



**Table III.** Products from the Decomposition of Phenyliodine Bis(diphenylacetate)<sup>a</sup>

Products <sup>b,c</sup>	—Initial concn of reagent, <i>M</i> —		
	0.097	0.052	0.011
Tetraphenylethane	16	28 (0) <sup>c</sup>	62
Phenyl diphenylacetate	4.9	5.3	5.1
Benzhydryl diphenylacetate	68	54 (10) <sup>c</sup>	20
Iodobenzene	94	93	95

<sup>a</sup> In dry, degassed C<sub>6</sub>H<sub>6</sub>Cl at 100°. Yields in % moles per mole of reagent. <sup>b</sup> The following were found to be absent: diphenylacetic acid, tetraphenylethylene, and diphenylmethane. <sup>c</sup> Figures in parentheses are for a run with added O<sub>2</sub>.

law,  $k = (7.33 \pm 0.15) \times 10^{-5} \text{ sec}^{-1}$ , 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<sub>2</sub> (98%). Triphenylacetic 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<sup>2</sup> 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<sup>3</sup>

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<sup>-1</sup> in CS<sub>2</sub>.

**Phenyliodine Bis(phenylacetate) (Method B).**<sup>4</sup> 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<sub>4</sub> 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).**<sup>5</sup> To a solution of 25.2 g of diphenylacetic acid in dry CHCl<sub>3</sub> was added 13.5 g of iodobenzene. The heterogeneous mixture was refluxed for 75 min under a Soxhlet extractor containing MgSO<sub>4</sub> 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<sub>3</sub>–hexane it melted at 133° dec. It is sensitive to light in the solid state; equiv wt 312 (calcd 313). *Anal.* Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>I: 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 iodobenzene derivatives used in this work, see Table IV.

(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.

**Table IV**

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

<sup>a</sup> Based on iodometric titration.

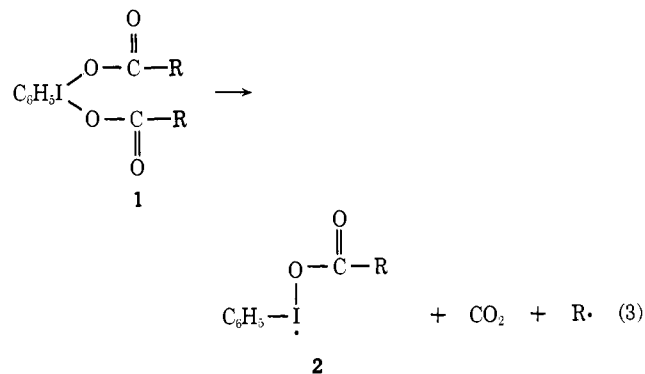
**Kinetics and Products.** In the kinetic runs sealed, degassed ampoules were quenched by cooling and analyzed for remaining trivalent iodine by reaction with KI in carbonated acetic acid, dilution with carbonated water, and titration to a starch–iodine end point with rapid stirring.<sup>6</sup>

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 phenylacetate 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(triphenyl-



acetate) 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.

(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	
	Phenyl iodine diacetates <sup>a</sup>	<i>tert</i> -Butyl peracetates <sup>b</sup>
0	[1]	[1]
1	1.4	$1.6 \times 10^4$
2	26	$9 \times 10^6$
3	$1 \times 10^3$	$4 \times 10^7$

<sup>a</sup> Relative to the rates of phenyl iodine diacetate decomposition calculated for 79.8, 100, and 140° using  $\Delta H^\ddagger = 28.9 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -10.2 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . <sup>b</sup> 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<sup>7-9</sup> in Table V. At each step in the series the effect is smaller for the phenyl iodine 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.<sup>10</sup>

A further consequence of the stability of radical **2** is a marked shift to more ester ROOCR at the expense

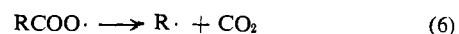
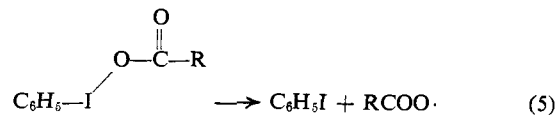
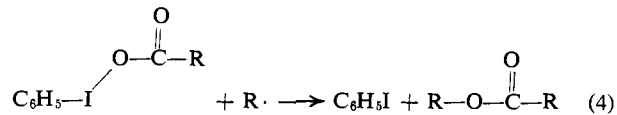
(7) P. D. Bartlett and D. M. Simons, *J. Amer. Chem. Soc.*, **82**, 1753 (1960).

(8) P. D. Bartlett and R. E. Hiatt, *ibid.*, **80**, 1398 (1958).

(9) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

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

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.



In the decomposition of *tert*-butyl triphenylperacetate,<sup>9</sup> 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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## Stable Carbocations. CXXXV.<sup>1,2</sup> 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  $-\text{OH}_2^+$  or  $\text{CH}_3\text{O}(\text{H})^+$  substituent at the meta position and (ii) protonated or alkylated oxocyclohexenyl dication. 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.<sup>1</sup> 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  $\text{HF}-\text{SbF}_5$  solution.<sup>3</sup> These benzenium ions (**1** and **2**)

(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.