Reactions of Peroxides: II. Reaction of Carboxylic Acids With Iodine and Peroxides[1]

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Abstract

Aroyl peroxides and *t*-butylperoxy isopropyl carbonate decarboxylate aliphatic carboxylic acids in the presence of iodine to form iodides in high yields. The aroyl peroxides also abstract carboxylic acid hydrogen from aromatic and perfluorocarbon acids. A proposed scheme is presented for the reaction of aroyl peroxides with carboxylic acids illustrating homolytic decarboxylation as taking place in an equilibrium between a pair of acyloxy radicals. These radicals are derived from the peroxide and acid and maintained in association by hydrogen bonding and iodine complexation.

Introduction

In a preceding paper we reported our results on the application of acyl and aroyl peroxide decompositions in iodine solutions as a limited preparative method for alkyl and aryl iodides (1):

$$(RCOO)_2 + I_2 \xrightarrow{\Delta} 2RI + 2CO_2 \qquad [1]$$

This paper reports the preparation of alkyl iodides in high yields by decomposing benzoyl peroxide or *t*-butylperoxy isopropyl carbonate (BPIC) in solutions of aliphatic carboxylic acids and iodine. Conversions of some aromatic acids to aryl iodides are also achieved but these reactions serve more usefully in probing the decomposition mechanism.

These reactions, aside from their synthetic application, demonstrate free radical hydrogen abstraction from the notoriously unreactive (2,3,4) O–H function. Generally, free radicals most offen abstract hydrogen from α-carbons in aliphatic acids (5–8) and from nuclear positions in aromatic acids (7). The comparative ease of abstracting hydrogen from the C–H bond has been attributed to this group's lower bond energy (2,3).

Prior to this work two peroxide reactions on the O–H position of carboxylic acids had been reported. In one case, trifluoroacetic acid was decarboxylated with benzoyl peroxide in the presence of iodine in isooctane solution to form CF_3I (3). This acid represents a special case in which O–H remains available to free radical attack owing to the resistance of C–F bonds. In the second case, homolytic decarboxylation of aromatic acids, e.g., free radical hydrogen abstraction and decarboxylation of the aroyloxy radical, was achieved in aromatic solvents under vigorous conditions with di-*t*-butyl peroxide or *t*-butyl hydroperoxide, oxygen and cobalt catalyst at the relatively high temperatures (180 C) necessary for decomposing the peroxide (9,10). Neither of these reactions indicates the feasibility of decarboxylating aliphatic and aromatic acids in the presence of iodine nor offers insights as to a mechanism under these conditions.

Experimental Procedures

All solvents were fractionally distilled. 1,1,2,2,-Tetrafluorodichloroethane (Freon 112) was supplied by E. I. du Pont and Co.

Octanoic acid was fractionally distilled and stearic acid crystallized until pure by GLC. The preparation of pure pelargonic acid has been reported (11). All other acids were used as supplied from commercial sources.

Benzoyl peroxide (Eastman White Label, 99.2% purity) and *t*-butylperoxy isopropyl carbonate (BPIC) (Pittsburgh Plate Glass Company, Inc., 85% peroxygen content) were each used as supplied. The preparation of pelargonyl and octanoyl peroxide (12) and *p*-nitrobenzoyl peroxide (13) and precautions on handling the latter peroxide (1,14) have been reported. Anisoyl and *m*-chlorobenzoyl peroxides were prepared by similar procedures.

Analytical

Gas Chromatography. GLC analyses of alkyl and aryl iodides were performed on an F & M Model 720 chromatograph. In the majority of analyses a steel column (8 ft, ¼ in.) packed with silanized 60/80 Chromosorb W (acid washed) and coated with SE 30, 10%, was used. The injection port temperature was maintained below 190 C to suppress decomposition of alkyl iodide. Standard solutions of known concentration for each compound measured in the reaction solutions were separately injected as external standards. Peak integrations were obtained with a Daystrom Attenumatic Integrator.

Iodometry. Iodine was determined by a standard method (15). Differential analyses of iodine and peroxide were unnecessary for the majority of the experiments as most peroxide decompositions were carried to completion. In the few cases where differential analyses were required they were determined as described for diacyl peroxide (12) and *t*-butyl peroxyester (16) analyses using traces of iron salt in acetic acid to accelerate the liberation of iodine. Unreacted peroxide was calculated from the difference between total and unreacted iodine.

Procedures. Two experiments describing reaction with benzoyl peroxide and BPIC are typical of the general sets of experiments. Changes in iodine concentration, time and temperature in other experiments were adjusted accordingly. 1,3-Dichloropropane was the preferred solvent in these experiments. Conversions of peroxides and acids to the corresponding iodides were calculated from GLC determinations on volumetric solutions of the products.

Use of Benzoyl Peroxide. Iodine (1.905 g, 0.0075 m), octanoic acid (1.442 g, 0.01 m) and benzoyl peroxide (1.211 g, 0.005 m) were weighed into a volumetric flask (50 ml) that was attached to a semi-micro condenser and stirred magnetically. 1,3-Dichloropropane (8.3 ml) was added and the ensemble and contents briefly sparged with nitrogen to dispel

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[1] Presented at the AOCS Meeting, Washington, D.C., March 1968.
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most of the oxygen. The system was maintained under nitrogen and the reactants stirred for 2 hr at 110 C, a time and temperature adequate for complete benzoyl peroxide decomposition. After cooling the reactants to room temperature, the condenser and joints were carefully rinsed and drained into the flask with a lower boiling rinse solvent, preferably benzene or chloroform. The flask was filled to its mark with rinsing solvent for subsequent GLC and iodometric analyses.

Use of t-Butylperoxy Isopropyl Carbonate. t-Butyl alcohol and acetone (and presumably some isopropyl alcohol), low boiling products of this reaction, must be distilled from the reaction zone as they are generated to prevent low iodide yields and tar formation by their reaction with the peroxide. Iodine (2.540 g, 0.01 m), octanoic acid (1.442 g, 0.01 m) and BPIC (85% concentration, 2.072 g, 0.01 m) were weighed into a two-neck, semi-micro R.B. flask (50 ml capacity) equipped with a nitrogen inlet, a distillation head (cold finger and stopcock type), and a magnetic microbar for stirring. The mixture was stirred magnetically, heated at the appropriate temperature range (125–135 C), and a nitrogen stream admitted to aid distillation of the lower boiling components. After completing the reaction (2–3 hr) the contents were cooled to room temperature and carefully transferred to a volumetric flask (50 ml). The joints and flask were carefully rinsed with benzene or chloroform. Rinsings were added to the flask which was then filled to mark with rinsing solvent for analyses.

Heptadecyl Iodide Preparations

The two previous methods were modified slightly for their application to a long chain fatty acid.

Decarboxylations with Benzoyl Peroxide. Iodine (12.7 g, 0.05 m), stearic acid (14.2 g, 0.05 m), and benzoyl peroxide (6.05 g, 0.025 m) were weighed into a round bottom flask (200 ml) equipped with a small distillation head. 1,3-Dichloropropane (42 ml) and Freon 112 (25 ml) were added as cosolvents. Freon added as a lower boiling solvent minimizes the volume requirement of the higher boiling dichloropropane. If it is not used, the additional equivalent volume of dichloropropane is added to moderate the peroxide decomposition. A homogeneous solution was attained within 10 min on approaching the Freon boiling point. The solution was maintained at reflux for 1 hr and the Freon then distilled within 30 min with only minor losses of iodine. Heating was continued for 1½ hr on reaching 110 C. The solvents were completely distilled off and some benzoic acid was sublimed by careful reduction of pressure and controlled heating.

The residue was dissolved in ether, iodine reduced by aqueous sodium sulfite treatment and the ether evaporated. The bulk of the heptadecyl iodide was separated from residual benzoic acid by elution of the crude product (20 g) with petroleum ether through a chromatographic column of silica gel. Heptadecyl iodide was recovered by evaporation of the main fraction (17.3 g; theory 18.3 g). Recrystallization from a mixture of acetone (70 ml) and 95% ethanol (25 ml) at 40 C yielded the analytically pure product (13.0 g, 71% yield); mp 34.8–35.3 C (reported 33.6 C) (17).

Analysis. Calculated for $C_{17}H_{35}I$: C, 55.73; H, 9.63; I, 34.64. Found: C, 56.03; H, 9.58; I, 34.34.

Decarboxylations with BPIC. Iodine (0.05 m) and stearic acid (0.05 m) were dissolved at 70 C in 1,3-dichloropropane (45 ml) in a round bottom flask (200 ml) equipped with a nitrogen inlet and distillation head. BPIC (0.05 m) was added, and the mixture heated for 3 hr at 125 C to distill the alcohols and acetone. The temperature was then elevated to 145 C to distill the solvent (including some iodine) under increased nitrogen flow. The residue was cooled, dissolved in petroleum ether and filtered from some insoluble compound (1.5 g). The solution was washed with sodium sulfite solution to remove the remaining iodine, passed through a small quantity of silica gel and evaporated. The white product (15 g) was crystallized to analytical purity from acetone-alcohol solution as described in the previous experiment.

Results and Discussion

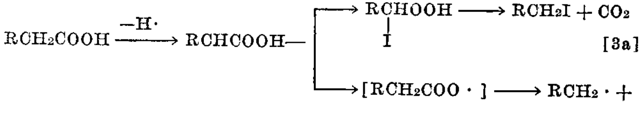
Decarboxylations With Aroyl Peroxides

The mole per cent conversion of octanoic acid and benzoyl peroxide to their corresponding iodides are reported in Table I. The amount of iodine consumed is in agreement with the sum of the two iodides indicating little, if any, iodine lost to side reactions. The results support the stoichiometric formulation in Equation 2.

$$2RCOOH + (\varnothing COO)_2 + I_2 \longrightarrow 2RI + 2\varnothing COOH + 2CO_2 \qquad [2]$$

Results of reactions between acids and acyl or aroyl peroxides are recorded in Table II. Conversions of peroxide and acid to iodides are reported as the mole per cent iodobenzene and companion iodide derived from them. Before presenting a general decarboxylation scheme in explanation of the results, a possible alternate route involving the α-methylene position, which is specific to aliphatic acids, is shown as follows to be unacceptable.

α-Carbon radicals generated by free radical attack on aliphatic acids may dimerize to succinic acid derivatives (5,6) or add to olefins in a synthesis of α-branched acids (18,19). Even homophthalic and homoterephthalic acids arising from benzoyl peroxide decomposition in acetic acid are traceable to α-carbon reactions (7). This preferred formation of α-carbon radical, should it be formed in the presence of iodine, suggests that it may be scavenged by iodine to produce α-iodoacid as an intermediate. Thermal decarboxylation of the latter which would account for the alkyl iodide [3a]. This scheme was tested experimentally on α-iodostearic acid under conditions analogous to reaction conditions for the peroxide/iodine reactions, e.g., 0.3 M α-iodostearic acid in 1,3-



$$RCH_2COOH \xrightarrow{-H\cdot} RCHCOOH - \begin{cases} \xrightarrow{I_2} \underset{\displaystyle I}{RCHOOH} \xrightarrow{\Delta} RCH_2I + CO_2 & [3a] \\ \longrightarrow [RCH_2COO\cdot] \longrightarrow RCH_2\cdot + CO_2 \xrightarrow{I_2} RCH_2I & [3b] \end{cases}$$

TABLE I

Reaction of Octanoic Acid With Iodine and Benzoyl Peroxide[a] Effect of Iodine Concentration on Conversion to Iodides

I_2/ Peroxide	1-Iodo-heptane, %[b]	Iodo-benzene, %[c]	I_2 Consumed, %[d]
1.0	74	18	94
1.5	83	9	95
3.0	90	3	100

[a] Peroxide 0.4 M, Acid 0.8 M, 1,3-Dichloropropane, 110 C, 2 hr.
[b] Based on conversion of acid.
[c] Based on conversion of peroxide.
[d] Calculated as I_2 (consumed) 100/I_2 (theory); theoretical iodine is equivalent to benzoyl peroxide or acid.

TABLE II

Reaction of Acids With Iodine[a] and Acyl or Aroyl Peroxides
Test of Hydrogen Exchange by Ratio of Iodide Yields

Peroxide	Acid	Iodobenzene, % (A)	Companion, Iodide (B)	A/B	Consumed[b] Iodine %
Octanoyl	Benzoic	0	67, Iodoheptane		63
Octanoyl	None	....	63, Iodoheptane		65
Pelargonyl	Octanoic	....	68, Iodooctane and ~ 0.01, Iodoheptane		....
Benzoyl	*m*-Chlorobenzoic	38	34, Chloroiodobenzene	1	79
m-Chlorobenzoyl	Benzoic	49	22, Chloroiodobenzene	2	79
Benzoyl	*p*-Nitrobenzoic	55	13, Iodonitrobenzene	4	88
p-Nitrobenzoyl	Benzoic	61	16, Iodonitrobenzene	4	80
Benzoyl	Anisic	32	11, Iodoanisole	3	53
p-Anisoyl	Benzoic	12	~ 1, Iodoanisole	~10	35
Benzoyl	Pentafluorobenzoic	21	0.8, Iodopentafluorobenzene	~25	53
Benzoyl	Perfluorooctanoic	8	67, Iodoperfluorooctane	....	67

[a] Peroxide 0.4 M, Acid 0.8 M, Iodine 0.6 M, 1,3-Dichloropropane, 110–125 C, 2–3 hr.
[b] Calculated as I_2 (consumed) $100/I_2$ (theory); theoretical iodine is equivalent to benzoyl peroxide or acid.

dichloropropane heated for 2 hr at 110 C. Iodoacid was recovered unchanged with no detectable presence of iodoheptadecane, thus eliminating this mechanism.

An optional path available to α-carbon radicals would lead to indirect formation of acyloxy radicals as shown in Equation 3b. In this scheme acyloxy radicals would arise by inter- or intramolecular O–H abstraction. This path was not explicitly tested but is rejected from prior observations on the preference of α-carbon radicals to dimerize rather than isomerize (5,6). It may also be argued that the α-carbon radical, which is preferentially formed because of the lower C–H bond energy, would in turn favor C–H rather than O–H attack. The direct formation of acyloxy radical is energetically the more favorable process than the indirect one.

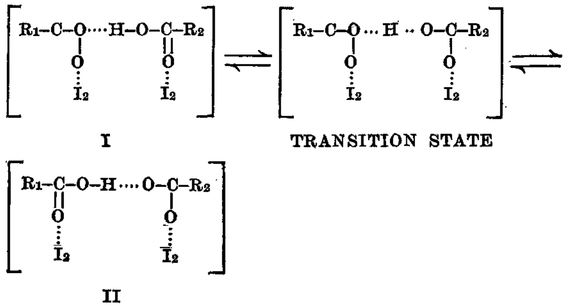
The homolytic decarboxylation of carboxylic acids is schematically presented as the interaction of acid and free radical taking place in a complex maintained by hydrogen bonding and iodine complexation (also called charge-transfer or π-complexation). The interaction of acid and free radical through hydrogen bonding is reviewed in the literature as the identity reaction (4). [The identity reaction is defined as the transfer of one atom from a molecule to the interacting free radical leading to regeneration of each species. It is formulated by the general equilibrium equation $RX + R\cdot \rightleftharpoons R\cdot + RX$ (20)]. The identity reaction describes the stepwise transfer of hydrogen between acyloxy radical and acid proceeding in an equilibrium process through an intermediate associate [4]. This exchange takes place to an insignificant degree, since hydrogen transfer by either benzoyloxy or acyloxy radicals is completed to the extent of only 1–2% (4a) and to only 3–7% in the example of benzoyloxy radical abstracting hydrogen from either acetic or propionic acid (3). These examples clearly show that the interaction of acid and radical by hydrogen bonding alone is inadequate for efficient transfer of hydrogen within the associate and that an additional association involving iodine complexation must also be considered.

$$RCOOH + RCOO\cdot \rightleftharpoons [RCOOHOOCR] \rightleftharpoons RCOO\cdot + RCOOH \quad [4]$$

A recent review on oxidation reactions documents the significant influence of iodine complexations and hydrogen bonds on the kinetics and mechanism of liquid phase radical reactions (21). Charge-transfer complexations are now recognized in reactions for their importance in the energy transfer process (22). Iodine's role in charge-transfer is well established (22–26) and evidence of peroxide participation in similar complexations is slowly accumulating (27).

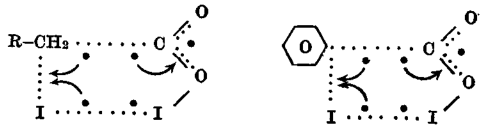
The association energies of hydrogen bonding (3–7 kcal/mole) (28) and iodine complexations (~1–12 kcal/mole) (23) are relatively strong for oxygen functions (~6 kcal/mole in each case). The combined energy of these associations (~12 kcal/mole) should be more effective than either one alone for maintaining the reactants in intimate involvement essential to their reactive roles. The molecular complexes of maleimide and quinol provide an illustration in which the bonding properties are considered to be principally of charge-transfer character stabilized by hydrogen bonding between the component molecules (29). Our scheme depicts the interaction of acid, free radical and iodine in a complex of charge-transfer character stabilized by hydrogen bonding.

The proposed scheme is a modified adaptation of the identity equilibrium:



[5]

The initially formed radical $R_1COO\cdot$ derived by homolytic scission of the aroyl peroxide is hydrogen bonded to acid R_2COOH in Complex I in which both components are associated by iodine (Eq. 5). Hydrogen is transferred through a transition state, represented by two radicals, $R_1COO\cdot$ and $R_2COO\cdot$ equally sharing the hydrogen atom, to give the conjugate Complex II between radical $R_2COO\cdot$ and acid R_1COOH. The equilibrium equation indicates that the transition state may be approached from either side by the appropriate acid and peroxide. Decomposition of one of the radicals in reaction with iodine completes the transfer as depicted by a 5 membered ring configuration of redistributed electron charge in which the C–C bond is simultaneously extended (and CO_2 eliminated) as the C–I bond is formed [6].



[6]

The relative stability of the radical pair in the transition state [5] determines the degree of hydrogen transfer, e.g., the more stable radicals generally receive the hydrogen atom and the less stable radicals decarboxylate, which determines the relative ratio of the iodide pair. Benzoyloxy radical, which is 18 kcal/mole more stable than acyloxy radical (2),

TABLE III

Reaction of Acids With Iodine and BPIC:[a] Experimental Conditions and Results

Acid	Molar ratio			Reactants consumed, %			Iodide[b]	Reaction conditions	
	Acid:	I_2:	Perester	Acid	I_2	Perester		Time Hr	Temperature C
Octanoic	2	1.5	1	15	88	99	16[c]	2	120[d]
Octanoic	2	1.5	1	51	72	100	42[c]	2	125[e]
Octanoic	1	1	1	....	128[f]	97	81[c]	2	135[e]
Octanoic	1	1.5	1	....	......	....	47[g]	3	125–135[e]
Sebacic	0.5	1	1	....	140[f]	93	82[h]	2	135[e]
Benzoic	1	1	1	....	130[f]	94	72[i]	2	135[e]
Anisic	1	1	1	....	......	....	20[j]	3	125–135[e]

[a] *t*-Butylperoxy isopropyl carbonate.
[b] Based on conversion of acid to iodide.
[c] Iodoheptane.
[d] In situ reaction.
[e] Alcohols distilled off as reaction proceeded.
[f] See Results and Discussion for explanation of iodine consumption exceeding 100%.
[g] Experiments were not reproducible at this mole ratio because of excessive tar formation. Some experiments gave no iodoheptane.
[h] 1,8-Diiodooctane.
[i] Iodobenzene.
[j] Iodoanisole.

could have been predicted to be a good abstractor of hydrogen from aliphatic acids. The stabilities of substituted aroyloxy radicals are determined by resonance and inductive interactions of their substituents with the aromatic ring and carboxyl radical function (30,31). These substituted radicals are generally more stable than the parent benzoyloxy radical.

The equilibrium concept is tested by reacting conjugate pairs of peroxide-acid combinations corresponding to Complexes I and [5]. The relative ratio of the iodide pair (A:B = iodobenzene-substituted iodobenzene) should be the same for reactions carried out by appropriate combinations at either side of the equation. Results of that test for a limited set of experiments are reported in Table II. In all cases, including the perfluoroaromatic and perfluoroaliphatic acids, the less stable radical has decomposed more extensively to form iodide in the greater quantity. Agreement in iodide ratios for the chloro- and nitro-substituted sets of experiments is satisfactory but seems less concordant for the methoxy-set which is explained as follows.

These free radical reactions are complicated by the susceptibility of the aromatic nucleus to undergo σ-attack (32) to form such hydroaromatic compounds as the tetrahydroquaterphenyls (33). Aroyl hypoiodite will add to the unsaturation to give products containing iodine (1). Similar black insoluble side-products were obtained in the current reactions accounting in part for disagreements between the iodine consumed and the total yields of iodide as well as for low overall conversions to iodides in several cases. The methoxy group is a particularly effective directing group for activating the nucleus to substitution and addition radical reactions (32,34).

Acyl (aliphatic) peroxides contrast with aroyl peroxides by their complete inability to abstract carboxylic hydrogen from either aliphatic or aromatic acids (Table II), even from acids providing identical radicals (octanoyloxy from octanoic acid and nonanoyloxy from pelargonyl peroxide). Two factors underlie this failure: acyl peroxides are an inefficient source of acyloxy radicals, since they may decompose by a mechanism of multicenter cleavages to generate alkyl as well as acyloxy radicals (35); and the latter radicals are so poorly stabilized as to decompose in the complex prior to hydrogen transfer. This instability of acyloxy radicals accounts for the high iodide yields and for the irreversibility of Complex II.

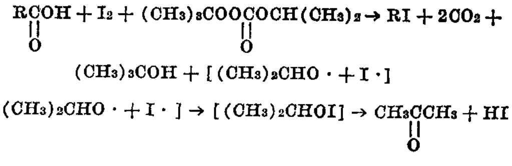
The relative increase in yield ratio of iodoheptane to iodobenzene with increase in iodine concentration (Table I) may be explained on the basis of iodine association. Aromatic compounds have larger formation constants than the corresponding aliphatic compounds (25). Accordingly, higher iodine concentrations are required to effectively complex the less favored aliphatic component for its reaction in the transition state.

An interesting comparison is observed between iodoalkane products obtained by homolytic decarboxylation of aliphatic acids and by decomposition of acyl peroxides. 1-Iodoheptane, derived from octanoic acid, is free of isomers in contrast to 1-iodooctane, derived from pelargonyl peroxide. The latter iodide shows gas chromatographic peaks corresponding to the 2- and 3-iodoalkane isomers (1). Isomer formation from the latter may be attributed to free radical rearrangement of an intermediate alkyl radical (36). In comparison the acyloxy radical in Equations 5 and 6 may not decarboxylate to a free alkyl radical since decarboxylation and C–I bond formation proceed concurrently.

Decarboxylations with BPIC

Results of *t*-butylperoxy isopropyl carbonate decompositions in solutions containing iodine and carboxylic acids are recorded in Table III. BPIC decompositions are completed (10 half-lives) within 2 hr at 135 C (37).

The *t*-butoxy radical is the active moiety of the peroxyester in these hydrogen abstractions [7] while the isopropoxy radical in comparison is



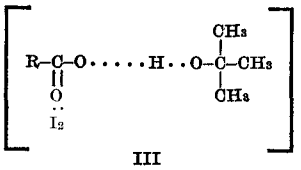
$$\mathrm{R\underset{\overset{\|}{O}}{C}OH + I_2 + (CH_3)_3COO\underset{\overset{\|}{O}}{C}OCH(CH_3)_2 \rightarrow RI + 2CO_2 +}$$

$$\mathrm{(CH_3)_3COH + [(CH_3)_2CHO\cdot + I\cdot]} \qquad [7a]$$

$$\mathrm{[(CH_3)_2CHO\cdot + I\cdot] \rightarrow [(CH_3)_2CHOI] \rightarrow CH_3\underset{\overset{\|}{O}}{C}CH_3 + HI} \qquad [7b]$$

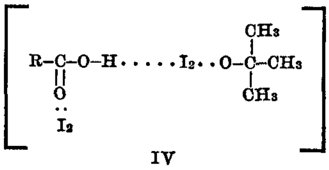
inefficient for this purpose. Isopropoxy radical would be partially consumed by decomposition owing to its lower stability [6 kcal/mole difference (36)] and partially by reaction with iodine [7] in analogy to the isopropyl hypochlorite decomposition to acetone and HCl (39). This would explain iodine consumption exceeding 100% (Table III) as theory is taken to be one half mole iodine for each mole of acid or peroxyester.

The best yields of iodoheptane are obtained at unit mole ratio of acid, peroxyester and iodine suggesting a hydrogen bonded state III between acyloxy and *t*-butoxy radicals. Iodine at this ratio is sufficient to complex only the acid and not *t*-butoxy radical. For



$$\left[R{-}\underset{\underset{\underset{I_2}{\cdot\cdot}}{O}}{\underset{\|}{C}}{-}O\cdots\cdots H\cdot\cdot O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3\right]$$

III



$$\left[R{-}\underset{\underset{\underset{I_2}{\cdot\cdot}}{O}}{\underset{\|}{C}}{-}O{-}H\cdots\cdots I_2\cdot\cdot O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3\right]$$

IV

reactions in excess iodine (1.5 moles of iodine per mole of acid) conversions are drastically reduced, nonreproducible and accompanied by much tar. Consequently, excess iodine may be associating with *t*-butoxy radical to obstruct or prevent hydrogen bonding as depicted in IV. The inability of acid to transfer its hydrogen in the presence of excess iodine results in tar formation by thermal destruction of the reagent.

Applications

The procedures described for decarboxylating octanoic acid were slightly modified for the larger scale preparations of heptadecyl iodide from stearic acid. Yields obtained with benzoyl peroxide reagent were about 10% higher than with BPIC. Perfluorooctanoic acid is decarboxylated by benzoyl peroxide to produce good yields of perfluoroheptyl iodide.

The peroxide methods are inapplicable to olefinic acids which are attacked at the double bond to form tar. In general, the methods are not suitable for preparative synthesis of aryl iodides from aromatic acids, although BPIC may be used to prepare iodobenzene from benzoic acid.

These homolytic decarboxylations help to explain the failure of benzoyl peroxide as an initiator for the addition of aliphatic carboxylic acids to olefins (18,19). It is now evident that benzoyl peroxide is consumed by O–H attack to generate acyloxy radical and the latter decarboxylates and terminates in unwanted reactions like dimerization, disproportionation and olefin polymerization (40).

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[Received September 19, 1968]