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ANOMALOUS ORIENTATIONAL EFFECTS DURING BENZOYLOXYLATIONS BY "SILVER BROMIDE DIBENZOATE"

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The solid complex formed from bromine and silver benzoate reacts with both arenes and alkanes to form aryl and alkyl benzoates, respectively. Highly unusual substituent effects are observed in the benzoyloxylations of arenes. Electron-withdrawing groups (e.g. $-NO_2$, -CN, -CO-) on the aromatic ring facilitate reaction though directing the attacking reagent exclusively to the meta position. In alkanes, tertiary positions are most prone to attack.

The action of halogen upon silver carboxylates is the basis of the Hunsdiecker halodecarboxylation procedure.$^{1)}$ It was earlier shown that aryl derivatives decarboxylate less readily than do the alkyl types and, that at or below room temperature in inert solvents such as dichloromethane, a solid complex is formed upon addition of bromine to silver benzoate.$^{2)}$ This has a somewhat variable composition approximating to $AgBr(OCOPh)_2$, 'silver bromide dibenzoate' 1. On warming or standing, the compound decomposes mainly to form bromobenzene but will react with arenes and even alkanes giving the respective products of bromination and benzoyloxylation.$^{2)}$ This Letter describes further properties of the complex which is an oxidising species apparently owing to the presence of an -O-Br bond. It will, for example, oxidise triethylamine to tribromoacet(N,N-diethyl)amide. Alkenes react instantaneously and analogously to the Prevost reaction with the formation of the 2-bromobenzoate evidently by a polar addition of electrophilic bromine followed by benzoate.$^{3)}$ Novel features appear in the reactions with arenes and alkanes. On stirring 1 with an aromatic compound at 25 °C for several hours, the oxidising properties disappear and the aryl benzoate, benzoic acid, and sometimes, aryl bromide, are formed (Table 1).

$$ArH + \text{"}AgBr(OCOPh)_2\text{"} \rightarrow ArOCOPh,\ PhCOOH,\ ArBr + AgBr$$

Table 1. Yields of Benzoate and Bromide Products Based on "$AgBr(OCOPh)_2$"

Substrate	Benzoate(%)	(position)	Bromide(%)	(position)
Benzene	10		16	
Toluene	5	α>>2,3,4	16	α>>2,3,4
Nitrobenzene	10	3	0	
Benzonitrile	30	3	0	
Pyridine	5	3	1	3
Benzoic acid	12	3	5-10	3
2-Methylbutane	6	2	5	2
Heptane	5	2,3,4	4	2,3,4
Cyclohexane	6.5		3.5	
Methylcyclohexane	8.5	1	7.5	1

Benzoyloxylation by this procedure shows the unusual feature of being promoted by electron-withdrawing groups such as $-NO_2$, -CN, or -COOH while at the same time retaining the meta- regiospecificity normally associated with electrophilic substitutions. Competition experiments confirm reactivity to be enhanced by -M groups; a partial rate factor of 250 for meta benzoyloxylation of nitrobenzene is found which argues strongly against conventional electrophilic substitution. Free radical substitutions in C_6H_5X are normally of low regioselectivity, e.g., for phenylation of nitrobenzene, benzonitrile and ethyl benzoate, o:m:p=60:10:30%[4] and partial rate factors are low. Furthermore, aromatic homolytic substitution by benzoyloxyl radicals is known to occur accompanied by products of phenylation and a strongly 'electrophilic' pattern of orientation. This possibility is ruled out by the absence of phenylation products and the implication from the order of total rate factors, $\underline{F}$, $(\underline{F}_{OMe} >> \underline{F}_{Me} > \underline{F}_{H} >> \underline{F}_{Cl})$[5] that nitro and cyano groups would be deactivating substituents contrary to the observations.

The present results are unique in that highly specific meta orientation is accompanied by activation of the system by -M,-I groups. By contrast, a +M substituent such as methyl (in toluene) leads to rather poor yields of benzoates and that mainly (4.9%) from (presumed) radical attack at the α-position to form benzyl benzoate. Minor benzoyloxylation of toluene occurs at all three positions, o:m:p=5:2:3, further suggestive of a radical reaction. Both ortho and para-bromotoluenes but not benzyl bromide are also formed in the reaction with toluene, evidently by an electrophilic bromination.

When the silver complex is stirred at room temperature with methylcyclohexane, low yields of both alkyl benzoates and bromides (8 and 9%, respectively) are formed. Tertiary, secondary, and primary attack occur in the approximate ratios, 200:1:0.1, normal for a rather selective radical. While in this case at least non-radical processes must seem highly unlikely, the absence of products of phenylation and high selectivity appears to rule out attack by free (as distinct from incipient) benzoyloxyl radicals. However, a radical transfer process from the complex species, providing effectively a radical of relatively low reactivity and high selectivity, is consistent with these observations. While a similar type of homolytic mechanism for the meta-benzoyloxylations of nitrobenzene, benzonitrile, and benzoic acid may be considered, the regiospecificity observed is far higher than has previously been observed even for electrophilic free radicals such as hydroxyl.[4] An alternative heterolytic mechanism may also be envisaged in which the reagent acts as a source of PhCO-OBr: this species undergoes reversible addition to the aromatic ring leading to an intermediate cyclohexa-1,3-diene. Substitution is then completed by rate-determining elimination of HBr, a process likely to be promoted by -M substituents.

References

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