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ON THE RELATIONSHIP BETWEEN THE HUNSDIECKER AND SIMONINI REACTIONS*

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Abstract—Silver carboxylates (RCO_2Ag) of varied structure have been degraded by chlorine, bromine, and iodine. The reactions yield halide RX and/or ester RCO_2R, the predominant product depending on the nature of the group R, the halogen used, and the reaction temperature. A correlation exists between the formation of ester and the success of the reaction $RX + RCO_2Ag \rightarrow RCO_2R + AgX$, implying that the alkyl halide is an intermediate in ester formation. Limitations to the synthetic applicability of the Hunsdiecker reaction are discussed.

THE DEGRADATION of silver carboxylates by the elemental halogens has been extensively investigated and reviewed.[1-3] With bromine, and it has been assumed also chlorine, the main product is an alkyl halide, which arises by the well-established reaction sequence 1–4 (Hunsdiecker reaction), involving the formation and subsequent free radical chain decarboxylation of an acyl hypohalite.

$$RCO_2Ag + X_2 \rightarrow RCO_2X + AgX \tag{1}$$

$$RCO_2X \longrightarrow RCO_2^{\bullet} + X^{\bullet} \tag{2}$$

$$RCO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2 \tag{3}$$

$$R^{\bullet} + RCO_2X \longrightarrow RX + RCO_2^{\bullet} \tag{4}$$

The use of iodine as the halogen usually leads to an ester; this is known as the Simonini reaction.

$$2RCO_2Ag + I_2 \rightarrow RCO_2R + 2AgI + CO_2$$

Some authors have considered that the Simonini reaction follows an ionic mechanism, but an attractive proposal is the sequence of the Hunsdiecker reaction leading to an alkyl iodide, followed by reaction of the iodide with more silver salt (eq. 5).

$$RX + RCO_2Ag \rightarrow AgX + RCO_2R \tag{5}$$

Consistent with either view are observations on the stereochemistry of the Simonini reaction;[4] optically active silver β-phenylisobutyrate gives a Simonini ester which may be hydrolysed to optically active β-phenylisobutyric acid and racemic β-phenylisopropyl alcohol.

An added complication mechanistically is that a complex of consistution $(RCO_2)_2AgI$ may often be isolated from reaction mixtures of silver salt and iodine.[5] The complex may subsequently be decomposed to give the ester, but neither the structure of the complex, nor its function, if any, in the reaction mechanism has been elucidated.

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One possibility might be that. on heating. the complex simply dissociates (eq. 6).

$$(RCO_2)AgI \rightleftharpoons RCO_2I + RCO_2Ag \qquad (6)$$

We became interested in the relationship between the Hunsdiecker and Simonini reactions through a study of the effects of temperature on the decomposition of benzoyl hypochlorite.[6] The relative difficulty of decarboxylation of benzoate radicals (eq. 3; R = Ph) makes the production of chlorobenzene efficient only at elevated temperatures. By contrast. the degradation of aliphatic silver carboxylates with halogen often proceeds more successfully on lowering the reaction temperature.* We proposed[6] that this might be the result of partial destruction of these halides at elevated temperatures. perhaps by some process such as shown in eq. 7.

$$Ag^+ + RX \rightarrow AgX + R^+ \rightarrow \text{byproducts} \qquad (7)$$

The present work was originally undertaken to investigate this proposal. to which end we have carried out a systematic study of the degradation of representative silver carboxylates with all three halogens under controlled conditions. examining byproducts as well as halides. This was necessary because most previous investigators have recorded only the yields of halides. and have neglected side products. We soon found that the Simonini ester frequently appeared as a product. and the results of our study lead us to new conclusions regarding the synthetic scope of the Hunsdiecker reaction. as well as confirming the reaction sequence 1–5 for the mechanism of the Simonini reaction.

RESULTS AND DISCUSSION

In the first series of experiments. we degraded the silver salts of valeric. isobutyric. pivalic. and phenylacetic acids. representing R of RCO_2Ag as primary. secondary. tertiary and benzylic. All three halogens were used. and the reaction conditions. notably temperature and reactant ratio $RCO_2Ag : X_2$. were varied. The main products of these reactions were the halide and the ester. though in some cases other products were also formed. A parallel study of the reaction between the alkyl halides and the starting silver salts was also carried out to determine whether the ester would be produced. In every case a correlation was noted between those silver salt-halogen reactions that afforded ester. with those silver salt-alkyl halide reactions that gave the same ester. The study is summarised in Table 1. and the results are consistent with the view that the alkyl halide is at least a plausible intermediate in ester production. In the following paragraphs we examine some of the results in more detail.

TABLE 1. PRODUCTS OF THE DEGRADATION OF SILVER CARBOXYLATES WITH HALOGEN

Silver Salt	Products from: Cl_2	Br_2	I_2
Valerate	RX	RX	RX + RCO_2R[a]
Isobutyrate	RX	RX + RCO_2R[a]	RCO_2R
Phenylacetate	RX	RX + RCO_2R[a]	RCO_2R
Pivalate	RX	RCO_2R	RCO_2R

[a] Significant amounts of ester were formed only at reflux in these reactions.

Note: Formation of ester from the reaction $RCO_2Ag + RX \rightarrow RCO_2R + AgX$ was observed *only* in those cases where the corresponding reaction between RCO_2Ag and X_2 afforded the same ester.

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* For examples and references see ref. 2 and Table 6 of ref. 6.

TABLE 2. ALKYL CHLORIDES FROM THE REACTION OF CHLORINE WITH SILVER CARBOXYLATES IN CCl_4

Silver Salt	Cl_2[a]	Conditions	RCl[a]
Valerate[b]	1·00	reflux. 1 hr	0·14[c]
	1·01	25°. 1 hr[d]	0·12
	1·03	−70°. 1 hr[d]	0·19[c]
Isobutyrate[b, e]	1·00	98°. 1 hr[d]	0·20[c]
	1·01	25°. 1½ hr[d]	0·18[c]
Pivalate[b]	0·99	25°. ½ hr[d]	0·17[c]
Phenylacetate[f]	0·96	reflux. 1 hr	0·41[c]
	0·99	25°. 1 hr	0·30[c]

For explanation of notes. see Table 6.

Chlorine as halogen (Table 2)

Reactions between alkyl chlorides and the silver carboxylates were generally unsuccessful. and correspondingly. ester formation does not complicate the reactions of chlorine with these salts. However. with this halogen. a different side reaction intervenes. The silver salts of valeric. isobutyric. and pivalic acid all afforded only low (< 20%) yields of alkyl chloride. together with starting acid. and the products of further chlorination of both acid and product alkyl chloride. In these systems gas evolution began immediately on mixing the reactants. and the polychlorides were not suppressed even in the dark at −70°. It seems clear that free radical chain chlorination is occurring. and the facile initiation of the reaction suggests that the decomposition of the acyl hypochlorite (eq. 2, $X = Cl$) is responsible. Acyl hypochlorites have previously[7] been shown to be thermally much less stable than their hypobromite counterparts. but it is not clear whether the chlorinating species is elemental chlorine (eq. 8–9) or the acyl hypochlorite itself (eq. 8–10) or both. The sequence 8–10 is suggested by analogy with the sequence proposed for the chlorination of alkanes by benzoyl hypochlorite.[8]

$$R'^{\bullet} + Cl_2 \rightarrow R'Cl + Cl^{\bullet} \tag{8}$$

$$Cl^{\bullet} + R'H \rightarrow HCl + R'^{\bullet} \tag{9}$$

$$HCl + RCO_2Cl \rightarrow Cl_2 + RCO_2H \tag{10}$$

(R′ is the alkyl group obtained by removal of hydrogen from any appropriate substrate).

In the case of silver phenylacetate and its product benzyl chloride. the only abstractable hydrogens are adjacent to a deactivating group. so that a better yield of the normal degradation product results. Likewise. the previously studied silver benzoate has no easily abstracted hydrogens and gives up to 60% of PhCl.[6]

The tendency towards polychlorination imposes a severe restraint on the use of chlorine as the halogen. and we predict that only if the group R contains hydrogens relatively inert towards abstraction can chlorine successfully be used in the Hunsdiecker reaction. This is in contrast to previous suppositions of the similarity of behaviour of chlorine and bromine; on the contrary. the reason for the successful application of bromine in the Hunsdiecker reaction is its relative unreactivity in hydrogen abstraction.

To try to overcome this limitation on the use of chlorine. we studied the reactions of silver benzoate and silver valerate with iodobenzene dichloride and sulphuryl chloride as potential chlorine carriers. Neither was successful; iodobenzene dichloride afforded only its own decomposition products. and sulphuryl chloride was unreactive under our conditions. Sulphuryl chloride has previously been observed to degrade silver benzoate to PhCl.[9] but only at about 200° in the gas phase;[10] our reactions were all carried out in refluxing or cold CCl_4.

TABLE 3. PRODUCTS OF THE DEGRADATION OF SILVER CARBOXYLATES WITH BROMINE IN CCl_4

Silver Salt	Br_2[a]	Conditions	RBr[a]	RCO_2R[a]	
Valerate[b]	0·97	reflux. 1 hr	0·86[c]	none[c]	
	0·52	reflux. 1 hr	0·43	none	
	1·03	25°. 6 hr	0·83[c]	none[c]	
Isobutyrate[b]	1·02	reflux. 1 hr	0·75	0·02	
	0·77	reflux. 1 hr	0·50	0·06	
	0·51	reflux. 1 hr	0·28	0·11	
	1·00	25°. 2 hr	0·77	<0·01	
	0·50	25°. 2 hr	0·34	0·05	
					RCO_2H[a]
Pivalate[g]	0·77	reflux. 1 hr	none[b]	0·12[f]	0·37[f]
	0·53	reflux. 1 hr	none[b]	0·02[f]	0·23[f]
	0·75	25°. 1 hr	none[b]	0·09[f]	0·28[f]
	0·75	0°. 1 hr	<0·01[b]	0·04[f]	0·18[f]
	0·60	0°. 1 hr	<0·01[b]	0·02[f]	0·45[f]
Phenylacetate[f]	1·02	reflux. 1 hr	0·58	0·11	0·10
	0·80	reflux. 1 hr	0·47	0·16	0·09
	0·51	reflux. 1 hr	0·05	0·30	0·17
	0·99	25°. 2 hr	0·25[c]	0·01[c]	0·31[c]

For explanation of notes. see Table 6.

Bromine as halogen (Tables 3 and 4)

These experiments affirm the great success that has been obtained using bromine as the halogen in the Hunsdiecker reaction. It is noteworthy that free radical bromination reactions are not observed. and that the further reaction of the alkyl bromide with more silver salt is significant only for the tertiary acid salt. silver pivalate. and for the silver salts of isobutyric acid and phenylacetic acid at elevated temperatures. One point that has not been remarked on previously is the formation of ester in these latter cases when a deficiency of bromine is used; for example. we obtained 60% of benzyl phenylacetate from silver phenylacetate and a half molar quantity of bromine.

The results with silver pivalate are consistent with those that have been obtained previously for other non-bridgehead tertiary acids. Usually such systems afford mainly the parent acid on an attempted Hunsdiecker degradation.[2] We found no

TABLE 4. PRODUCTION OF ESTER FROM THE REACTION OF SILVER CARBOXYLATES WITH ALKYL BROMIDES IN CCl_4

Silver Salt	RBr^a	Conditions	RCO_2R^a	RCO_2H^a
Valerate[b]	1·00	reflux. 4 hr	none[c]	
Isobutyrate[b]	2·12	reflux. 2½ hr	0·92[c]	
	2·06	25°. 3 hr	trace	
	1·92	25°. 19 hr	0·11	
Pivalate[f,g]	1·04	reflux. 3 hr	<0·03	0·98
	1·18	25°. 2 hr	0·45	0·50
	1·10	0°. 1 hr	0·50	0·47
	1·03	−70°. 1 hr	0·39	0·30
Phenylacetate[f]	1·04	reflux. 2½ hr	0·99[c]	
	1·01	25°. 2 hr	0·06[c]	

For explanation of notes. see Table 6.

more than traces of t-butyl bromide from silver pivalate and bromine even at 0°, but in addition to the free acid, we also found the Simonini ester, t-butyl pivalate. The ratio of pivalic acid to t-butyl pivalate is temperature dependent, relatively more of the acid being formed at high temperatures. From t-butyl bromide and silver pivalate the ratio of ester to acid ranged from <0·03 at reflux to 1·31 at −70°. This variation results from elimination from t-butyl bromide competing more successfully with nucleophilic substitution as the temperature is raised, and is not the result of decomposition of the ester, which we find is stable to at least 150° (*cf.* the decomposition of, for example, sec. butyl esters,[11] but only at a much higher temperature).

The fact that t-butyl bromide and silver pivalate react even at −70° makes it clear that t-butyl bromide may not be prepared from silver pivalate and bromine. Indeed the only related decarboxylations of pivaloyl derivatives to t-butyl halides have both involved reactions not proceeding through metal salts *viz.* formation and subsequent decarboxylation of the pivaloyl hypohalite by transhalogenation of the acid with another positive halogen compound. t-butyl hypoiodite[12] or bromine monoxide.[13] The lack of ester production in these latter reactions constitutes confirmatory evidence for the involvement of a metal salt/alkyl halide pathway in ester formation.

Iodine as halogen (Tables 5 and 6)

The Hunsdiecker reaction has only rarely been applied to the preparation of alkyl iodides. though perfluoroalkyl iodides may be prepared in good yield.[14–16] The reason usually advanced for lack of success with alkyl iodide formation is that ester production predominates. However, using more iodine than the 0·5 mole required by the Simonini reaction, preparation of primary alkyl iodides becomes feasible.[17, 18] We find for instance that on raising the iodine to silver salt reactant ratio from 0·42 to 1·82 the ratio of 1-iodobutane to butyl valerate produced increases from 0·16 to 3·81.

TABLE 5. PRODUCTS OF THE DEGRADATION OF SILVER CARBOXYLATES BY IODINE IN CCl_4

Silver Salt	I_2[a]	Conditions	RI[a]	RCO_2R[a]	
Valerate[b]	1·82	reflux. 1 hr	0·78	0·14	
	1·02	reflux. 1 hr	0·77	0·10	
	0·99	reflux. 3 hr	0·64[c]	0·19[c]	
	0·45	reflux. 3 hr	0·19	0·31	
	0·42	reflux. 3 hr	0·06	0·41	
	0·54	25°. 24 hr	none	none	(RCO_2I 0·40[a])
Isobutyrate[b,g]	0·75	reflux. 1 hr	<0·01	0·40	
	0·58	reflux. 1 hr	none	0·41	
	0·76	25°. 380 hr	0·03	0·38	
	0·60	25°. 380 hr	<0·01	0·28	
					RCO_2H[a]
Pivalate[g]	0·96	25°. 24 hr	none[b]	0·17[f]	0·29[f]
	0·76	25°. 24 hr	none[b]	0·16[f]	0·28[f]
	0·51	25°. 24 hr	none[b]	none[f]	(RCO_2I 0·26[a])
Phenylacetate[f]	0·54	reflux. 1 hr	0·03	0·39	0·06
	0·66	25°. 24 hr	trace	0·41	0·07

For explanation of notes. see Table 6.

TABLE 6. PRODUCTION OF ESTERS FROM THE REACTION OF SILVER CARBOXYLATES WITH ALKYL IODIDES IN CCl_4

Silver Salt	RI[a]	Conditions	RCO_2R[a]	
Valerate[b]	1·01	reflux. 4 hr	1·00[c]	
	1·07	25°. 4 hr	none[c]	
Isobutyrate[b,g]	1·10	25°. 2 hr	0·99[c]	
				RCO_2H[a]
Pivalate[f,g]	1·02	25°. 2 hr	0·14	0·68
	0·99	0°. 1 hr	0·23	0·31
	1·04	0°. 1 hr	0·18	0·61
Phenylacetate[f]	1·03	reflux. 2 hr	0·98	
	1·06	25°. 1½ hr	0·72	

[a] All quantities in mole/mole of silver salt
[b] products analysed by VPC
[c] average value from two experiments
[d] protected from the light
[e] reactions carried out in sealed ampoules
[f] products analysed by NMR
[g] solvent was Freon 113

However the method seems to have possibilities only for primary alkyl iodides; the silver salts of isobutyric. phenylacetic and pivalic acids gave no more than traces of iodides. and correspondingly. the reactions between silver salt and alkyl iodide were noted as being very facile.[*]

Reactions between the silver salts and iodine in the cold led to the Simonini complex. which decomposes very slowly at room temperature. though faster if excess iodine is present. Use of the volatile Freon 113 as reaction medium and filtration yielded a colourless solution which retained oxidising properties and appears to contain a mixture of the Simonini complex and the acyl hypohalite; in the case of the solution from silver valerate and iodine. decomposition at reflux yielded both iodide and ester together with AgI. However. the AgI was insufficient to account for all of the oxidant as $(RCO_2)_2AgI$. Attempts to obtain characterisable substances by removal of the volatile solvent were unsuccessful.

Aromatic systems (Tables 7 and 8)

The evidence presented so far is compatible with the reaction sequence 1-5 leading to the ester. with 6 as an unrelated side reaction. If this sequence were indeed operative it would follow that ester production should be suppressed when the nucleophilic

TABLE 7. DEGRADATION OF SILVER BENZOATE WITH THE HALOGENS[a]

Halogen	Conditions[b]	PhX	$PhCO_2Ph$
I	benzene. reflux	32%	17%
I	benzene. 5°	9	44
I	CCl_4. reflux	18	none
Br	benzene. reflux	26	2
Br	benzene. 5°	25	14
Br[c]	CCl_4. reflux	46	none
Br[c]	CCl_4. 3°	5	none
Cl	benzene. reflux	85	2
Cl	benzene. 5°	70	4
Cl[c]	CCl_4. reflux	65	none
Cl[c]	CCl_4. 3°	3	none

For explanation of notes. see Table 8.

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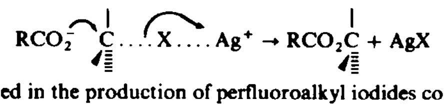
[*] An unresolved question is the nature of the nucleophilic reaction 5. The problem is complicated by the heterogeneity of the reaction. but in principle either a direct displacement (quasi S_N2) or the intermediate formation of a carbonium ion could be involved. Certainly a carbonium ion is involved in some cases. for example the observation of rearranged ester in the degradation of cyclobutanecarboxylic acid,[19] and is suggested by the ease of substitution which increases in the order R(prim.) < R(sec.) < R(tert.). However. the lack of rearrangement in other cases e.g. silver β-phenylisobutyrate cited above[4] argues against the involvement of carbonium ions in that case. Possibly substitution involves a displacement of the type envisioned by Swain[20] which we would formulate as 8. which in its extreme forms becomes either S_N1 or S_N2.



$$\mathrm{RCO_2^-}\ \mathrm{C}\cdots\mathrm{X}\cdots\mathrm{Ag^+} \rightarrow \mathrm{RCO_2C} + \mathrm{AgX} \tag{8}$$

Thus. the great success enjoyed in the production of perfluoroalkyl iodides could be the result of either of instability of R^+ or of the feeble nucleophilicity of the perfluorocarboxylate ion.

reaction 5 fails, and this is the case with the four acids studied and the perfluoroacids referred to above. A test of the mechanism is that ester production should also fail if the group R were either aryl or the bridgehead of a rigid bicyclic system.

TABLE 8. DEGRADATION OF SILVER *p*-NITROBENZOATE WITH THE HALOGENS[a]

Halogen	Conditions[b]	PhX	p-$NO_2C_6H_4X$	p-$NO_2C_6H_4CO_2Ph$
I	benzene, reflux	14%	1%	8%
I	benzene, 5°	4	none	<1
Br	benzene, reflux	58	none	1
Br	benzene, 5°	65	none	1
Br[c]	CCl_4, reflux	none	76	none
Br[c]	CCl_4, 3°	none	2	none
Cl	benzene, reflux	43	none	<1
Cl	benzene, 5°	65	1	<1

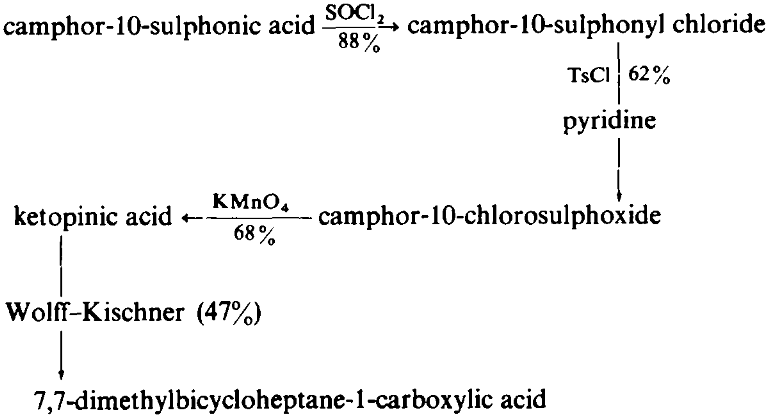
[a] equimolar ratios of silver salt to halogen
[b] reactions at reflux heated for 2–3 hr, those in the cold allowed to react for 7–15 days.
[c] data of ref. 6

In apparent contrast, the reaction of silver benzoate and iodine in benzene has been reported[21] to give a low yield of phenyl benzoate. We have confirmed this result, but we believe that the ester formed is not the Simonini ester but rather the product of attack of benzoate radicals on the solvent benzene, for the following reasons. First, no phenyl benzoate is formed in CCl_4 from either silver benzoate and iodine or the preformed Simonini complex. Second, phenyl benzoate production increases at lower temperatures, behaviour typical of the attack of benzoate radicals on benzene.[6,22] Third, the reaction of silver *p*-nitrobenzoate with iodine leads not to the Simonini ester, *p*-nitrophenyl *p*-nitrobenzoate, but to phenyl *p*-nitrobenzoate; thus the Ph group must have come from the solvent.

The reactions of silver *p*-nitrobenzoate with the halogens gave in addition to the unsymmetrical ester, the halobenzene and the *p*-nitrohalobenzene. The latter is the normal Hunsdiecker product, but the halobenzene is the result of electrophilic substitution of the solvent by the acyl hypohalite intermediate.[6,23] The extent of electrophilic substitution increases in the expected order for $I < Br < Cl$. In benzene solvent, the ester and the halobenzene completely overshadow the normal Hunsdiecker product, though changing the solvent to CCl_4 allows its production in good yield and the suppression of the ester and the halobenzene. Thus, in benzene solvent, the Hunsdiecker degradation has to compete both with another free radical reaction giving ester, and with an ionic reaction involving electrophilic substitution of the solvent.

Bicyclic systems

The inertness of the bridgehead of a rigid bicyclic system towards both S_N1 and S_N2 reactions[24,25] should make the production of the Simonini ester unlikely in such cases. The particularly inflexible bicyclo [2.2.1] heptane system is suitable for study; we prepared the bridgehead carboxylic acid of 7,7-dimethylbicycloheptane from camphor-10-sulphonic acid by the route shown.[26]



Recently.[27] a method involving the transformation of the sulphonyl chloride directly to ketopinic acid has been published. with only marginal sacrifice in yield.

Treatment with iodine in cyclohexane of the silver salt thus obtained gave an excellent yield of the bridgehead iodide, uncontaminated with ester. This behaviour is again consistent with a metal salt/alkyl halide route to the Simonini ester. since the bicycloheptyl system is so inert towards bridgehead nucleophilic substitution.

Degradation[28] of the corresponding bicyclo[2.2.2]octane-1-carboxylic acid has given a different result in that the Simonini ester was obtained but no iodide. The degradation was effected using HgO and iodine. but since we have shown[13] that this variant of the Hunsdiecker reaction is mechanistically similar to the Hunsdiecker reaction itself, the result is unexpected. Possibly the result may be explained in terms of the greater flexibility of the bicyclooctane compared with the bicycloheptane system making the former more amenable to nucleophilic substitution at the bridgehead.[29]

CONCLUSIONS

In summary. our studies strongly support the reaction sequence 1–5 for the formation of the Simonini ester. making the Simonini reaction simply a variant of the Hunsdiecker reaction. While the evidence is permissive only, there seems no reason to favour any other route. An unresolved problem is whether or not carbonium ion intermediates are formed in the nucleophilic substitution step 5. but this point cannot be resolved on the evidence at hand.

Additionally however our results lead us to new conclusions as to the synthetic scope of the Hunsdiecker reaction. The great success of the use of bromine in this degradation results from the fact that side reactions. which variously interfere with the corresponding reactions with chlorine and iodine. do not interfere in the case of bromine. With chlorine. the problem is the intervention of a readily initiated free radical chain chlorination; this makes the Hunsdiecker reaction for chlorine almost useless except where the silver salt does not bear readily abstractable hydrogen atoms.

Free radical bromination is so slow by comparison that the Hunsdiecker reaction may compete successfully in this case. With iodine on the other hand the difficulty lies in the lability of the first formed alkyl iodide, which contains the excellent potential leaving group I^- and is thus susceptible both to nucleophilic substitution, affording the Simonini ester, and to elimination. Again, for degradations by bromine this side reaction is usually unimportant because bromide ion is a poorer leaving group and thus confers greater stability on the halide product.

Finally the synthetic usefulness of the Hunsdiecker reaction may be compared with that of the variant degradation using the acid, HgO, and halogen, introduced by Cristol and Firth.[30] In a separate study in this laboratory we have shown[13] that the latter reaction involves formation of a mercuric carboxylate salt, followed by a Hunsdiecker type degradation with halogen. The reaction is thus parallel to the Hunsdiecker, rather than complementary in that limitations to the Hunsdiecker reaction such as those described above also apply to the HgO method. There is an additional limitation that a reasonably soluble mercuric carboxylate must be formed under the conditions of the reaction, and this in practice excludes many aromatic acids from success. Nevertheless, the simplicity of the HgO method, in particular the avoidance of separately preparing and drying the silver salt, makes it a very attractive alternative to the conventional Hunsdiecker reaction, even though the yields of halides obtained are usually slightly lower.

EXPERIMENTAL

Solvents were reagent grade materials, dried using activated molecular sieve type No. 3A. The carboxylic acids and most of the alkyl halides used as authentic samples for comparison with reaction products were obtained from British Drug Houses Ltd. or Aldrich Chemical Inc. For conversion to the silver salt a solution of the acid in EtOH aq was treated with an equimolar quantity of $AgNO_3$ aq and then neutralised with an equimolar quantity of NaOH aq, whereupon the silver salt was deposited as an off-white to grey powder. The mixture was filtered, washed with water then acetone, and dried at 65° for several days before use.

Vapour phase chromotographic (VPC) analyses were carried out using a Varian Aerograph Model A90-P3 instrument using helium as carrier gas. Quantitative determinations were made by adding a measured quantity of a standard substance to the reaction and comparing the ratio of the area of the standard substance with that of the unknown. All such analyses were carried out in triplicate, and reported values are the average. The response of the gas chromatograph was assumed to be equal toward isomers, but where necessary calibration curves were constructed to relate area ratios to molar ratios. When a product was first formed in a reaction, it was isolated and its identity checked by the standard procedures, usually by comparison with authentic material; thereafter, its VPC retention time was taken to be characteristic. NMR analyses involved the use of a Varian Associated A60-A instrument. A weighed quantity of a standard substance was added to the reaction, and the area under the resonance peak due to the standard was compared with that due to the compound in question.

Aromatic esters were prepared by interaction of equimolar quantities of the acid chloride, the phenol, and dry pyridine at reflux in benzene. After filtration to remove py. HCl the ester usually crystallised from the hot filtrate. Thus prepared were phenyl benzoate m.p. 67–69° (lit.[31] 69°), phenyl *p*-nitrobenzoate m.p. 126–128° (lit.[32] 129°), and *p*-nitrophenyl *p*-nitrobenzoate m.p. 156–162° (lit.[33] 159°).

BzI m.p. 22–23° (lit.[31] 24°) was prepared by the action of NaI on BzCl in acetone at reflux. *p*-Bromonitrobenzene m.p. 126–126·5° (lit.[31] 126°) and *p*-iodonitrobenzene m.p. 175–177° (lit.[31] 176°) were prepared from *p*-nitroaniline through the diazonium salt.

Preparation of silver 7,7-*dimethylbicyclo* [2.2.1] *heptane*-1-*carboxylate*

Camphor-10-*sulphonyl chloride.*[34, 35] The acid chloride was prepared from camphor-10-sulphonic acid (50g) by the action of $SOCl_2$ in the presence of powdered $CaCO_3$, according to the procedure of Warnhoff and Joshi. Recrystallisation from ligroin gave the chloride (47g, 88%) as off-white crystals m.p. 64–66°

(lit.[35] 68). The NMR spectrum ($CDCl_3$) showed the diastereomeric protons on C 10 as doublets centred on τ 5·67 and τ 6·25. J 14·5 c/s.

Camphor-10-chlorosulphoxide.[34,36,37] Dropwise addition of a hot dry dioxan solution of camphor-10-sulphonyl chloride (40 g) to a mixture of p-TsCl (30·6 g) and dry pyridine at 90° by the modified[34] procedure of Strating.[36] gave a dark viscous oil.* The chlorosulphoxide was extracted by refluxing with ether. followed by filtration. and evaporation of ether from the filtrate. The crude solid was recrystallised from ligroin to give. including a second crop of crystals. camphor-10-chlorosulphoxide (23 g) m.p. 83–85° (lit.[37] 86°) as off-white crystals.

Ketopinic acid.[26] To a 1 l beaker containing water (100 ml) and acetone (100 ml)† was added camphor-10-chlorosulphoxide (20 g). The solution was stirred and $Na_2CO_3.H_2O$ (22 g) added. $KMnO_4$ (63 g) was now added in small portions over 90 min, the exothermic nature of the reaction causing extensive frothing. After 1 hr. the solution was filtered using HyFlow Super Cel and the filtrate acidified with conc HCl. Repeated extraction with ether followed by evaporation of solvent and recrystallisation from water afforded ketopinic acid 12·5 g (68%) as colourless needles m.p. 233–235° (lit.[26] 234°). The IR spectrum ($CHCl_3$) showed C=O stretching frequencies at 1660 and 1725 cm^{-1}.

7.7-Dimethylbicyclo [2.2.1] *heptane-1-carboxylic acid.* In a two necked 250 ml flask equipped with an air reflux condenser and thermometer were placed diethylene glycol (100 ml), ketopinic acid (10 g), and KOH (2·0 g). Hydrazine hydrate (10 ml) was added and the mixture heated until the mixture reached 205°. water formed being thereby distilled. This temp was maintained for 4 hr. The cooled mixture was diluted with water. acidified. and extracted repeatedly with ether. but without success. The water was therefore distilled whereupon a white solid sublimed into the condenser. Further material crystallised from the solvent when distillation of the water was complete. Recrystallisation from water afforded the acid (4·6 g. 47%) m.p. 210–213° (lit.[26] 218°). The IR spectrum ($CHCl_3$) showed C=O absorption only at 1715 cm^{-1}.

Silver salt of 7.7-dimethylbicyclo [2.2.1] *heptane carboxylic acid.*[38] The acid (4·61 g) was allowed to react with $AgNO_3$ (4·76 g) in a solution of NH_3 aq after the procedure of Wilder and Winston.[38] The precipitated silver salt was dried for several days at 62° and was obtained as 6·5 g (86%) of an off-white powder. (Calc. for $C_{10}H_{15}O_2Ag$: C. 43·26; H. 5·41. Found: C. 42·76; H. 5·67%).

Degradations of silver salts with halogens (Tables 2, 3, 5, 7 and 8)

The following procedures are typical.

Silver valerate with iodine at reflux. To a mixture of silver valerate (0·840 g. 4·02 m moles) and dry CCl_4 (15 ml) at reflux in a 25 ml flask equipped with reflux condenser and $CaCl_2$ tube was added I_2 (1·040 g. 4·09 m moles). The mixture was maintained at reflux for 1 hr then 1-bromobutane (0·327 g. 2·39 m moles) was added as a VPC standard. Analysis by VPC (10% SE30 on acid washed 60/80 Chromosorb W. 90°) indicated the presence of 1-iodobutane (3·09 m moles) and butyl valerate (0·41 m moles). A titration with standard sodium thiosulphate solution showed that 0·63 m mole of I_2 had not been consumed.

Silver phenylacetate with bromine at reflux. To a mixture of silver phenylacetate (0·912 g. 3·77 m moles) and dry CCl_4 (10 ml) at reflux was added 3·0 ml of a 1·01 M solution of Br_2 in dry CCl_4. After 1 hr at reflux. 2·0 ml of a 0·52 M solution of BzCl in CCl_4 was added as standard. and the solvent evaporated. NMR analysis indicated the presence of BzBr (τ 5·7. 1·76 m moles). benzyl phenylacetate (τ 5·0 and τ 6·5. 0·60 m moles). and free phenylacetic acid (τ-2·0 and τ 6·6. 0·35 m mole).

Silver pivalate with t-butyl bromide at 25°. To a mixture of silver pivalate (4·2 g. 20 m moles) and dry Freon 113 (30 ml) in a 50 ml Erlenmeyer flask was added t-butyl bromide (3·0 g. 22 m moles). The flask was stoppered and the contents stirred for 2 hr. Filtration. followed by evaporation of solvent afforded a residue (3·2 g) which showed C=O absorption in the IR at 1700 and 1720 cm^{-1}. The NMR spectrum showed resonances at τ 2·0 and τ 8·8 (pivalic acid, 12·6 m moles) and τ 8·6 and τ 8·9 (t-butyl pivalate, 11·3 m moles). The mixture was redissolved in Freon 113 and extracted with $NaHCO_3$ aq to give, after evaporation, a residue which showed C=O absorption at only 1720 cm^{-1} in the IR and an NMR spectrum consisting only of two resonances of equal area at τ 8·6 and τ 8·9 (t-butyl pivalate).

Reaction of silver valerate with iodine at 25°

A mixture of silver valerate (3·703 g. 17·7 m moles). dry Freon 113 (50 ml) and I_2 (2·254 g. 8·87 m moles)

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* Strating[36] obtained a solid at this point. We always obtained an oil which was treated according to the earlier procedure of Wedekind *et al.*[37]

† The use of a mixture of acetone and water. taken from the procedure for isoketopinic acid[34] avoids the use of a large quantity of solution.[37]

in a stoppered Erlenmeyer flask was stirred at 25° for 45 min. by which time the colour of I_2 was discharged. Filtration afforded 44 ml of a colourless solution, a portion of which was analysed iodometrically indicating the presence of 4·41 m moles of (I^+). After the iodometric titration VPC analysis of the organic phase (SE30. 90°) showed that neither 1-iodobutane nor butyl valerate was present. Another portion (10 ml) of the filtrate was heated to reflux for 20 min. AgI (~0·10 g) was precipitated. and VPC analysis (SE30. 90°) after the addition of 1-bromobutane (0·190 g) as a standard indicated that 1-iodobutane (0·57 m mole) and butyl valerate (0·60 m mole) had been formed. After reflux, this portion of the filtrate assumed the colour of molecular iodine. which was shown iodometrically to be present to the extent of 0·06 m mole.

Isolation of isobutylene from the reaction of bromine with silver pivalate

Silver pivalate (50 m moles) and CCl_4 (50 ml) were heated to reflux in a 100 ml three necked flask equipped with reflux condenser, dropping funnel, and N_2 gas inlet. The N_2 was saturated with CCl_4 by passing through a wash bottle containing the solvent. Through the dropping funnel was added dropwise a 1 M solution of Br_2 in CCl_4 until the Br_2 colouration persisted in the solution. The exhaust gases were led from the top of the condenser into a solution of Br_2 in CCl_4. After reaction the excess of Br_2 and most of the CCl_4 were removed; the residue on examination by NMR showed the two singlet resonances τ 8·1 and τ 6·1 characteristic of isobutylene dibromide.

Reaction of iodine with silver 7.7-*dimethylbicyclo* [2.2.1] *heptane*-1-*carboxylate*

A mixture of 2·0 g of the silver salt and I_2 (4·0 g) in 11 ml cyclohexane* was heated to reflux for 1 hr. A portion of the solution was analysed by VPC (SE30. 110°) using bromocyclohexane as standard. One main product. assigned to 7.7-dimethyl-1-iodobicyclo [2.2.1] heptane was present (80%). The remaining solution was washed successively with sodium thiosulphate. Na_2CO_3, and water. then dried. Examination of the residue by IR indicated that no C=O containing material was present. Preparative VPC, followed by vacuum sublimation gave the iodide. m.p. 128–129·5 (lit.[12] 132°). (Calc. for $C_9H_{15}I$: C. 43·20; H. 6·05; I. 50·75. Found: C. 43·47; H. 6·07; I. 50·53%). Repetition of the experiment gave the iodide (86%) and again no ester.

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* The use of CCl_4 as solvent leads to considerable formation of alkyl chloride in addition to the iodide.[38] Even using cyclohexane some abstraction from the solvent occurs. since iodocyclohexane (9%) was produced.

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