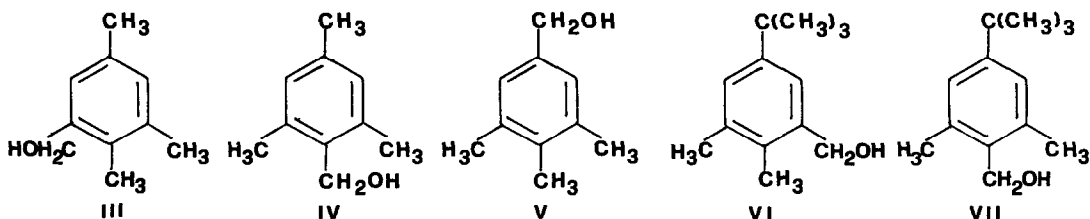
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Electrophilic side-chain substitutions¹ of alkylaromatic compounds are characterized by a very high positional selectivity. Thus, the side-chain chlorination^{2a} and nitration^{2b} of isodurene(I) occur nearly exclusively at the methyl group located in the 5-position, and the side-chain nitration^{2b} of 5-t-butylhemimellitene (II) concerns only the methyl group in the 1-position. Since it seemed interesting to acquire information on the positional selectivity and the orientation of side-chain reactions which occur by non heterolytic mechanisms, we have determined the product distribution in the reactions of (I) and (II) with Ce(IV) and N-bromosuccinimide (NBS).

The isomeric distribution of the products was determined by converting all substances initially formed (mainly acetates in the case of the reaction with Ce(IV)) into the corresponding alcohols (III-V from I, and VI VII from II), which were quantitatively analyzed by g.l.c.. The results (collected in the Table together with the data for the electrophilic side-chain reactions) show that the reactions with Ce(IV) and NBS exhibit a smaller positional selectivity than electrophilic side chain substitutions. Moreover, the orientation is sharply different since the main product, with both I and II, is that substituted at the methyl group located in the 2-position. The absence of this product in the side-



chain reactions of Cl_2 and AcONO_2 , provides further support to the heterolytic nature of these reactions.

Table

Distribution of isomeric alcohols (mole, %) ^a obtained (see text) in the side-chain reactions of isodurene and 5-t-butylhemimellitene with Ce(IV), NBS and some electrophilic reagents.

Reagent	Isodurene			5-t-Butylhemimellitene	
	III	IV	V	VI	VII
Ce(IV) ^b	13	77	10	5	95
NBS ^c	30	60	10	32	68
Cl_2 ^d	< 2	-	> 98		
AcONO_2 ^e	-	-	(100) ^f	(100) ^f	-

a) The error in the analysis is $\sim \pm 2\%$. b) As cerium ammonium nitrate. In acetic acid at $80 \pm 1^\circ$. The molar ratio hydrocarbon/Ce(IV) was 0.5. c) In refluxing CCl_4 with benzoylperoxide as initiator. The molar ratio hydrocarbon/NBS was 3, in order to minimize dibromination. d) In acetic acid, in the dark at room temperature ^{2a}. e) In acetic anhydride, at room temperature ^{2b}. f) In this case the reaction products were not converted to alcohols. However it was shown that for I and II the methyl groups involved in the reaction were those located in the positions 5 and 1, respectively.

The orientation and low selectivity in the reactions with NBS are in agreement with the generally accepted reaction mechanism ³. Ce(IV) exhibits a larger selectivity than NBS, while orientation remains unchanged. This reagent probably reacts through an electron-transfer mechanism, similar to that postulated for cobaltic acetate oxidation of alkylbenzenes ⁴.

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References

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