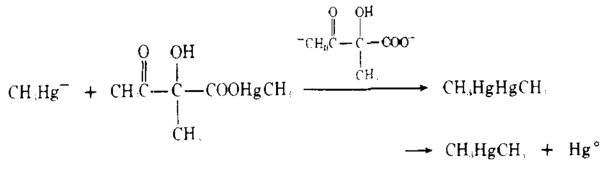

$$CH_3Hg^- + CH_3\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{OH}{C}}-COOHgCH_3 \xrightarrow{^-CH_2\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{OH}{C}}-COO^-} CH_3HgHgCH_3 \longrightarrow CH_3HgCH_3 + Hg^\circ$$

However, this is considered to be an unlikely prospect in the aqueous environment.

(16) See ref 10a, p 125. This statement holds when such ligands are present in excess over the satisfaction of mercury(II) coordination.

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Radical Isomerization and Hydrogen–Deuterium Exchange in Reactions of Silver *p-tert*-Butylbenzoate

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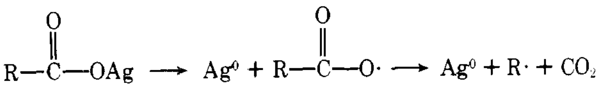
Silver *p-tert*-butylbenzoate decomposes at 300 °C to products that retain the *tert*-butyl group intact. Among these products are five isomeric di-*tert*-butylbiphenyls, evidently resulting by isomerization of the first-formed *p-tert*-butylphenyl radical. With labeled benzophenone and benzene, the silver salt gives products in which much protium–deuterium exchange has occurred. The photolyzed silver salt arylates 1,2,4-trichlorobenzene; thermal decomposition in benzonitrile yields triphenyltriazine in addition to the radical arylation product.

We discovered that silver carboxylates decompose at 200–400 °C according to eq 1. We have described the formation and reactions of mono- and polyradicals from silver arenecarboxylates in a previous publication.[1] More recently, we wished to find if a thermally labile group such as *tert*-butyl could survive the elevated temperatures at which silver salts decompose. Accordingly, we pyrolyzed 8.55 g (30 mmol) of silver *p-tert*-butylbenzoate (294 °C dec) at 300 °C under nitrogen and obtained 4.2 g of a distillate composed of the products listed in Table I. All products apparently retained the *tert*-butylphenyl group intact.



$$R-\overset{O}{\overset{\|}{C}}-OAg \longrightarrow Ag^0 + R-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow Ag^0 + R\cdot + CO_2 \quad (1)$$

Table I. Products from Silver *p-tert*-Butylbenzoate at 300 °C

product	relative concentration[a]
tert-butylbenzene	38.6
tert-butylbenzoic acid	4.5
di-*tert*-butylbiphenyl	30.1
di-*tert*-butylbenzocoumarin	2.2
tri-*tert*-butylterphenyl	5.6
tetra-*tert*-butylquaterphenyl	0.7

[a] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum.

In addition to demonstrating the survival of the *tert*-butyl groups at the pyrolysis temperature, analyses of the products presented two other points of interest.

The presence in a single spectrum of *tert*-butylbenzene and of biphenyl, terphenyl, and quaterphenyl with a *tert*-butyl group on each ring offered a clear illustration of the effect of molecular size on a favored decomposition in the mass spectrum. All *tert*-butylarenes have a marked tendency to lose CH_3 under electron impact. In a small molecule such as *tert*-butylbenzene, the intensity ratio of $[M^+ - CH_3]/[M^+]$ in 70 eV spectra usually is about 4 or 5:1. With increase of molecular size, this ratio tends to drop, presumably because of the increased number of degrees of freedom. The ratios are shown in Table II.

Directly coupled gas chromatography/mass spectrometry revealed the presence of five isomeric di-*tert*-butylbiphenyls, whose partial spectra are shown in Table III. The high intensity at *m/z* 195 for $(M - CH_3 - C_4H_8)^+$ ions in isomers 1 and 2 suggested that these contained two and one *tert*-butyl groups, respectively, ortho to the second ring and that isomers **3**, **4**, and **5** contained no *tert*-butyl group ortho to the second ring. The absence of ortho substitutions in **3**, **4**, and **5** was confirmed by synthesis of authentic 3,3′- and 4,4′-di-*tert*-butylbiphenyl and of a mixture containing known amounts of the 3,3′, 3,4′, and 4,4′ isomers; this allows firm identification by retention time of isomers **3**, **4**, and **5**, respectively, as the 3,3′-, 3,4′-, and 4,4′-di-*tert*-butylbiphenyls. The relative amount of each isomer formed from silver *tert*-butylbenzoate, as determined by gas chromatography, is shown in Table IV.

One might expect 3,4′-di-*tert*-butylbiphenyl to be the

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Table II. Intensity Ratio of [$M^+ - CH_3$]/[M^+] in *tert*-Butylarenes[a]

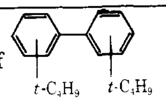
tert-butylarene	mol wt	intensity ratio [$M^+ - CH_3$]/[M^+]
tert-butylbenzene	134	4.6:1
di-*tert*-butylbiphenyl[b]	266	2.4:1
tri-*tert*-butylterphenyl[b]	398	0.8:1
tetra-*tert*-butylquaterphenyl[b]	530	0.4:1

[a] In 70 eV spectrum. [b] Isomeric distributions are uncertain.

Table III. Partial Spectra of Di-*tert*-butylbiphenyls

m/z	relative intensities				
	isomer, in order of elution				
	1	2	3	4	5
266	145	66	50	35	32
251	100	100	100	100	100
195	200	61	4	2	4

Table IV. Concentration of Di-*tert*-butylbiphenyl Isomers from Silver *p*-*tert*-Butylbenzoate

isomer of 	% of total
2,2′	1.7
2,3′ and/or 2,4′	1.5
3,3′	75.0
3,4′	19.2
4,4′	2.6

predominant isomer formed in view of the structure of the attacking radical I and steric constraints. Seemingly there has been a considerable amount of isomerization of the 4-*tert*-butylphenyl radical to the 3 isomer, even in the brief time span of the rapid pyrolysis.

In another context, we found a somewhat related rapid transformation. Silver *tert*-butylbenzoate was refluxed 3 min at 305 °C in separate experiments with benzophenone and benzophenone-d_{10} in a 1:2 mole ratio. The products are shown in Tables V and VI. A considerable amount of hydrogen–deuterium exchange took place during formation of *tert*-butylphenyl radical and its reactions with benzophenone-d_{10}.

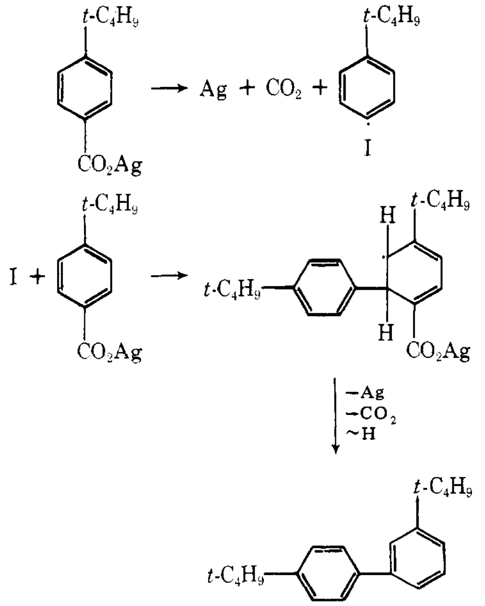


Table V. Products from the Reaction of Silver *p*-*tert*-Butylbenzoate with Benzophenone

product	relative concentration[a,b]
tert-butylbenzoic acid	2.4
benzophenone	76.3
di-*tert*-butylbiphenyl	2.9
tert-butylphenylbenzophenone	6.6
benzophenone dehydro dimer	2.4
bis(*tert*-butylphenyl)benzophenone	0.3

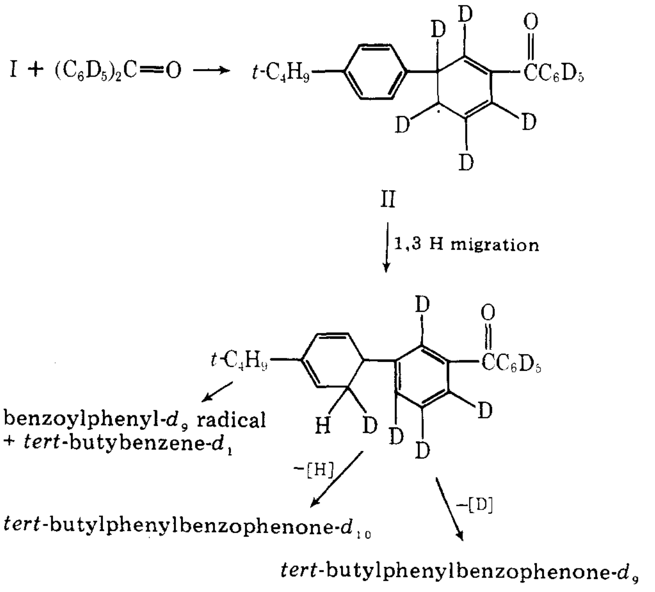
[a] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum. [b] A small amount of the relatively volatile *tert*-butylbenzene, if formed, was presumably lost during workup.

Table VI. Products from the Reaction of Silver *p*-*tert*-Butylbenzoate with Benzophenone[a]

product	isotopic distribution, %[b]	relative concentration[b]
tert-butylbenzene	38 d_1	1.9
	31 d_2	
	31 d_3	
benzophenone	1 d_5	75.7
	1 d_6	
	3 d_7	
	13 d_8	
	35 d_9	
	47 d_{10}	
di-*tert*-butylbiphenyl	14 d_1	6.7
	27 d_2	
	35 d_3	
	24 d_4	
tert-butylphenylbenzophenone	19 d_8	5.1
	32 d_9	
	33 d_{10}	
	16 d_{11}	
benzophenone dehydro dimer	29 d_{16}	2.0
	39 d_{17}	
	32 d_{18}	
bis(*tert*-butylphenyl)benzophenone	100 d_{10}	0.7

[a] Isotopic composition: 88.9% d_{10}, 10.4% d_9. [b] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum.

Reversible formation of the cyclohexadienyl radical II, followed by loss of either protium or deuterium in rearomatization, could account for the scrambling.[2]



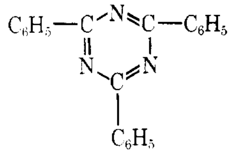
To evaluate a possible catalytic role of some of the products from silver *p-tert*-butylbenzoate pyrolysis, we refluxed mixtures of benzophenone and benzophenone-d_{10} with *tert*-butylbenzoic acid and silver metal from a prior pyrolysis, each at 300 °C for 5 min. The mixtures were recovered unchanged. Under the same conditions, 2 mol % of silver *p-tert*-butylbenzoate brought about appreciable exchange. The ratio of benzophenone-d_9/-d_{10} went from 11.7% in the original sample to 31.7% in the product, and benzophenone went from 100% d_0 to 2% d_1 and 0.2% d_2, presumably through the mechanism outlined.

Under more drastic conditions, silver *p-tert*-butylbenzoate brought about extensive deuterium exchange. A mixture of 5 mmol of silver salt with 50 mmol of benzene-d_6 in a bomb at 300–310 °C for 30 min gave the products shown in Table VII.

The same mixture at 175–200 °C for 1 h underwent no exchange, showing that the silver salt per se was not catalyzing the exchange.

The solubility of silver *p-tert*-butylbenzoate in organic reagents at elevated temperatures made possible its photolysis in 0.076 M solution in 1,2,4-trichlorobenzene at 200 °C. The major products, other than recovered trichlorobenzene and *tert*-butylbenzoic acid, were *tert*-butyltrichlorobiphenyl (25%) and pentachlorobiphenyl (56%), presumably via arylation of trichlorobenzene by *tert*-butylphenyl and dichlorophenyl radicals, respectively. The dichlorophenyl radical forms by the action of ultraviolet light on trichlorobenzene.

With benzonitrile, silver *p-tert*-butylbenzoate gave the products shown in Table VIII. *tert*-Butylbenzonitrile results apparently by transfer of a CN group to the *tert*-butylphenyl radical. Triphenyltriazine has been made from benzonitrile



through trimerization by a strong acid, fuming sulfuric acid,[3] or molten sodium at reflux.[4] Dicyanobenzene was formed in small amounts in the gas-phase reaction of phenyl and nitrophenyl radicals from nitrobenzene and *m*-dinitrobenzene with benzonitrile at 600 °C,[5] but triphenyltriazine was not among the products of these reactions. The species responsible for trimerization may be a transient complex formed at the pyrolysis temperature between the silver salt and benzonitrile, which goes quantitatively to triphenyltriazine at 190 °C.[6]

Table VII. Products from Silver *p-tert*-Butylbenzoate with Benzene-d_6[a]

product	isotopic distribution, %	relative concentration[b]
benzene	16 d_5 84 d_6	27.8
tert-butylbenzene	15 d_0 29 d_1 32 d_2 21 d_3 3 d_4	27.2
tert-butylbenzoic acid	30 d_0 40 d_1 30 d_2	14
tert-butylbiphenyl	19 d_4 26 d_5 33 d_6 22 d_7	7.2
di-*tert*-butylbiphenyl	14 d_1 21 d_2 34 d_3 24 d_4 7 d_5	11.5
di-*tert*-butylterphenyl	36 d_6 36 d_7 28 d_8	1.9
tri-*tert*-butylterphenyl	68 d_4 32 d_5	1.3

[a] 96.6% d_6, 3.4% d_5. [b] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum. Fragment ions attributed to the loss of CH_3 from *tert*-butylbenzene and *tert*-butylbenzoic acid are included.

Table VIII. Products from the Reaction of Silver *p-tert*-Butylbenzoate and Benzonitrile[a]

product	relative concentration[b]
tert-butylbenzene	9.4
tert-butylbenzonitrile	7.9
tert-butylbiphenyl	4.1
tert-butylphenylbenzonitrile	13.8
di-*tert*-butylbiphenyl	18.7
triphenyltriazine	13.2

[a] Conditions: 20 mmol of silver salt, 200 mmol of benzonitrile, 300 °C, in a bomb for 30 min. [b] Percent of total ions in the low-voltage (7.5 eV nominal) mass spectrum.

The *tert*-butyl group was retained also in the pyrolysis of silver 4-*tert*-butylphthalate (323 °C dec). The products are shown in Table IX.

Ether-soluble products from 30 mmol of silver 4-*tert*-butylphthalate weighed 3.3 g, in contrast to 0.18 g of such products from 30 mmol of silver terephthalate. The latter salt went 98% to carbon-like polymer, as was the case with most silver arene polycarboxylates. This result suggests considerably more stepwise rather than concerted decomposition of silver *tert*-butylphthalate, with concomitant H abstraction by intervening radicals.

The driving force for the isomerization of *tert*-butylphenyl radical remains unclear. Formation of the isomeric di-*tert*-butylbiphenyls is not due to thermal rearrangement; a sample of 4,4′-di-*tert*-butylbiphenyl at 300 °C for 4 h was recovered unchanged. The behavior of *tert*-butylphenyl radicals from sources other than silver *p-tert*-butylbenzoate as well as the apparent lability of the CN group of benzonitrile in radical reactions at elevated temperatures are being investigated further.

Experimental Section

Silver *p-tert*-butylbenzoate was prepared in quantitative yield by adding an aqueous solution of the sodium salt of *tert*-butylbenzoic acid (Aldrich Chemical Co.) to aqueous silver nitrate in 5% molar excess at 20 °C with rapid stirring. The precipitated silver salt was collected on a filter, washed with water, and dried in vacuo at 90 °C. It was crystallized from *o*-xylene as white needles, mp 294 °C dec.

For pyrolysis, the silver salt, 20 mmol, was spread evenly in a Pyrex tube, swept with dry nitrogen, and heated in a furnace. The cooled products were extracted with ether, the ether solutions were filtered and evaporated, and the residues were analyzed by gas chromatog-

Table IX. Products from Pyrolysis of Silver 4-*tert*-Butylphthalate

product	yield, wt %[a]
tert-butylbenzene	9
di-*tert*-butylbiphenylene	4
di-*tert*-butylbiphenyl	28
di-*tert*-butylbenzocoumarin	15
tri-*tert*-butyltriphenylene	3
tri-*tert*-butylterphenyl	6

[a] Based on total weight of ether-soluble products and relative concentrations of ions in the low-voltage (7.5 eV nominal) mass spectrum.

raphy, 70 eV and low-voltage mass spectrometry (low-resolution), supplemented by high-resolution precise mass measurements as needed, and directly coupled gas chromatography/mass spectrometry. Low-resolution mass spectra were measured on a DuPont Model 21-104 instrument using electrical scanning, with normal and low-voltage electron energies set at 70 and 7.5 eV nominal and with inlet and source temperatures of 350 and 250 °C, respectively. Directly coupled gas chromatography/mass spectrometry utilized a 5 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W coupled via a jet orifice separator to a DuPont Model 21-491 mass spectrometer; electron energy was 70 eV, and ion source temperature was 250 °C. High-resolution measurements were made on a CEC Model 21-110B mass spectrometer with 70 eV electrons and inlet and source temperatures approximating those used for the low-resolution spectra. Mass measurements were obtained via the A.E.I. DS50 system at a resolution of 10 000 (10% valley definition), except in cases where peaks of interest, especially some due to chlorinated species, were poorly resolved from perfluoroalkane reference peaks. In such cases, we resorted to peak matching at a resolution of 20 000.

Synthesis of Di-*tert*-butylbiphenyl Isomers. 4,4′ Isomer. A 100-mL (0.667 mol) amount of *tert*-butylbenzene was iodinated with 49.8 g (0.1962 mol) of iodine and 46 mL (1.02 mol) of nitric acid, at 70 °C for 3 h according to the method of Dains and Brewster.[7] The product distilling at 249–254 °C, 48 mL, was stirred with 25 g of iron filings, 35 mL of water, and 5 mL of concentrated hydrochloric acid to reduce any nitro compounds. Filtering, washing, drying, and distilling gave 51.4 g boiling at 249–254 °C, which analyzed as 97.3% pure 4-iodo-*tert*-butylbenzene. The iodo compound, 10 g, was heated with 10 g of copper powder in a bomb at 325 °C for 4 h to yield 1.5 g of white crystals of 4,4′-di-*tert*-butylbiphenyl: mp 127–128 °C, after crystallization from methanol (lit.[8] mp 127–128 °C).

3,3′ Isomer. 3-Bromo-*tert*-butylbenzene, bp 222–225 °C, was prepared in 65% yield from 3-*tert*-butylphenol (Aldrich), triphenylphosphine, and bromine by the method of Schaefer and Higgins.[9] A Grignard reagent from 2.88 g (0.12 mol) of Mg turnings, 21.3 g (0.1 mol) of 3-bromo-*tert*-butylbenzene, and 150 mL of anhydrous ether was added rapidly to a stirred mixture of 2.2 g (0.010 mol) of anhydrous cobaltous bromide and 7.46 mL (0.1 mol) of ethyl bromide in 20 mL of anhydrous ether.[10] The mixture was refluxed for 2 h and decomposed with ice, water, and acetic acid, and the ether layer was washed, dried, and evaporated on a steam bath to give 13.4 g of product that analyzed for 43.6 wt % of 3,3′-di-*tert*-butylbiphenyl and 1.7 wt % of 3,4′-di-*tert*-butylbiphenyl.

Mixed 3,3′, 3,4′, and 4,4′ Isomers. A solution of 2.24 g (0.010 mol) of palladium acetate and 75 mL (0.5 mol) of *tert*-butylbenzene in 100 mL of trifluoroacetic acid was stirred at 20–25 °C for 26 days.[11] The solution was still red, although a good deal of palladium metal had precipitated. The mixture was poured into water, ether was added, and the ether extract was washed successively with water, 10% potassium hydroxide, and water, dried, and distilled. The residue at 214 °C, 4.2 g, analyzed by gas chromatography, contained 8.3% 3,3′-, 21.2% 3,4′-, and 17.5% 4,4′-di-*tert*-butylbiphenyl, closely duplicating Norman et al.,[11] who gave the composition as 5% 3,3′, 20% 3,4′, and 17% 4,4′ isomers.

Relative retention times for 3,3′, 3,4′, and 4,4′ isomers were 2.67, 2.87, and 3.07, respectively, relative to biphenyl. A 5 ft column of 10% OV-17 on 80–100 mesh Chromosorb W was used, temperature-programmed from 150 to 300 °C at 8 °C/min with a flow rate of 25 mL/min of helium.

Benzophenone-d_{10} was prepared from benzoyl-d_5 chloride and benzene-d_6 (Stohler Isotope Chemicals) with aluminum chloride in 95% yield.[12]

Photochemical Reaction of Silver *p-tert*-Butylbenzoate and 1,2,4-Trichlorobenzene. A mixture of 14.25 g (50 mmol) of silver salt and 660 mL (4.4 mol) of 1,2,4-trichlorobenzene was stirred and heated to 200 °C in a quartz flask irradiated by a 550 W Hanovia medium-pressure mercury vapor lamp (no. 6515-36) in an aluminum reflector (no. 6531-16), 7.5 cm distant. The flask was rotated 25° every hour to expose a fresh surface during 14 h of irradiation. The cooled mixture was filtered and distilled, leaving 19.5 g of residue.

Acknowledgment. The authors are happy to acknowledge the considerable assistance of Dr. Richard E. Pauls, Standard Oil Company (Indiana), in the many gas chromatographic analyses.

Registry No.—Silver *p-tert*-butylbenzoate, 46203-44-5; benzophenone, 119-61-9; benzophenone-d_{10}, 22583-75-1; benzene-d_6, 1076-43-3; benzonitrile, 100-47-0; silver 4-*tert*-butylphthalate, 67872-67-7; *tert*-butylbenzene, 98-06-6; 4-iodo-*tert*-butylbenzene, 35779-04-5; 4,4′-di-*tert*-butylbiphenyl, 1625-91-8; 3-bromo-*tert*-butylbenzene, 3972-64-3; 3,3′-di-*tert*-butylbiphenyl, 53692-24-3; 3,4′-di-*tert*-butylbiphenyl, 53692-25-4; 1,2,4-trichlorobenzene, 120-82-1.

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