Substituent Effects on the Rate and Mechanism of the Decomposition of Phenyliodine Dicarboxylates

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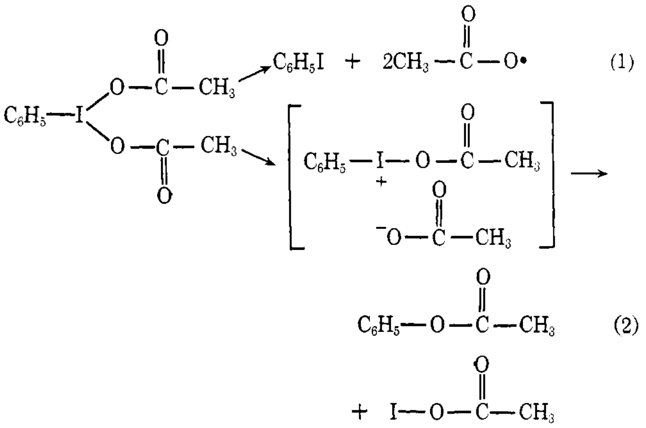
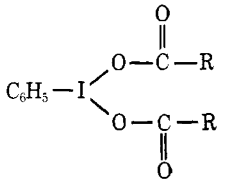
Abstract: As phenyl substituents are introduced into the acetoxy moieties of phenyliodine diacetate, the decomposition is accelerated and the reaction shifts from a predominantly ion-pair process giving phenyl acetate to a radical process giving alkyl esters ROOCR (*p*-chlorophenyl *p*-chlorophenylacetate, benzhydryl diphenylacetate, and trityl triphenylacetate) or alkyl dimers RR. The ester is favored over the hydrocarbon by high initial reagent concentrations, an effect attributed to the stabilization of the acyloxy radicals against decarboxylation while they are still part of a divalent iodine radical. The accelerations produced by one, two, and three phenyl substituents are less than those in the decomposition of the analogous substituted *tert*-butyl peracetates by a factor of 10^4.

In the decomposition of phenyliodine diacetate there are two paths, one leading to phenyl acetate and iodine acetate by way of an ion-pair intermediate, the other leading to iodobenzene and acetoxy radicals[1]



This paper is concerned with the mechanistic consequences of weakening the bond between the carbonyl and alkyl groups of **1** by the successive introduction of phenyl substituents.



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Results

Phenyliodine Bis(phenylacetate) and Derivatives. The decomposition of phenyliodine bis(*p*-chlorophenylacetate) in dry, degassed chlorobenzene at 140° obeys a first-order rate law over a range of initial concentrations from 0.005 to 0.09 *M*. The rate constant is (2.60 ± 0.12) × 10^{-5} sec^{-1} (standard deviation). As in the case of phenyliodine diacetate, traces of water accelerate the decomposition because of hydrolysis to iodosobenzene which then disproportionates to iodobenzene and iodoxybenzene. Initial rate constants for phenyliodine bis(phenylacetate) and other substituted phenylacetates are shown in Table I.

Table I. Initial[a] Rate Constants for the Decomposition of Substituted Phenyliodine Bis(phenylacetate)[b]

Substituent[c]	$k \times 10^5$ sec^{-1}	Substituent[b]	$k \times 10^5$ sec^{-1}
p-Cl	2.60	*m*-Cl	3.13
m-NO_2	4.98	H	3.80
p-CH_3O	13.4	*p*-NO_2	5.37
m-CH_3O	4.41		

[a] In some runs the rate constant increased after the first half-life. [b] 0.03 *M* in C_6H_5Cl at 140°. [c] Substituted in both phenylacetate groups.

The products of the decomposition of phenyliodine bis(*p*-chlorophenylacetate) are shown in Table II.

Table II. Products of the Decomposition of Phenyliodine Bis(*p*-chlorophenylacetate) in Dry Chlorobenzene at 140° [a]

Product	Initial concn of reagent, *M* 0.096	0.047
p,p'-Dichlorobibenzyl	19	24
p-Chlorobenzyl *p*-chlorophenylacetate	33	23
Phenyl *p*-chlorophenylacetate	13	15
p-Chlorophenylacetic acid	21[b]	27
Iodobenzene	85	81
p-Chlorotoluene	<1	<1

[a] Yields in per cent moles per mole of reagent. [b] In the presence of 1.0 *M* $CHCl_3$ the yield of this product increased to 86 mol %.

Phenyliodine Bis(diphenylacetate). The decomposition of this compound was studied at 100°. In chlorobenzene the rate constant is (1.56 ± 0.10) × 10^{-5}, independent of initial concentrations in the range from 0.005 to 0.10 *M*. The fit to a first-order law is good. In contrast to the diacetate and bis(phenylacetate) the bis(diphenylacetate) is not sensitive to traces of water in the solvent. The reaction products are shown in Table III.

Phenyliodine Bis(triphenylacetate). The decomposition of this compound was studied at 79.8°. In degassed benzene the reaction follows a first-order rate

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(1) J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967). The benzoate (J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, **31**, 1153 (1966)) and the anisate (T. T. Wang and J. E. Leffler, *ibid.*, **36**, 1531 (1971)) behave similarly.

Table III. Products from the Decomposition of Phenyliodine Bis(diphenylacetate)[a]

Products[b,c]	Initial concn of reagent, *M*: 0.097	0.052	0.011
Tetraphenylethane	16	28 (0)[c]	62
Phenyl diphenylacetate	4.9	5.3	5.1
Benzhydryl diphenylacetate	68	54 (10)[c]	20
Iodobenzene	94	93	95

[a] In dry, degassed C_6H_5Cl at 100°. Yields in % moles per mole of reagent. [b] The following were found to be absent: diphenylacetic acid, tetraphenylethylene, and diphenylmethane. [c] Figures in parentheses are for a run with added O_2.

law, $k = (7.33 \pm 0.15) \times 10^{-5}$ sec^{-1}, independent of initial concentration in the range from 0.007 to 0.07 *M*. The rate is insensitive to traces of water.

The products from the decomposition in dry benzene at 79.8°, initial concentration 0.027 *M*, were iodobenzene (99% yield), trityl triphenylacetate (94% yield), and CO_2 (98%). Triphenylacetaic acid (4%) is presumed to have come from hydrolysis of the trityl ester during work-up. The phenyl ester, trityl iodide, and triphenylmethane were absent.

Heating a solution of phenyliodine bis(triphenylacetate) to 100 or 125° in degassed benzene produces a transient yellow substance whose visible and esr[2] spectra are identical with those of triphenylmethyl.

Photolysis of phenyliodine bis(triphenylacetate) in degassed benzene (350 nm) gave trityl triphenylacetate in 60% yield provided that illumination was not continued too long.

Experimental Section[3]

Most of the phenyliodine dicarboxylates used in this study were made by metathesis of phenyliodine diacetate with the corresponding carboxylic acid, as in the procedure given for phenyliodine bis(triphenylacetate).

Phenyliodine Bis(triphenylacetate) (Method A). To a mixture of 5.76 g (0.02 mol) of triphenylacetic acid and 150 ml of anhydrous ether was added 3.22 g (0.01 mol) of phenyliodine diacetate The mixture was stirred for 6 hr, after which the fine white precipitate was collected and recrystallized from chloroform–petroleum ether: yield 6.25 g (80%); mp 138.5–140° dec; equiv wt 387 (calcd 389); carbonyl stretching frequency, 1640 cm^{-1} in CS_2.

Phenyliodine Bis(phenylacetate) (Method B).[4] To a mixture of 4.88 g (0.02 mol) of the Ag salt of phenylacetic acid in 50 ml of acetonitrile (or anhydrous ethanol) was added 2.75 g (0.01 mol) of phenyliodine dichloride. The yellow mixture was stirred at room temperature for 30 min, after which the AgCl precipitate was filtered out and the solvent stripped off. The residual oil was crystallized from a mixture of CCl_4 and low boiling petroleum ether, giving 3.2 g (68%) of the bis(phenylacetate), white needles, mp 55–59°, 58–60° after recrystallization; equiv wt 239 (calcd 237).

Phenyliodine Bis(diphenylacetate).[5] To a solution of 25.2 g of diphenylacetic acid in dry $CHCl_3$ was added 13.5 g of iodosobenzene. The heterogeneous mixture was refluxed for 75 min under a Soxhlet extractor containing $MgSO_4$ to remove water formed in the reaction After filtration and removal of solvent, 33 g (88.5% yield) of the crude bis(diphenylacetate) was obtained. After three recrystallizations from $CHCl_3$–hexane it melted at 133° dec. It is sensitive to light in the solid state; equiv wt 312 (calcd 313). *Anal.* Calcd for $C_{34}H_{27}O_4I$: C, 65.18; H, 4.34. Found: C, 64.87; H, 4.11. This compound was also made by method A, which gave material melting at 134–136° dec.

For data on the other iodosobenzene derivatives used in this work, see Table IV.

Table IV

Group R in 1	Mp, °C	Equiv wt[a]: Calcd	Found	Synthetic method
p-Chlorobenzyl	124–125	271.5	272	A
m-Chlorobenzyl	85–87	271.5	274	B
p-Nitrobenzyl	145–147	282	283	A
m-Nitrobenzyl	134–136	282	284	A
p-Methoxybenzyl	78–80	267	269	B
m-Methoxybenzyl	46–48	267	270	B
p-Methylbenzyl	93–95	251	255	B

[a] Based on iodometric titration.

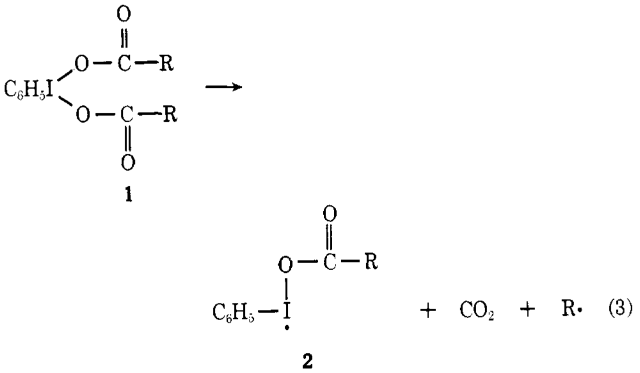
Kinetics and Products. In the kinetic runs sealed, degassed ampoules were quenched by cooling and analyzed for remaining trivalent iodine by reaction with KI in carbonated acetic acid, dilution with carbonated water, and titration to a starch–iodine end point with rapid stirring.[6]

Most of the products were determined by conventional glc using internal standards. *p*-Chlorophenylacetic acid was determined from its infrared intensity. Trityl triphenylacetate was determined gravimetrically.

Discussion

The first-order rate law and the products are compatible with a unimolecular decomposition into radicals as the major reaction. The acceleration on successive introduction of phenyl substituents is compatible with a process in which at least one of the alkyl to carbonyl bonds is weakened in the transition state for the rate-determining step. The effect of substituents in the phenyl groups of the phenylacetoxy moieties of phenyliodine bis(phenylacetate) is also consistent with a rate-determining step leading to benzyl radicals: *both* *p*-nitro and *p*-methoxy accelerate the reaction. Finally, in the case of phenyliodine bis(triphenylacetate), the intermediate trityl radical was detected by its visible and esr spectra.

We suggest that a decomposition with concerted decarboxylation as in eq 3 is followed by the bis(triphenylacetate) and bis(diphenylacetate) and at least in part by the bis(phenylacetate). The relative rates for the series (Table V) show a modest acceleration for one phenyl substituent, a larger one for two, and a 1000-fold acceleration for three. In the case of the mono- and diphenyl-substituted compounds the products still reflect some of the process that is the main decomposition mode for the diacetate, namely, the formation of phenyl esters from ion pairs (eq 2). The yields of the phenyl ester diminish in the series 75, 14, 5, 0% for zero, one, two, and three phenyl substituents in the acetoxy moiety.



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(2) D. B. Chesnut and G. J. Sloan, *J. Chem. Phys.*, **33**, 637 (1960).

(3) D. C. Ward, Dissertation, Florida State University, 1971.

(4) A modification of a procedure developed by N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 4103 (1963).

(5) P. W. Inward, this laboratory.

(6) J. P. Wibaut, H. B. van Leewen, and B. van der Wal, *Recl. Trav. Chim. Pays-Bas*, **73**, 1033 (1954).

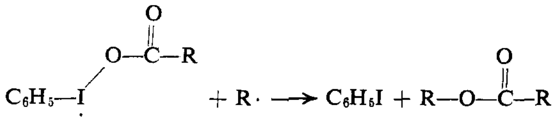
Table V. Effect of Phenyl Substitution on Relative Rates

Number of phenyl substituents	Reaction	
	Phenyliodine diacetates[a]	*tert*-Butyl peracetates[b]
0	[1]	[1]
1	1.4	1.6×10^4
2	26	9×10^5
3	1×10^3	4×10^7

[a] Relative to the rates of phenyliodine diacetate decomposition calculated for 79.8, 100, and 140° using $\Delta H^{\ddagger} = 28.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.2$ cal mol^{-1} deg^{-1}. [b] Recalculated from the activation parameters given in ref 7–9.

The accelerations produced by phenyl substituents in this reaction series are compared with those for the decomposition of the corresponding *tert*-butyl peracetates[7–9] in Table V. At each step in the series the effect is smaller for the phenyliodine diacetates than for the *tert*-butyl peracetates by a factor of about 10^4. We interpret this as meaning that the alkyl to carbonyl bond is much less weakened at the transition state in the former series. Because the radical **2** is more stable than a *tert*-butoxy radical, the transition state is reached earlier in the reaction, in accord with the principle that transition states tend to resemble the products more closely when the products are of higher energy.[10]

A further consequence of the stability of radical **2** is a marked shift to more ester ROOCR at the expense of dimer RR in reactions with higher initial concentrations (Tables II and III). The divalent iodine radical persists long enough to give ester by reaction 4 at high steady-state concentrations, but dissociates into iodobenzene and unstable acyloxy radicals at lower concentrations. The latter decarboxylate and combine to give dimer at the expense of ester.



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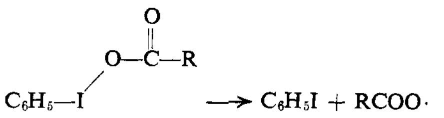

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$$\mathrm{RCOO}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{CO_2} \qquad (6)$$

$$2\mathrm{R}\cdot \longrightarrow \mathrm{R{-}R}$$

In the decomposition of *tert*-butyl triphenylperacetate,[9] Lorand and Bartlett found both trityl *tert*-butyl ether and an "abnormal" para coupling product *p*-*tert*-butoxytriphenylmethane among the products. In contrast, we find only the normal trityl triphenylacetate ester. This may reflect a hidden step in eq 4 in which a transient phenyltrityliodonium triphenylacetate is formed before the ester and iodobenzene.

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(10) (a) J. E. Leffler, *Science*, **117**, 340 (1953); (b) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

Stable Carbocations. CXXXV.[1,2] Protonation of Trihydroxybenzenes and Their Methyl Ethers in Superacids

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Abstract: Protonation of isomeric trihydroxybenzenes and their methyl ethers in four different superacid media (I–IV) was studied. The sites of protonation were found at carbon and/or oxygen. Two different types of diprotonated ions were observed in strongest superacid media (I and II): (i) benzenium ions with a $-\mathrm{OH_2}^+$ or $\mathrm{CH_3O(H)}^+$ substituent at the meta position and (ii) protonated or alkylated oxocyclohexenyl dications. Isomeric monoprotonated benzenium ions derived from the same precursors were observed in weaker superacid media (III and IV).

In the preceding paper, we discussed the protonation of mono- and dihydroxybenzenes and their derivatives.[1] The behavior of trihydroxybenzenes and their methyl ethers in superacids has not yet been studied systematically. Our major interest in the course of this study was directed to establish the site of protonation, the possibility of diprotonation, and the formation of isomeric ions through the influence of substituents in the benzenium ions.

On the other hand, diprotonated 2,4,6-trimethylaniline and 2,4-dimethylaniline were observed in HF–SbF$_5$ solution.[3] These benzenium ions (**1** and **2**)

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(1) Part CXXXIV: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, submitted for publication.

(2) For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 2, 1970, p 845; see reference to unpublished results. Similar results were also obtained in our laboratories.