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THE ACTION OF SILVER BENZOATE AND BROMINE ON AROMATIC COMPOUNDS AND ALKANES

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تأثير بنزويتات الفضة والبروم على الهيدروكربونات العطرية والالكينية

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تعرض هذه الدراسة طريق تفاعل بنزيوتات الفضة والبروم فى وسط غير متجانس من الهيدروكربونات . ومن نواتج التفاعل ونسبة الاستيرات والبرومينات وشدتها فى التفاعل مع الهيدروجينات الأحادية والثنائية والثلاثية تم التوصل الى تحديد طريقة التفاعل والتى وجد بأنها رادكل موجبة تكونت فى وسط من $(PhCO_2)_2AgBr$ و $PhCO_2\ Br$

ABSTRACT

Silver benzoate and bromine were used to react in heterogenous phase with certain aromatic compounds and alkanes. From the data on the ratios of bromination and bencoylоxylation products and the extent of reaction on primary, secondary and tertiary hydrogens, a mechanism has been suggested in which an electrophilic radical attack is considered most probable in the presence of $(PhCO_2)_2AgBr$ *and* $PhCO_2$ *as intermediates.*

INTRODUCTION

Several accounts of substitution reactions of aromatic compounds brought about by silver benzoate and halogens have appeared in the literature. Three different types of substitution in the ring have been observed, namely phenylation, benzoyloxy lution and helogentian. Birchenbach and Meisenheimer(1) obtained aryl benzoates and iodides from reactions of silver benzoate and iodine with anisol and with chlorobenzene at 135°C. Chlorobenzene gave a moderate yield (30%) of ortho and para-chloro-phenyl benzoates together with a little chlorobenzene.

Anisole yielded only iodoanisole in 60% yield. No evidence as to the nature of this reaction was provided.

Bryce-Smith and Clark(2) re-examined this reaction and reported the production of a solid reactive species, insoluble in most solvents with the empirical formula $(C_6H_5CO_2)_2AgI$ which appeared to cause these substitution reactions with aromatic compounds such as benzene, anisole, t-butylbenzene, chlorobenzene and nitrobenzene. The evidence for this complex was based on the analytical results from the hydrolysis of the solid.

$$3AgI(OCOC_6H_5)_2 + 3H_2O \rightarrow 6C_6H_5CO_2H + 2gI + AgIO_3$$

The analytical results support this formula for the iodide, but they are inconclusive in the case of the bromide. Similar types of complexes were suggested by Simonini(3) by Simond(4) and by Prevost(5).

Benzoly hypobromite have been postulated by previous workers as a reactive intermediate in reactions of silver benzoate and bromine but never isolated or fully characterized. The evidence for its existence was based on their addition reaction to alkanes.(6)

In this study, an attempt has been made to investigate this reaction futher and to study its mechanism as well as its synthetic potential. Five different aromatic compounds (Benzene, toluene, nitrobenzene, benzonitrile and pyridine) were chosen as substrates because of their distinct orientational behaviour towards both electrophilic and radical attack.

Alkanes are likely to be subject to hydrogen abstraction by reactive radicals and so are not unlikely to yield alkyl benzoates. Therefore, alkanes, heptane, 2 methyl butane, cyclohexane were chosen as substrates because these compounds provided examples of primary, secondary and tertiary hydrogens with an expected pattern of radical reactivity.

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Table 1. Products of Reaction of Silver Benzoate and Bromine with aromatic and aliphatic compounds

Substrate Reaction Temperature	Benzene 25°C 8 hrs Reaction Time		Toluene 20°C 6 hrs		Nitrobenzene 25°C 5 hrs		Benzonitrile 25°C 5 hrs		Pyidine 25°C over 12 hrs		2-methylbutane 25°C 8 hrs		n-heptane 25°C 6 hrs		cyclohexane 25°C 6 hrs		methyl-cyclo-hexane 25°C 6 hrs	
Strarting materials	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%	mole	mole%
Bromine	0.0265	-	0.0184	-	0.017742	-	0.01319	-	0.03353	-	0.01255	-	0.0590	-	0.0330	-	0.05413	-
Silver Benzoate	0.0530	-	0.03579	-	0.0355	-	0.03665	-	0.0670	-	0.0062	-	0.0295	-	0.0164	-	0.05418	-
Organic products																		
Aryl & Alkyl bromides	0.0086	16.6	0.00583	16.3	0.0	0.0	0.0	0.0	0.0	0.0	0.00069	5.4	0.0025	4.6	0.002	6.3	0.005	8.4
Aryl & Alkyl Benzoate	0.00533	10..	0.00163	4.2	0.0028	8.	0.0093	25	0.003	4.5	.00072	-	0.002	4.2	0.0013	3.5	0.0023	7.5
Benzoic Acid	0.03169	59.6	0.0206	53..	0.0246	69	0.025	68	0.0368	55	0.00603	49.0	0.0025	42.5	0.028	87.3	0.029	49.0
Silver Benzoate	not calculated		0.0132	39..	0.005	1.4	0.005	0.0	0.0	0.0	0.0054	24.0	0.02	33.0	not		not calculated	

EXPERIMENTS AND RESULTS

Substitution reactions of some aromatic and aliphatic hydrocarbons

Bromine was added dropwise to a well stirred suspension of two equivalent moles of dry silver benzoate in excess substrate (benzene, toluene, introbenzene, benzonitrile, pyridine, 2-methyl butane, hexane, methyl hexane and heptane) at OC° in the dark.

The mixture was allowed to reach room temperature and maintained in that condition until the reaction was completed. The silver benzoate and silver bromide were removed by filtration. Free benzoic acid was extracted from the reaction mixture with saturated sodium hydrogen carbonate.

Unreacted substrate was removed from the organic phase by rotary evaporation. The neutral residue from the evaporation of solvent was examined by g.l.c., t.l.c. mass spect., I.R. and N.M.R where appropriate.

The products from this reaction were compared with the authentic samples and the results obtained are summarized in tables 1, 2, and 3.

DISCUSSION

Owing to the insolubility of silver benzoate in both aromatic and saturated hydrocarbons the reaction occurs under heterogencous conditions and as can be seen from tables 1 and 2 two types of substitution may result, benzoates and bromides.

The benzoate products formed from nitrobenzene and from benzonitrile were found to be exclusively the meta isomers. These observations are compatible with electrophilic but not with typical radical displacement. Benzoyloxylation of toluene by contrast occured mainly in the side chain (97%) forming benzyl benzoate which might at first sight be considered typical of radical abstraction. The small proportion of ring benzoyloxylation that did ocur was of low selectivity (1.5% orto 0.89% meta, and 0.65% para) and of pattern similar to that of radical substitution of toluene. The benzyl benzoate obtained could arise from recombination of benzoate and benzyl radicals.

$$PhCH_2 + PhCO_2 \rightarrow PhCH_2O_2CPh$$

Table 2. Orientational preference for bromination and benzoyloxylation of aromatic compounds

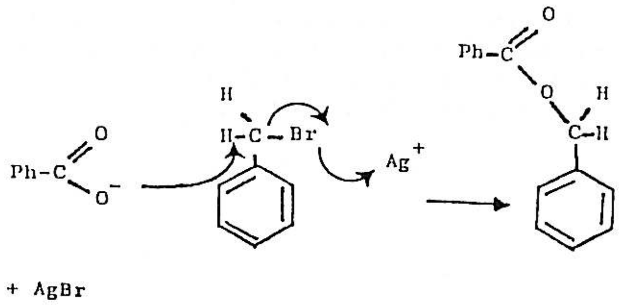
	Bromination				Benzoyloxylation			
SUBSTRATE	O-%	m-%	p-%	O attack	O-%	m-%	p-%	O attack
Toluene	30%	-	70-%	-	1.5%	0.85%	0.65%	97%
Nitrobenzene	-	-	-	-	-	100%	-	-
Benzonitrile	-	-	-	-	-	100%	-	-
Pyridine	Only 3-bromopyridine detected				Only 3-pyridyl benzoate			

Table 3. The relative amounts of primary, secondary and tertiary attack of alkanes with silver benzoate

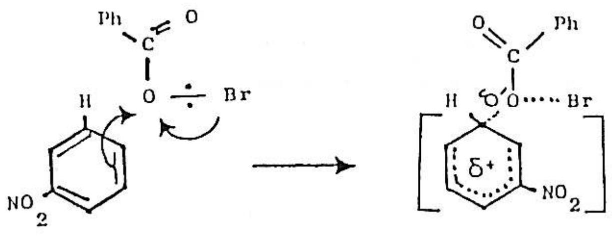
SUBSTITUTION	SUBTRATE	TERTIARY ATTACK	SECONDARY ATTACK	PRIMARY ATTACK
Benzoates	2-methylbutane	13.6	1	traces
	methlylcyclohexane	13.7	1	"
Bromides	2-methylbutane	10.4	1	"
	methylcyclohexane	28.2	1	"

This may be considered improbable because, in the present case, each reaction is at a very low concentration and phenylation products are absent.

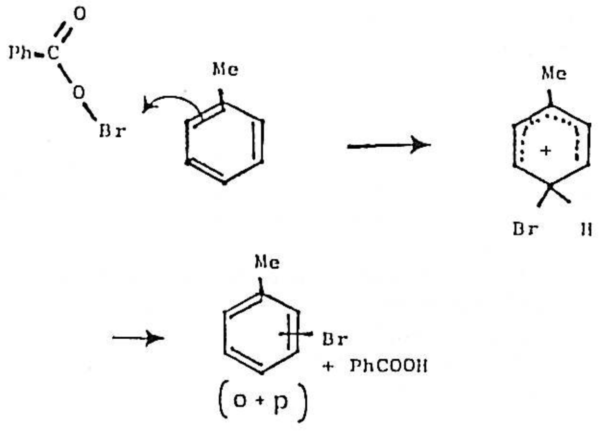
A second possible route to benzoyl benzoate could be by SN ^{2} process. In a control experiment we found that indeed, benzoyl benzoate was obtained in good yield from the reaction of silver benzoate with benzyl bromide.

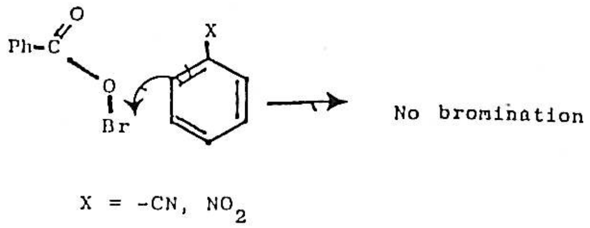


However, the unusual feature of these reactions is the oriention al preference of attack. In each case the isomer distribution remains clearly that which is normally associated with electrophilic attack. It may be inferred from these results that the radical has electrophilic character or that the transition state partakes of a degree of charge polorisation.



Nitrobenzene and benzonitrile, known to be strongly deactivated towards electrophilic attack, give no products of bromination when treated with silver benzoate and bromine while toluene yielded 16% of mixed bromotoluenes of which the ortho/para ratio was 0.43. No meta bromotaluenes were observed. This product distribution is compatible with electrophilic substitution. Furthermore the partial rate factors for bromination of toluene in this study are similar to electrophilic substitution reaction.(7)



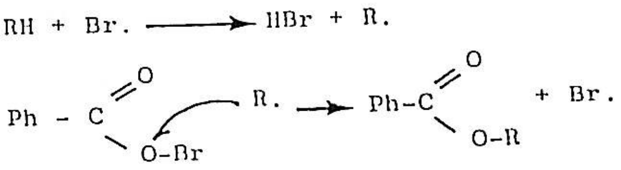


The total rate factors for benzoyloxylation are much smaller. K toluene/K benzen is 7.0. It appears that the brominating agent is highly selective while the benzoyloxylating species is of low selectivity arguing in favour of electrophilic and radical attack respectively.

In this work the benzoate and bromide products formed from alkanes which contained tertiary, secondary and primary hydrogens such as 2-methyl bou tane and methyl cyclohexane amounted to 5.4-8.4%. The ratio selectivity was heavily in favour of attack at tertiary position (95%) with only little secondary (5%) and traces of primary attack. Benzoyloxylation of the secondary positions of heptane (4.5%) yield was not random, but gave as the major product 2-heptyl benzoate (65%) together with the 3 and 4-isomers (35%).

There are no available data from the literature concerning benzoyloxylation of alkanes but the product distribution is very similar to that obtained for other radical substitution reactions such as phenylation or bromination. A further possibility, however, remains to be considered. The alkyl benzoates could in principle result from a nucleophilic displacement between alkyl bromides formed by radical bromination and silver benzoate probably by a silver ion catalysed SN^2 process. In a control experiment we have investigated this possibility but found that under the reaction conditions not much displacement occurs between cylohexyle bromide and silver benzoate, in contrast to the results obtained with bromotoluene.

These results suggest that benzoyloxylation and bromination of both aromatic compounds and alkanes by silver benzoate and bromine has the general character of a radical reaction though, again, a benzayloxy radical transfer from some covalent species must be inferred. The following scheme is consistent with the facts :



The attack of an alkyle or aryl radical on the silver benzoate was considered unlikely since it would result in the deposition of metallic silver which was not formed.

The production of 2-bromobenzoyloxyalkane from the addition of cyclohexene or ethylene to the clear yellow solution from reaction of silver benzoate and bromine in carbon tetrachloride, suggests the presence of benzoyl hypobromite in the mixture which is either formed as such by an ionic reaction between bromine and silver benzoate or is present in equilibrium with solid in suspension, the so called "Silver bromide dibenzoate".

Therefore, we conclude that the reaction mixture consists of two components, one being the Solid intermediate $(PhCO_2)_2AgBr$ and the other appears to be a solution of benzoyl hypobromide $PhCO_2Br$.

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