The infrared and nmr spectra were identical with those of the compound obtained from N,N-diethyl 2-(dimethylsulfuranylidene)acetamide and a mixture melting point was also undepressed, 66–67°. The thetin was dried *in vacuo*, mp 138–140°.

Attempted Rearrangement of 2-(Dimethylsulfuranylidene)-acetyl-4′-chloroacetophenone (22).—The above ylide was added to 200 ml of water and the mixture refluxed for 6 days. The nmr spectrum of the insoluble oil was unchanged from starting material.

Solvent Effects.—The rearrangement of 2-(dimethylsulfuranylidene)acetophenone was repeated in absolute ethanol. Nmr spectra indicated complete reaction only after 66 hr. The solution was concentrated and the residue extracted with ether. Concentration of the ether gave 1-(methylthio)methoxystyrene in 81% yield. Heating the above ylide in DMSO for 13 days gave no rearranged product by nmr analysis.

Registry No.—**6**, 14236-72-7; **7**, 14439-02-2; **8c**, 14679-47-1; **8e**, 14679-48-2; **9a**, 14439-02-2; **9b**, 14680-04-7; **9c**, 14679-93-7; **9d**, 14679-94-8; **9e**, 14679-95-9; **11**, 14679-96-0; **12**, 14679-97-1; **13**, 14679-98-2; **15b**, 10271-55-3; **15c**, 14680-00-3; **18**, 4727-41-7; 2-methylsulfonyl-3-phenylpropiophenone, 3708-06-3; α-(propylthio)methoxystyrene, 14680-03-6; **20**, 14680-21-8.

Photochemical Decarboxylation of Acids with Thallium(III)

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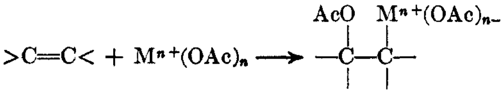
Tl(III) carboxylates generated by the facile metathesis of Tl(III) acetate and a variety of carboxylic acids are photolyzed at 2537 and 3500 A in benzene solutions. Photolysis yields Tl(I) carboxylate and CO_2 quantitatively together with products derived from the alkyl moiety of the acid. These are alkane, alkene, dialkyl and alkyl esters, and alkylbenzene. The relative amounts of each depend on the irradiating source. Alkyl dimers are formed in high yields with 2537-A light, whereas at 3500-A alkanes are the major products. These products are considered to arise from free alkyl radicals generated by photolytic homolysis of Tl(III) carboxylates stepwise to Tl(II) carboxylates, followed by further fragmentation to the Tl(I) product. The good yields of dimers particularly from primary acids using 2537-A irradiation is attributed to high local concentrations of radicals due to the instability of the Tl(II) species generated in an excited state. These alkyl radicals can be trapped by hydrogen donors of scavenged by Cu(II). The rearrangement of 5-hexenyl radical from 6-heptenoic acid to cyclopentylmethyl radical is not reversible and direct molecular processes do not obtain in the dimerization.

Thallium(III) acetate is an oxidant easily prepared from its readily obtainable oxide.[1] As the middle member of the post-transition triad, Hg, Tl, and Pb, Tl(III) exhibits properties intermediate between its isoelectronic analogs, Hg(II) and Pb(IV), toward organic substrates. Thus, arenes are more readily mercurated[2] than thallated,[3] and plumbation[4] occurs only in selected cases. Alkenes such as cyclohexene also react with this group of heavy metal carboxylates in approximately the same order of reactivity.[5] In most cases, products can be considered to arise *via* electrophilic addition of the metal moiety and acetate to the unsaturated linkage, followed by further reactions of the alkyl metal carboxylates.[6]



$$>C{=}C< + M^{n+}(OAc)_n \longrightarrow -\overset{\overset{\large AcO}{|}}{\underset{|}{C}}-\overset{\overset{\large M^{n+}(OAc)_{n-1}}{|}}{\underset{|}{C}}- \qquad \text{etc.} \quad (1)$$

On the other hand, in a variety of other types of oxidations, Pb(IV) acetate[6a] is a powerful, as well as versatile, oxidant under conditions in which neither Hg(II) nor Tl(III) acetates are effective. The mechanism of the facile decarboxylation of acids by Pb(IV) has been shown to be a free-radical chain process which can be induced thermally or photochemically.[7] The relevant propagation steps in the proposed mechanism are given by eq 2 and 3.[8] In this sequence a metastable Pb(III)[9] species plays an important role

$$R\cdot + RCO_2Pb(IV) \longrightarrow [R^+] + RCO_2Pb(III) \qquad (2)$$

$$RCO_2Pb(III) \longrightarrow Pb(II) + CO_2 + R\cdot \text{ etc.} \qquad (3)$$

in the oxidation. The oxidation of alcohols by Pb(IV) has also been shown to proceed *via* free radicals and Pb(III) intermediates are also implicated.[10]

The reactions of these heavy metal carboxylates with organic substrates superficially appear to involve at least two mechanisms: metallation which is *electrophilic* in character in contrast to electron transfer which is *free radical* in nature. In oxidation processes, the former may involve a direct 2-equiv oxidation of the metal moiety: Hg(II) → Hg(0),[11] Tl(III) → Tl(I),[5b] and Pb(IV) → Pb(II).[12] In electron-transfer reactions of Pb(IV), the oxidation which also requires 2 equiv over-all may proceed in two discrete 1-equiv steps: Pb(IV) → Pb(III) → Pb(II).

The electron-transfer mechanism is not common in chemistry of Tl(III) compounds. These are generally

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(1) R. Meyer and E. Goldschmidt, *Ber.*, **36**, 238 (1903).

(2) R. Schramm, W. Klapproth, and F. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951); H. Brown and C. McGary, *J. Am. Chem. Soc.*, **77**, 2300, 2306, 2310 (1955); **84**, 1650 (1950).

(3) V. Glushkova and K. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **103**, 615 (1955); **116**, 233 (1957); *Izv. Akad. Nauk SSSR*, 1186, 1391 (1957). H. Gilman and R. Abbott, *J. Am. Chem. Soc.*, **65**, 122 (1943); K. Ichikawa, S. Uemura, and T. Sugita, *Tetrahedron*, **22**, 407 (1966).

(4) D. Harvey and R. Norman, *J. Chem. Soc.*, 4860 (1964).

(5) (a) Hg: G. Wright, *J. Am. Chem. Soc.*, **69**, 697 (1947); W. Treibs, C. Lucious, H. Kogler, and H. Breslauer, *Ann.*, **581**, 59 (1953). (b) Tl: J. Lee and M. Price, *Tetrahedron*, **20**, 1017 (1964); H. Kabbe, *Ann.*, **656**, 204 (1962); C. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963). (c) Pb: R. Criegee, *Ann.*, **481**, 263 (1930).

(6) (a) R. Criegee, "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 5; (b) P. Henry, *J. Am. Chem. Soc.*, **87**, 990, 4423 (1965); (c) K. Pande and S. Winstein, *Tetrahedron Letters*, 3393 (1964).

(7) J. Kochi, J. Bacha, and T. Bethea, submitted for publication.

(8) J. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

(9) In subsequent presentations, the coordination around the metal atoms will be unspecified unless required for clarity. Tl(III) compounds exhibit a variety of structural possibilities: F. Cotton, B. Johnson, and R. Wing, *Inorg. Chem.*, **4**, 507 (1965); T. Spiro, *ibid.*, **4**, 1290 (1965).

(10) D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 206, 1961 (1964); K. Heusler, *Tetrahedron Letters*, 3975 (1964); W. Starnes, *J. Am. Chem. Soc.*, **89**, 3368 (1967).

(11) F. Jensen and R. Oullette, *ibid.*, **85**, 364 (1963); A. Brook and G. Wright, *Can. J. Res.*, **28B**, 623 (1950).

(12) K. Alder, H. Flock, and H. Wirtz, *Ber.*, **91**, 609 (1958); R. Criegee, P. Dimroth, K. Noll, and C. Weis, *ibid.*, **90**, 1070 (1957).

considered 2-equiv oxidants and reactions are facile when they are coupled with a 2-equiv reductant.[13] However, kinetics of the oxidation of V(III) and Fe(II) by Tl(III) in aqueous solutions are simple second order, and Tl(II) has been proposed as an intermediate in both reactions.[14] Other catalytic reactions involving similar transient species have been proposed.[15] More direct evidence for Tl(II) species has recently been obtained by voltammetry in electrooxidations[16] and spectral studies in pulse radiolysis[17] of Tl(I) and Tl(III) compounds.

Bivalent thallium has never been prepared as a stable species in quantities amenable to chemical characterization. It is isoelectronic with Pb(III) and Hg(I); the former is also uncharacterized and the latter is known only as dimeric compounds. Since the preferred route to electron-transfer reactions of Pb(IV) is through oxidation of acids,[8] we sought to examine the decarboxylation of acids as a means of studying these processes in Tl(III).[18] Furthermore, Tl(III) is not so powerful an oxidant as Pb(IV).[19] Since both are 2-equiv oxidants, we sought to examine their differences in the over-all course and mechanism of decarboxylation of acids.

Results

Thallium(III) acetate was readily metathesized with a variety of carboxylic acids in benzene solutions. Tl(III) acetate is rather insoluble in benzene but

$$Tl(III)(OAc)_3 + 3RCO_2H \rightleftarrows Tl(O_2CR)_3 + 3HOAc \qquad (4)$$

carboxylates of the higher homologs are readily soluble in this medium. These Tl(III) carboxylates, $Tl(O_2CR)_3$, can be synthesized as crystalline materials by a procedure similar to that employed to prepare Pb(IV) carboxylates.[20] However, in order to facilitate the examination of a variety of Tl(III) carboxylates, we found it more convenient to prepare these esters *in situ* by adding an excess of the appropriate carboxylic acid to Tl(III) acetate in the solvent. The resulting clear and colorless homogeneous solutions were photolyzed directly.

The absorption spectrum of Tl(III) valerate was examined in cyclohexane solutions. The spectrum exhibited only a broad structureless tail extending from the near ultraviolet to slightly beyond 3600 A. At 2537 A the extinction coefficient for Tl(III) valerate was 5×10^3 l. mole^{-1} cm^{-1}, and the ultraviolet band is probably associated with a charge-transfer transition(s). The reflectance spectrum of crystalline Tl(III) acetate was also examined relative to a standard CaF_2 plaque from 2500–6500 A. It showed essentially the same features as the absorption spectrum in cyclohexane.

Photolytic Decarboxylation of Tl(III) Carboxylates.—Photolysis of a solution of Tl(III) acetate (0.11 *M*) and valeric acid (1.2 *M*) in benzene at 30° with 2537 A irradiation produced 2 moles of carbon dioxide. The butyl moiety was identified as *n*-butane (31%), butene-1 (10%), *n*-octane [33% (66%[21])], *n*-butyl acetate (1.5%), *n*-butyl valerate (5%), *n*-butylbenzene (1%), and *n*-pentane (5%), together with a small amount (4%) of methane as given in eq 5.[22] The same

$$\begin{aligned}(CH_3CH_2CH_2CH_2CO_2)_3Tl \xrightarrow[C_6H_5]{h\nu} TlO_2CCH_2CH_2CH_2CH_3 &+ \\ CO_2 + [CH_3CH_2CH_2CH_3 + CH_3CH_2CH{=}CH_2 &+ \\ (CH_3CH_2CH_2CH_2)_2 + CH_2CH_2CH_2CH_2O_2CR &+ \\ CH_3CH_2CH_2CH_2C_6H_5] & \qquad (5)\end{aligned}$$

products were obtained, although in different amounts, if the photolysis was carried out at 3500 A. The relative amounts of products generated at 2537 and 3500 A are compared in Table I.

Prolonged photolysis at 3500 A caused no further change of Tl(I) valerate. However, at 2537 A, Tl(I) was very slowly reduced to thallium metal with further evolution of CO_2. The secondary photolysis was sufficiently inefficient to cause no difficulty with the decarboxylation of Tl(III). Preliminary measurements of quantum yields indicate that photolysis of Tl(III) carboxylates are nonchain processes, unlike the radical-chain decarboxylation of the Pb(IV) analogs. Detailed quantum yield studies will be presented later.

The stoichiometry of the decarboxylation of a Tl(III) ester is complex, since a variety of simultaneous reactions is represented. These differ largely in the formal oxidation state of the product, and the electron balance determines the stoichiometric requirements for Tl(III). Thus, octane is a dimeric product of decarboxylation which generates 2 moles of CO_2 and requires 1 mole of Tl(III) (eq 6). The mixed coupling product, *n*-pentane, from valerate and acetate is an equivalent reaction. The formation of butene-1, butyl acetate and valerate is an oxidative process which requires 1 mole of Tl(III) and generates 1 mole of CO_2 (eq 7).

$$(RCO_2)_3Tl(III) \longrightarrow R{-}R + 2CO_2 + Tl(I)O_2CR \qquad (6)$$

$$\begin{tikzcd} & R(-H) + CO_2 + RCO_2H + Tl(I)O_2CR \\ (RCO_2)_3Tl(III) \arrow[ur, "a"] \arrow[dr, "b"'] & \\ & RO_2CR + CO_2 + Tl(I)O_2CR \end{tikzcd} \qquad (7)$$

On the other hand, alkane (RH) and methane derived from decarboxylation of the acid (RCO_2H) and acetic acid, respectively, *formally* do not consume Tl(III) (eq 8), although the latter is important since

$$RCO_2H \xrightarrow{Tl(III)} RH + CO_2 \qquad (8)$$

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[13] H. Halvorson and J. Halpern, *J. Am. Chem. Soc.*, **78**, 5562 (1956); A. Sykes, *J. Chem. Soc.*, 5549 (1967); J. Halpern and L. Orgel, *Discussions Faraday Soc.*, **29**, 7 (1960); M. Ardon and R. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[14] (a) K. Ashurst and W. Higginson, *J. Chem. Soc.*, 3044 (1953); (b) N. Daugherty, *J. Am. Chem. Soc.*, **87**, 5026 (1965); (c) see, however, F. Baker, W. Brewer, and T. Newton, *Inorg. Chem.*, **5**, 1294 (1966).

[15] R. Betts, *Can. J. Chem.*, **33**, 1780 (1955); K. Ashurst and W. Higginson, *ibid.*, **33**, 1780 (1955); D. Rosseinsky and W. Higginson, *J. Chem. Soc.*, 31 (1960).

[16] H. Catherino and J. Jordan, *Talanta*, **11**, 159 (1964). See also O. Farver and G. Nord, *Chem. Comm.*, 736 (1967).

[17] B. Cercek, M. Ebert, and A. Swallow, *J. Chem. Soc.*, A612 (1966).

[18] We hope to present studies of the photochemistry of Hg (II) compounds later.

[19] This only refers to the two-electron process in water. The one-electron potentials are unknown. *Cf.* E. Collinson, F. Dainton, D. Smith, G. Trudel, and S. Tazuke, *Discussions Faraday Soc.*, **29**, 189 (1960), and ref 16 and 17.

[20] W. Mosher and C. Kehr, *J. Am. Chem. Soc.*, **75**, 3176 (1953).

[21] Yields are based on 1 mole of product from 1 mole of Tl(III) reduced (*vide infra*). The higher figure for octane is based on the butyl moiety. Other products are all derived from only one butyl group.

[22] Equation is not balanced.

TABLE I

PRODUCTS FROM PHOTOLYSIS OF *n*-VALERATOTHALLIUM(III) AT 2537 AND 3500 A[a]

Irradiation, A	Products[b]								
	CH_4	CO_2	$n\text{-}C_4H_{10}$	$C_4H_8\text{-}1$	$n\text{-}C_8H_{18}$	*n*-BuOAc	*n*-BuOVal	$n\text{-}BuC_6H_5$	$n\text{-}C_5H_{12}$
2537	3.5	200	31	10	33	1.5	5	1	5
3500	4.8	180	69	1	7	1.5	4	6	<0.2

[a] In benzene solutions containing 0.11 *M* Tl(III) acetate and 1.2 *M* *n*-valeric acid at 30°. Carried to 100% conversion, irradiated 12 hr at 2537 and 40 hr at 3500 A. [b] All yields based on mole of product per mole of Tl(III) consumed.

TABLE II

PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF PRIMARY ACIDS WITH THALLIUM(III) ACETATE IN BENZENE SOLUTION AT TWO WAVELENGTHS[a]

Acid	Products							
	Methane	Alkane	Alkene	Dimer	Acetate ester	Higher ester	Alkyl benzene	Other
				At 2537 A				
n-Butyric	3.3	34[b]	10[c]	30[d]	Not determined	1.3[e]	1.1[f]	4[g]
n-Valeric	3.5	31[g]	10[h]	33[i]	1.4[j]	5.1[k]	0.8[l]	
Isovaleric	2.7	26[m]	7.1[n]	38[o]	Not determined	0.6[p]	1.6[q]	5[r]
Phenylacetic[y]	1.6	16[s]		49[t]	2.4[u]	14[v]	0.7[w]	0.4[x]
				At 3500 A				
n-Butyric	4.7	96[b]	1.7[c]	5.3[d]	Not determined	6.1[e]	1.4[f]	
n-Valeric	4.8	69[g]	1.2[h]	7.1[i]	1.5[j]	3.3[k]	6.0[l]	
Isovaleric	3.6	59[m]	1.8[n]	7.5[o]	Not determined	0.6[p]	4.4[q]	
Phenylacetic[y]	4.1	30[s]		41[t]	2.4[u]	23[v]	1.4[w]	

[a] In solution containing 0.10 *M* Tl(III) acetate and 1.1 *M* carboxylic acid at 30°. Reactions carried to 100% conversion and quantitative CO_2 obtained. Product conversions are expressed in percentage as moles of product per mole of thallium(III) reacted. [b] Propane. [c] Propene. [d] Hexane. [e] Propyl butyrate. [f] Propylbenzene. [g] Butane. [h] Butene-1. [i] Octane. [j] *n*-Butyl acetate. [k] *n*-Butyl valerate. [l] *n*-Butylbenzene. [m] Isobutane. [n] Isobutene. [o] 2,5-Dimethylhexane. [p] Isobutyl isovalerate. [q] Isobutylbenzene. [r] 2-Methylbutane. [s] Toluene. [t] Bibenzyl. [u] Benzyl acetate. [v] Benzyl phenyl acetate. [w] Diphenylmethane. [x] Ethylbenzene. [y] Carbon dioxide yield near 200%.

these acids are not otherwise decarboxylated. It is likely that alkane is derived *via* alkyl radicals by hydrogen abstraction (*vide infra*) from the α position of the acid.

$$R\cdot + SH \longrightarrow RH + S\cdot \qquad (9)$$

The Tl(III) requirements for alkane formation would then depend on the fate of the radical (S·) derived from transfer. If S· disappears by dimerization, the over-all stoichiometry is given by eq 6; if it is oxidized, the stoichiometry given by eq 7 is applicable.

These complexities, thus, lend ambiguity to a valid assignment of the stoichiometric requirements of Tl(III) for each product. The Tl(III) requirement may formally vary from 0 to 2 and until *all* the products are resolved, it is misleading to reckon yields on the usual basis. With these limitations in mind we have taken the simple expediency of assigning conversions on a molar basis, *i.e.*, moles of product formed (regardless of its oxidation state) per mole of Tl(III) consumed.

Primary Acids.—The photolysis in benzene solution of other carboxylato Tl(III) species derived from such primary acids as *n*-butyric, isovaleric, octanoic, nonanoic, and phenylacetic are compared in Tables II and III. In all cases the thallium(III) was reduced to thallium(I) and the carbon dioxide yields were near quantitative (that is, 200%) unless otherwise noted. The relative yields of product in these photolyses were not altered materially by concentration of reactants, conversion of Tl(III), or intensity of the irradiation.

It is noteworthy that on photolysis at 2537 A, aliphatic primary acids and Tl(III) afforded relatively high yields of dimeric products (eq 6). At lower energies (3500 A), these dimers were relatively minor products and were replaced principally by alkanes (eq 8). The small amounts of mixed coupled products (homologs) with the methyl fragment from acetic acid were detectable only in reactions induced by 2537-A irradiation. Phenylacetic acid was an exception in that high yields of dimers and respectable amounts of esters were formed in reactions carried out at both wavelengths. Phenylacetic acid was also unique in that of all acids studied, the Tl(III) ester was the only one which was reduced completely to thallium metal (300% CO_2) with 2537-A irradiation under our experimental conditions.

Secondary Acids.—The secondary acids used in this study include isobutyric acid, 2-methylbutyric acid, and cyclohexanecarboxylic acid. The products obtained upon photolysis of these acids and thallium(III) acetate in benzene solution at the two wavelengths are shown in Table IV. In all cases the Tl(III) species were reduced to Tl(I) carboxylates and yields of carbon dioxide were close to quantitative (*i.e.*, 200%).

The relative amounts of products from secondary acids uniformly differ from those derived from primary acids. At 2537 A, dimers are formed in diminished yields from secondary acids and alkenes are more dominant products. The latter are also more important at 3500 A with secondary acids compared to primary acids.

Tertiary Acids.—Trimethylacetic acid and 2,2-dimethylbutyric acid were the representatives of tertiary acids studied. The products obtained after photolysis of these acids and thallium(III) acetate in benzene solution at two wavelengths are listed in Table V.

The trend in the distribution of products derived from the photolysis of Tl(III) derivatives developed with primary acids compared to secondary acids was continued with tertiary acids. Although the difference between reactions carried out at 2537 and 3500 A persisted, the difference was even smaller than those observed with secondary acids. Thus, alkene was a

TABLE III

HYDROCARBONS OBTAINED FROM THE PHOTOLYSIS OF OCTANOIC ACID AND NONANOIC ACID WITH THALLIUM(III) ACETATE IN BENZENE SOLUTION AT TWO WAVELENGTHS[a]

			Products				
Acid	Wavelength, A	% conversion	CO_2	Methane	Alkane	Alkene	Dimer
Octanoic	2537	98	193	6.2	22[b]	9.2[c]	18[d]
Nonanoic	2537	96	189	7.0	22[e]	4.6[f]	21[g]
Octanoic	3500	98	182	6.8	52[b]	Not determined	<0.2
Nonanoic	3500	96	187	6.9	48[e]	3.4[f]	<0.2

[a] Contains 0.10 *M* Tl(III) acetate and 1.1 *M* carboxylic acid at 30°. Products are given in percentages expressed as moles of product per mole of thallium(III) reacted; numerous unidentifiable products were produced in addition to those reported here. [b] Heptane. [c] Heptene-1 and *cis* and *trans*-heptene-2; complete separation could not be achieved. [d] Tetradecane. [e] Octane. [f] Octene-1 and *cis*- and *trans*-octene-2, complete separation could not be achieved. [g] Hexadecane.

TABLE IV

PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF SECONDARY ACIDS WITH THALLIUM(III) ACETATE IN BENZENE SOLUTION AT TWO WAVELENGTHS[a]

	Products							
Acid	Methane	Alkane	Alkene	Dimer	Acetate ester	Higher ester	Alkylbenzene	Other
At 2537 A								
Isobutyric	4.6	52[b]	50[c]	16[d]	Not determined	Not determined	0.9[e]	2[f]
2-Methylbutyric	2.9	35[g]	25[h] 11[i] 9.5[j]	19[k]	Not determined	1.3[l]	0.8[m]	3[n]
Cyclohexanecarboxylic	4.8	27[o]	17[p]	7.6[q]	1.7[r]	6.9[s]	0.8[t]	0.2[u]
At 3500 A								
Isobutyric	3.2	84[b]	26[c]	3.2[d]	Not determined	Not determined	3.6[e]	
2-Methylbutyric	4.9	49[g]	11[h] 6.9[i] 6.2[j]	5.6[k]	Not determined	1.7[l]	3.6[m]	
Cyclohexanecarboxylic	2.6	48[o]	13[p]	2.8[q]	1.6[r]	5.8[s]	2.2[t]	

[a] In solutions containing 0.11 *M* Tl(III) acetate and 1.2 *M* carboxylic acid at 30°. Conversions were 100% and CO_2 found in 180–200%. Percentages are expressed as moles of product per mole of thallium(III) reacted. [b] Propane. [c] Propene. [d] 2,3-Dimethylbutane-1. [e] Isopropylbenzene. [f] Isobutane. [g] *n*-Butane-1. [h] *trans*-2-Butene. [i] *cis*-2-Butene. [j] 3,4-Dimethylhexane. [k] *sec*-Butyl 2-methylbutyrate. [m] *sec*-Butylbenzene. [n] 2-Methylbutane. [o] Cyclohexane. [p] Cyclohexene. [q] Dicyclohexyl. [r] Cyclohexyl acetate. [s] Cyclohexyl cyclohexanecarboxylate. [t] cyclohexylbenzene. [u] Methylcyclohexane.

TABLE V

PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF TERTIARY ACIDS WITH THALLIUM(III) ACETATE IN BENZENE SOLUTION AT TWO WAVELENGTHS[a]

	Products						
Acid	Methane	Alkane	Alkene	Dimer	Acetate ester	Higher ester	Alkylbenzene
At 2537 A							
Trimethylacetic	4.6	33[b]	55[c]	6.4[d]	3.5[e]	3.3[f]	0.2[g]
2,2-Dimethylbutyric	Not determined	43[h]	45[i] 18[j]	6.0[k]	0.5[l]	1.4[m]	1.5[n]
At 3500 A							
Trimethylacetic	0.6	29[b]	36[c]	3.9[d]	10	8.2	Not determined
2,2-Dimethylbutyric	Not determined	35[h]	35[i] 19[j]	4.2[k]	1.8[l]	2.8[m]	1.1[n]

[a] Reactions carried to 100% conversion; 150–170% formed from reactions containing 0.11 *M* Tl(III) acetate and 1.2 *M* carboxylic acid at 30°. Percentages are expressed as moles of product per mole of thallium(III) reacted. [b] Isobutane. [c] Isobutene. [d] 2,2,3,3-Tetramethylbutane. [e] *t*-Butyl acetate. [f] *t*-Butyl trimethyl acetate. [g] *t*-Butylbenzene. [h] 2-Methylbutane. [i] 2-Methyl-1-butene. [j] 2-Methyl-2-butene. [k] 3,3,4,4-Tetramethylhexane. [l] *t*-Amyl acetate. [m] *t*-Amyl 2,2-dimethyl butyrate. [n] *t*-Amylbenzene.

major product at both wavelengths, and higher yields of esters were also obtained. Although dimers were still significant products, they were generated in amounts less than those observed from secondary and primary acids under comparable conditions.

Trapping of Alkyl Radicals as Intermediates.—Alkyl radicals are possible precursors for all the observed products. Various amounts of hydrogen donors were employed as part of the solvent to trap possible alkyl radicals as alkanes. These systems are described in Table VI for cumene, dibenzyl ether, and chloroform with valeric acid and Tl(III) in benzene. Cu(II) acetate, known to be a particularly effective *oxidant* of alkyl radicals, was also employed as a radical trap in benzene as well as chloroform solutions.

The yields of only the hydrocarbon products, alkane, alkene, and dimer, and carbon dioxide were determined since these were the products necessary for the diagnosis of the cage reaction. The variation of these products with the amount of hydrogen donor and copper(II) acetate added is shown in Table VI.

With cumene present, the amount of butane formed was greater than that formed in its absence. The diminution of all products with increasing cumene concentration (except butane with cumene as the solvent) may be explained by assuming that some of

TABLE VI

THE VARIATION OF BUTANE, BUTENE-1, AND OCTANE FROM PHOTOLYSIS OF Tl(III) AND VALERIC ACID IN THE PRESENCE OF HYDROGEN DONORS[a]

Hydrogen[b] donor	Donor/Tl(III), mole/mole	Products, % Butane	Butene-1	Octane	Carbon dioxide[d]
Cumene	1	42.4	12	32.3	200
Cumene	12	40.3	10	27.8	207
Cumene	37	39.8	7.9	17.7	174
Cumene	S[c]	44.6	6.1	11.4	154
Dibenzyl ether	1	33.5	7.4	26.2	193
Dibenzyl ether	11	53.2	2.4	6.6	107
Dibenzyl ether	S[c]	35.2	0	0.3	46
Chloroform	1	46.5	8.5	Not determined	206
Chloroform	9.4	100	5.2	10.6	239
Chloroform	S[c]	205	0	3.2	276
Cu(II)	0.053	10	81.7	3.4	150
Cu(II)	0.50	7.2	86.9	3.0	Not determined
Cu(II)	0.046[e]	132	3.0	2.7	233
None		31	10	33	200

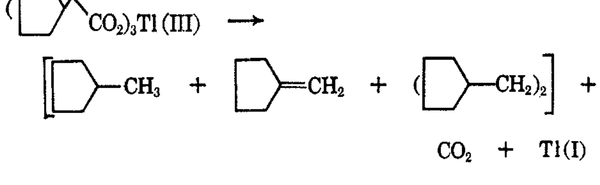
[a] In solutions containing 0.11 *M* Tl(III) acetate and 1.1 *M* valeric acid at 30° irradiated with 2537 A light. [b] In benzene solvent [c] Solvent. [d] Yields of carbon dioxide were determined using an 8-ft Porapak Q column at 65° with ethane as the marker. These analyses are perhaps more reliable than those performed using the silica gel column; the carbon dioxide peak observed using the silica gel suffered from rather severe post tailing. [e] Chloroform solvent.

the thallium was reacting with cumene, or radicals derived from it, by hydrogen abstraction (*i.e.*, the cumyl radical), rather than undergoing decarboxylation. (Small amounts of α-methylstyrene were observed but not determined quantitatively.) The solution was quite viscous with dibenzyl ether as the solvent, and if a cage reaction were to take place, it should be in evidence here. However, decarboxylation appeared to be the minor reaction as indicated by the very low yield of carbon dioxide.

Chloroform was perhaps the best hydrogen donor of the compounds studied. Increasing the chloroform concentration greatly enhanced the butane formation. However, with large quantities of chloroform present, the thallium was reduced to the metal. In those cases where butene-1 was not found (with both dibenzyl ether and chloroform as solvents), the radicals reacted mainly with the solvent.

Of the radical traps employed, the effect of copper (II) is the most readily understood. In the Cu(II)-catalyzed thermal decarboxylation of valeric acid with Pb(IV) acetate, butene-1 was practically the sole product.[8] In the photolytic (2537 A) decarboxylation employing Tl(III) acetate, however, significant quantities of butane and octane were formed even when the Cu(II) to Tl(III) ratio was as high as 1:2.

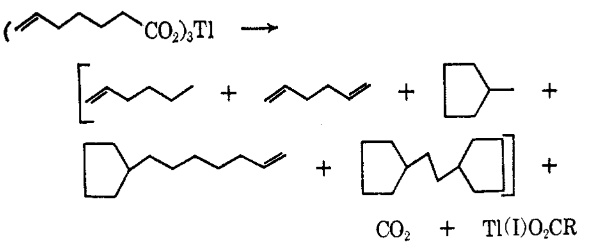
Decarboxylation of 6-Heptenoic and Cyclopentylacetic Acids with Tl(III).—A solution of 0.95 *M* cyclopentylacetic acid and 0.11 *M* Tl(III) in benzene was readily photolyzed at 2537 A. The principal



(10)

products were CO_2, methylcyclopentane (56%), methylenecyclopentane (4%) and 1,2-dicyclopentylethane (37%).[22] No evidence for any of the open-chain hexenes was found.

The unsaturated 6-heptenoic acid (0.94 *M*) reacted with 0.11 *M* Tl(III) in benzene solution slowly at room temperature without liberating CO_2. After 12 hr the Tl(III) concentration dropped to less than 0.01 *M* even when the reaction was kept in the dark. An insoluble thallium containing compound was formed, but not characterized further. However, if the solution of this acid was prepared and then photolyzed immediately a photoinduced decarboxylation could be performed. As expected, however, less than quantitative CO_2 was liberated due to the competing thermal reaction. Products derived from the 5-hexenyl moiety (see eq 11) were produced in 30% yield; they were hexene-1 (6%), methylcyclopentane (17%), biallyl (6%), 7-cyclopentylheptene-1 (1%), and 1,2-dicyclopentylethane (1%).[22] No 1,11-hexadecadiene (<0.3%) was found. The absence of the latter and yields of the other alkenes cannot be taken as definitive since it is possible that reaction of the unsaturated linkage with Tl(III) led to unidentified products.



(11)

Thermal Decarboxylation of Acids by Tl(III).—Qualitatively, tertiary aliphatic acids undergo photolysis more easily than their secondary alkyl or primary alkyl counterparts in the presence of Tl(III). Attempts were made to decarboxylate pivalic acid thermally with Tl(III) acetate in benzene. Unlike Pb(IV) pivalate the decomposition of Tl(III) pivalate was less than 50% complete in refluxing benzene solution after one week. Even the addition of sodium acetate, pyridine or Cu(II) acetate which are effective catalysts in the decarboxylation of Pb(IV) pivalate was of little value.

The thermal decarboxylation, however, was markedly catalyzed by strong acids in the carboxylic acid as solvent. Addition of perchloric acid, trifluoroacetic acid, and boron trifluoride induced rapid decarboxylation of isobutyric and *n*-butyric acids in the presence of Tl(III). Alkanes and alkenes were minor products and esters were formed in the largest amounts. Acid catalysis also pertains to decarboxylation of Mn(III), Co(III), Pb(IV), and Ce(IV) esters and we will describe these reactions in further detail at a later time.

Discussion

Results given in Tables II and III reveal some most interesting differences in the amounts of products formed during the photolysis of primary acids and Tl(III). The irradiation at shorter wavelength, 2537 A, produces greater amounts of alkene and dimer than does the reaction at 3500 A. The latter irradiation, in turn, affords high yields of alkanes. Most unique in the reaction at 2537 A, however, is the formation of products, *e.g.*, butane from *n*-butyric acid and pentane from *n*-valeric acid, which may be considered as originating from the coupling of a methyl radical and the radical produced from the decarboxylation of the acid. Also noteworthy is the relatively small quantities of esters and alkylbenzenes formed at both of these wavelengths. The alkane–dimer ratio in each example, except phenylacetic acid from which no alkene is possible, is approximately 0.3. This is close to the ratio (0.4) of these products formed in the vapor phase disproportionation–recombination of primary radicals.[23] Although photolytic reactions in solution and thermal gas phase reactions probably are highly dissimilar, the correspondence between these ratios is quite striking.

The amounts of alkene and dimer formed in the 2537-A reaction in both the secondary acid and tertiary acid photolyses are also greater than in the reaction carried out at 3500 A, as seen from Tables IV and V. Even in the case of tertiary acids, relatively small quantities of acetates and alkylbenzenes are formed. The yields of alkene from tertiary acids are significantly, though not much, greater than those from secondary acids. This points out the apparent inefficiency of Tl(III) to oxidize alkyl radicals, be they primary, secondary, or tertiary.

The yields of alkanes at 2537 A and the alkenes at both wavelengths show a general *increase* on going from primary to secondary to tertiary acids. The alkanes at 3500 A and the dimers at both wavelengths show a general *decrease* in this same sequence as the structure of the acid is varied. Substantial quantities of dimers are formed even with tertiary acids and relatively low yields of products of oxidation (except alkenes) are formed in all cases. This indicates to us a largely radical nature to these reactions.

Of all the acids studied and reported here, the photolysis of phenylacetic acid at 2537 A is the only case in which the thallium(III) appeared to be reduced to the metal. The 300% yield of carbon dioxide bears this out; this anomaly is under further investigation.

A Scheme for Photolysis of Tl(III) Esters.—These varied results for photolysis of primary, secondary, and tertiary acids in the presence of Tl(III) can be encompassed in a coherent pattern if free alkyl radicals are generated by the photolytic process illustrated in eq 12 and 13.

$$(\mathrm{RCO_2})_3\mathrm{Tl(III)} \xrightarrow{h\nu} (\mathrm{RCO_2})_2\mathrm{Tl(II)} + \mathrm{R}\cdot + \mathrm{CO_2} \qquad (12)$$

$$(\mathrm{RCO_2})_2\mathrm{Tl(II)} \xrightarrow{\text{fast}} \mathrm{RCO_2Tl(I)} + \mathrm{R}\cdot + \mathrm{CO_2} \qquad (13)$$

The products derived from the alkyl moiety are attributed to first- and second-order processes involving alkyl radicals. Dimers, prevalent in reactions at 2537 A, are derived by coupling of radicals. Similarly, alkanes and alkenes, particularly the latter, arise mainly by disproportionation.

We postulate further that dimers are mainly products of alkyl radicals derived from the homolysis of the *same* Tl(III) species by rupture of several bonds. Under

$$(\mathrm{RCO_2})_3\mathrm{Tl} \xrightarrow{2537\ \mathrm{A}} 2\mathrm{R}\cdot + \mathrm{CO_2} + \mathrm{Tl(I)O_2CR} \qquad (14)$$

these circumstances two alkyl radicals are born in close proximity and offer optimal opportunity for bimolecular reactions. The high local concentrations of radicals produced in photolysis at 2537 A is further manifested in the mixed coupling product between methyl and alkyl radical derived from acetic and the added acid, respectively. These homologs are probably generated from mixed esters such as Tl(III) $(\mathrm{OAc})_{3-n}(\mathrm{O_2CR})_n$ derived by incomplete metathesis (*cf.* eq 4), and are more important at lower concentrations of carboxylic acid.

It is unlikely in eq 14 that one quantum induces a four-bond homolysis. We suggest that the higher energies inherent with 2537 A irradiation[24] are sufficient to leave the initially formed (eq 12) metastable Tl(II) species in an excited state from which subsequent homolysis (eq 13) is rapid.[25] These pairs of alkyl radicals are not geminate in the usual sense,[26] since they can be rather thoroughly scavenged by such active hydrogen donors as dibenzyl ether and chloroform and efficient alkyl radical traps as Cu(II) (see Table VI).[27] In the latter case, Cu(II) is only necessary in catalytic quantities since the facile oxidation of the alkyl radical is followed by a rapid reoxidation of Cu(I) by Tl(III).[28]

$$\mathrm{R}\cdot + \mathrm{Cu(II)} \longrightarrow \mathrm{R(—H)} + \mathrm{Cu(I)} + \mathrm{H^+} \qquad (15)$$

$$\mathrm{Cu(I)} + \mathrm{Tl(III)} \longrightarrow \mathrm{Cu(II)} + \mathrm{Tl(II)} \qquad (16)$$

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[23] J. Kerr and A. Trotman-Dickinson, *Progr. Reaction Kinetics*, **1**, 107 (1961); J. Kraus and J. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

[24] The photophysical processes are, of course, not determined by these experiments. No doubt that in benzene considerable energy at 2537 A is transferred to the $\pi-\pi^*$ of the solvent. Energy transfer from either the singlet $^1\mathrm{B_{2u}}$ or triplet $^2\mathrm{B_{1u}}$ to Tl(III) is possible. Further studies in other solvents are in progress: A. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); M. DeGroot and van der Walls, *Mol. Phys.*, **6**, 545 (1963); S. Leach and R. Lopez-Delgado, *J. Chim. Phys.*, **61**, 1636 (1964); *cf.* also D. Bryer-Smith and H. Longuet-Higgins, *Chem. Commun.*, 593 (1966); J. Calvert and J. Pitts, "Photochemistry," John Wiley and Sons, New York, N. Y., 1966, p 321 ff.

[25] (a) Tl(II) carboxylate, like its Pb(III) analog,[8] should be thermally unstable and decompose spontaneously to Tl(I). We postulate here that its rate of fragmentation may be dependent on its vibronic state. The aquo Tl(II) ion disproportionates rapidly.[16] (b) It is also possible to entertain the notion of complexes between radicals and Tl(II) or Tl(III) as intermediates which affect radical reactivity: *cf.* J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

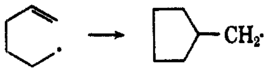
[26] W. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 87 ff.

[27] Low concentrations of Cu(II) are sufficient to remove most of the dimer. However, a large amount of Cu(II) does not obviate its formation entirely, and a primary recombination may be in order: R. Noyes, *J. Phys. Chem.*, **65**, 763 (1961); **22**, 1349 (1954); H. Waits and G. Hammond, *J. Am. Chem. Soc.*, **86**, 1907 (1964).

[28] Theoretically, reactions 15 and 16 together with 13 constitute a scheme for the radical-chain decomposition of Tl(III) carboxylates (*cf.* Pb(IV) decarboxylations[8]). We have not yet shown such a chain process and other factors must be involved.[29]

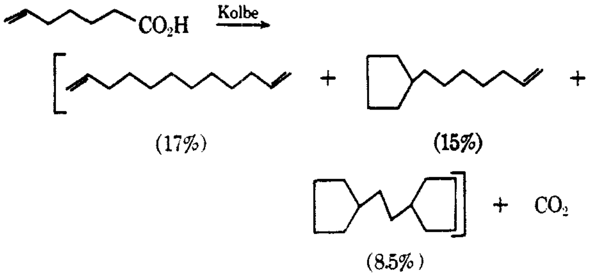
[29] In aqueous solution Tl(II) is alleged[16] to be a more powerful oxidant than Tl(III). Of course, this cannot be extrapolated to nonaqueous systems for a variety of reasons. It is possible that Tl(II) *is* responsible for oxidation of alkyl radicals.

There is further evidence that dimer is not formed by a molecular process. We observe extensive rearrangement of the 5-hexenyl moiety derived from 6-heptenoic acid. The 5-hexenyl radical is known to rearrange rapidly to the cyclopentylmethyl radical.[30] This rearrangement is unique with free radicals since the carbonium ion cyclizes to the isomeric cyclohexyl cation.[31] The absence of ring-opened products from the decarboxylation of cyclopentylacetic acid shows that the rearrangement (eq 17) is irreversible, which is consistent with other studies[29] on this system.



(17)

The results of the decarboxylation of 6-heptenoic acid by Tl(III) can be compared to the Kolbe electrolysis of this acid at Pt electrodes in methanol.[32] Cyclopentylacetic acid afforded only 1,2-dicyclopentylethane as coupled product, whereas the isomeric 6-heptenoic acid gave a mixture of rearranged products.[33] We could find no unrearranged dimer, 1,11-hexadecadiene, but the rearranged cyclopentylmethyl moiety was quite in evidence, as dimeric and monomeric products.



(18)

In addition to disproportionation, the imbalance of alkane produced at 2537 A relative to alkene is attributed to reactions of single alkyl radicals by hydrogen transfer with the milieu (eq 9). Photolyses at 3500 A generate predominantly alkanes, and these first-order reactions of alkyl radicals by hydrogen transfer processes are even more important than they are at 2537 A. The Tl(II) intermediate under these conditions may be in a less energetic state than that produced at 2537 A and fragment (eq 13) sufficiently slowly to reduce the incidence of bimolecular radical interactions.[33]

Alkenes are formed largely by disproportionation of alkyl radicals. Consistent with this formulation, alkene is more important for reactions at 2537 than 3500 A, since the former generates radicals in an environment in which they are more likely to collide with each other. Furthermore, disproportionation increases in importance relative to dimerization on going from primary radicals to secondary and to tertiary radicals, which is in accord with the well-known behavior of alkyl radicals in the gas phase.[23]

Disproportionation of radicals alone, however, does not account for all the alkene, especially those derived from tertiary alkyl and benzyl systems. In the former, alkene exceeds alkane and in the latter, disproportionation is not possible. This discrepancy also generally follows the increasing yields of esters in the order: primary < secondary < tertiary < benzyl. Other studies have shown that rates of oxidation of radicals by Pb(IV) increases in the same order. Thus, benzylic and tertiary alkyl radicals are selectively oxidized by Pb(IV) in preference to secondary and primary radicals.[7,8] Tl(III) is a less potent oxidant than Pb(IV) and oxidation of alkyl radicals by Tl(III) may be rather slow compared to other pathways for radicals in this system[29]

$$\mathrm{Tl(III)} + \mathrm{R}\cdot \longrightarrow \mathrm{Tl(II)} + [\mathrm{R}^+] \text{ etc.} \qquad (19)$$

(eq 19). Nonetheless, we postulate that some of the alkene and the esters, albeit minor and quantitatively indeterminant, are generated by such an oxidative route.[34]

The minor amounts of alkylbenzenes are derived by attack of the solvent by alkyl radicals. Similar processes were observed in the decarboxylation of acids by Pb(IV).

Experimental Section

Acids.—*n*-Butyric and isobutyric acids were Fisher Certified reagents, redistilled through a 4-ft helix packed column. Cyclohexanecarboxylic, *n*-valeric, isovaleric, and 2-methylbutyric acids were Eastman Kodak White Label, redistilled. The latter contained a small amount (<1%) of isovaleric acid. Octanoic and heptanoic acids were Matheson Coleman and Bell reagents redistilled before use. Pivalic acid was generously supplied by Enjay Chemial Co. and used directly. Cyclopentylacetic acid was from Aldrich Chemical Co.

2,2-Dimethylbutyric acid was prepared from *t*-amyl chloride and magnesium followed by carbonation (bp 186–187°). 6-Heptenoic acid was prepared from methyl suberate by oxidative decarboxylation with lead tetraacetate and cupric acetate[35] (bp 82–84° at 1.5 mm).

All acids were analyzed by gas-liquid partition chromatography (glpc) for isomeric impurities. The methyl ester (diethyleneglycol succinate) or the acid itself (FFAP, Varian Aerograph Co.) was examined.

Benzene, thiophene-free, was redistilled through a 22-plate Oldershaw column. It contained traces of cyclohexane but no toluene. Cumene, dibenzyl ether, and chloroform were redistilled before use under a nitrogen atmosphere. Glacial acetic acid (B & A, General Chemical reagent) was used as such.

Thallium(III) Acetate.—The methods of preparation of pure thallium(III) acetate reported in the literature were not desirable because of the poor quality and purity of the product[1,5b] or because of the inapplicability to large-scale production.[36]

A modified procedure was developed for the large-scale production of pure (>95% Tl(III) by titration) thallium(III) acetate in reasonably good yield. The following procedure is representative.

Thallium(III) oxide (457 g, 1 mole), obtained from the American Smelting and Refining Co., New York, N. Y., was added slowly with stirring to a hot (80–90°) solution of 2 l. of glacial acetic acid containing 110 ml of acetic anhydride. After addition was complete, the walls of the flask were washed down with about 500 ml of glacial acetic acid. Stirring and heating (90–100°) were continued until all of the brown oxide had dissolved (about 2 hr). While the solution was still hot, the solution was filtered through a medium, sintered-glass frit. The filtrate was allowed to cool to room temperature. The precipitate was removed by filtration through a sintered-glass frit. The collected solid was dissolved in the smallest possible volume (about 800 ml) of glacial acetic acid at 80–90°. The hot solution was again filtered through a sintered-glass frit and allowed to cool to room temperature and then to about 15° by cooling in cold water. The thallium(III) acetate was removed by filtration,

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(30) R. Lamb, P. Ayers, and M. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963); J. Garst, J. Pacifici, and R. Lamb, *ibid.*, **88**, 4260 (1966); C. Walling, J. Cooley, A. Ponaras, and E. Racah, *ibid.*, **88**, 5361 (1966); M. Julia, *Rec. Chem. Progr.*, **25**, 3 (1964).

(31) P. Bartlett, W. Closson, and T. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965).

(32) R. Garwood, C. Scott, and B. Weedon, *Chem. Commun.*, 14 (1965).

(33) An alternative explanation involves higher quantum yields and/or more intense irradiation at 2537 than at 3500 A (see, however, Results).

(34) If such an oxidative pathway were important, a radical-chain process (eq 13 and 19) similar to that for Pb(IV) would obtain.

(35) Unpublished results (*cf.* ref 8).

(36) R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

was spread in a large glass dish, and was placed in a desiccator over solid potassium hydroxide pellets overnight. The material obtained, 467 g, 61%, showed a thallium(III) content of 97% (see analysis below).

Analysis.—The iodometric analysis for thallium(III) compounds reported[6b,37] was unsuitable because the end point, even in the presence of starch, was obscured by the intense yellow-orange thallium(I) iodide formed. Excellent analyses were obtained by reducing the thallium(III) with an excess of standardized iron(II) solution (ferrous ammonium sulfate) and titrating the excess iron(II) with a standardized cerium(IV) solution (ceric ammonium sulfate) to the ferrous *o*-phenanthroline end point.[14b] Since reaction between Fe(II) and Tl(III) is not fast, it is important to use excess Fe(II) in these titrations.

Thallium(I) compounds, organic acids, and solvents were shown not to interfere in the analysis.

Photolyses.—A chamber reactor (Rayonet RPR-100, Southern New England Ultraviolet Co.) was used in all studies. Provisions for 16 interchangeable lamps placed peripherally enabled us to carry out intensity studies qualitatively by using different numbers of lamps. The lamps at 3500 A, according to the manufacturers, emitted an approximately gaussian distribution of light with a half-band width of ± 150 A at 3520 A. Each 2537- and 3500-A lamp emitted approximately 1.5 w in its spectral region. In general, a 20-ml solution of 0.1 *M* Tl(III) and 1 *M* acid contained in a 11 × 450 mm cylindrical quartz tube required 4 hr for photolysis at 2537 A (35 w) and 20 hr at 3500 A (24 w).

General Procedure.—Stock solutions were prepared for duplicate runs so that each reaction mixture (20 ml) contained approximately 2.0 mmoles of thallium(III) acetate and approximately 20 mmoles of the appropriate acid. Except where indicated to the contrary, the clear, colorless solutions remained so throughout the reaction with no solids precipitating from solution. Each stock solution was analyzed for thallium(III) content before irradiation. After the reaction was considered over, an aliquot of each reaction solution was analyzed for unreacted thallium(III).

An aliquot (20 ml) of the solution was transferred by pipet to quartz tubes with total capacity of about 40 ml. After filling the tubes, each one was covered with aluminum foil and the contents were flushed by bubbling an inert gas, nitrogen or argon, through the solution for 10–15 min by means of a glass capillary extending to the bottom of the tube. The tubes were stoppered with a securely fastened rubber septum stopper. The tubes were placed in the photochamber equipped with lamps to produce light of desired wavelength and were photolyzed for a period of time previously determined to be long enough to ensure complete disappearance of the thallium(III). After the photolysis was completed, the tube was placed in liquid nitrogen to freeze the contents and to condense the gases. The appropriate markers for analysis of the gases were added, and the tubes brought to room temperature with thorough agitation. The gases were analyzed by glpc. Pressure was released from the tubes; the contents were removed quantitatively from the tubes and adjusted to a known volume, generally 30 ml, with glacial acetic acid. Aliquots were taken from this diluted solution for analysis of any unreacted thallium(III) and of the remaining products.

Photolyses of solutions of 0.10 *N* Tl(III) acetate ahd 1.0 *M* valeric acid were carried out to 15, 30, 50, and 100% conversion of Tl(III). The relative amounts of products were the same within ±3% in all runs. Photolyses were also carried out using 4, 8, and 16 lamps (6, 12, and 24 w, respectively) for approximately 12, 6, and 3 hr using the 2537-A lamp. Equivalent results were obtained in all of these runs.

Glpc analyses were performed using the internal standard method. In the following sequence, the compound(s) (marker), and column are given serially. Methane, CO_2 (ethane), 8-ft. Porapak Q at 30°; propane, propylene, *n*-butane, butene-1, *cis*- and *trans*-butene-2,2-methylbutane (isobutane), 15-ft 30% Dowtherm/firebrick at 15°; isobutane, isobutylene (butane), Dowtherm; 2-methylbutane, 2-methyl-1-butene, 2-methyl-2-butene (*n*-pentane), 10-ft 30% Dowtherm on firebrick, 42°; 2,3-dimethylbutane, (*n*-octane), 8-m, 20% DEGS on Chromosorb W, 70°; isopropylbenzene (*sec*-butylbenzene), 9-ft 20% DEGS on acid-washed firebrick, 71°; 3,4-dimethylhexane (*n*-octane), 8-ft 20% SF-06 on Chromosorb W, HMDS, 67°; dicyclohexyl, cyclohexyl acetate, cyclohexylbenzene (*n*-amylbenzene), 6-ft 5% triisodecyl trimellitate, 5% Bentone 34 on Chromosorb P, HMDS, 125°; cyclohexane, cyclohexene, methylcyclohexane (*n*-hexane), 8-m 20% DEGS on Chromosorb W, 55°; *t*-amyl acetate, 3,3,4,4-tetramethylhexane, *t*-amyl benzene, *t*-amyl 2,2-dimethyl butyrate (cyclohexyl acetate), 12-ft 20% SF-96 on Chromosorb W, HMDS, 165°; 2,2,3,3-tetramethylbutane, *t*-butyl acetate, *t*-butyl trimethylacetate (*n*-butyl acetate), 12-ft 20% SF-96 on Chromosorb W, HMDS, 90°; *t*-butylbenzene (*n*-butyl acetate), 7-ft 20% SF-96 on Chromosorb W, HMDS, 120°; *n*-propyl butyrate, *n*-propylbenzene (*sec*-butylbenzene), 9-ft 20% DEGS on acid-washed firebrick; isobutyl isovalerate, isobutylbenzene (*n*-butylbenzene), 9-ft 20% DEGS on acid-washed firebrick, 104°; *sec*-butyl 2-methylbutyrate, *sec*-butylbenzene (*n*-butylbenzene), 9-ft 20% DEGS on acid-washed firebrick, 71°; *n*-octane (*n*-heptane), 12-ft 15% didecyl phthalate, 5% Bentone 34 on Chromosorb W, 90°; hexane (octane), 8-m 20% DEGS on Chromosorb W, 70°; dibenzyl, diphenylmethane, benzyl acetate (dicyclohexyl), benzyl phenylacetate (phenyl benzoate), 6-ft 20% SF-96 on Chromosorb W, HMDS, 150°; cyclohexyl cyclohexanecarboxylate (*n*-heptyl cyclohexanecarboxylate), 4-ft 20% SF-96 on Chromosorb W, HMDS, 170°; *n*-butyl valerate (ethyl hexanoate), *n*-butylbenzene (isopropylbenzene), 9-ft 20% DEGS on acid-washed firebrick, 104°; 2,5-dimethylhexane (*n*-octane), 8-ft 30% Dowtherm on firebrick, room temperature; toluene (ethylbenzene), ethylbenzene (toluene), 12-ft 15% didecyl phthalate, 5% Bentone 34 on Chromosorb W, 120°.

In every case authentic compounds were used for direct comparisons with products of the reaction. In a number of cases several types of columns (polar and nonpolar) were employed to substantiate assignment.

Electrolysis of Cyclopentylacetic and 6-Heptenoic Acids.—A small piece of freshly cut sodium metal (about 0.1 g) was added to 16 ml of anhydrous methanol. After the sodium reacted, two drops of distilled water and 2.02 g (15.8 mmoles) of cyclopentylacetic acid were added. The beaker was surrounded by ice and the solution electrolyzed between platinum electrodes at approximately 75 v and 0.35 amp. Methanol was added from time to time to keep the volume constant. After 2 hr, the solution was basic to litmus. Distilled water was added to the reaction mixture followed by ether extraction. The ether solutions were combined, washed with distilled water, and dried over magnesium sulfate. Products were not determined quantitatively, but by glpc analysis 1,2-dicyclopentylethane was the sole dimeric product.

The same procedure was followed in the electrolysis of 2.03 g (15.9 mmoles) of 6-heptenoic acid. In this run, black material formed at the cathode and fluctuations in the amperage were difficult to control. Changing the polarity of the electrodes was helpful in keeping the amperage reasonably constant, but periodic cleaning by flaming was more helpful. This reaction was complete in approximately 4 hr. The dimeric products obtained were 1,11-dodecadiene (43%), 7-cyclopentyl-1-heptene, and 1,2-dicyclopentylethane (29%). Neither absolute yields nor other products were determined.

Registry No.—Thallium(III), 14627-67-9; thallium(III) acetate, 2570-63-0; thallium(III) valerate, 14627-69-1; *n*-butyric acid, 107-92-6; *n*-valeric acid, 109-52-4; isovaleric acid, 503-74-2; phenylacetic acid, 103-82-2; octanoic acid, 124-07-2; nonanoic acid, 112-05-0; isobutyric acid, 79-31-2; 2-methylbutyric acid, 116-53-0; cyclohexanecarboxylic acid, 98-89-5; trimethylacetic acid, 75-98-9; 2,2-dimethylbutyric acid, 595-37-9; cumene, 98-82-8; dibenzyl ether, 103-50-4; chloroform, 67-66-3; copper(III) acetate, 302-07-8; 6-heptenoic acid, 1119-60-4; cyclopentylacetic acid, 1123-00-8; benzene, 71-43-2.

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