phosphite to a "positive carbon atom" adjacent to the carbonyl function. Carboxylation reactions generally require proceeding *via* the α-keto carbanion. The differences in polarity of precursor species to the phosphonate and carboxylate, respectively, should be of utility for specific synthetic strategies.

Registry No.—1, 40463-76-1; **2,** 40463-77-2; dimethyl acetonylphosphonate, 4202-14-6; sodium iodide, 7681-82-5.

Induced Decomposition of Di-*tert*-butyl Peroxide Using Chlorotris(triphenylphosphine)rhodium(I)/Hydrogen

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Received March 2, 1973

Heterogeneous hydrogenation of peroxides using various metal systems is well known.[1] The fact that nearly quantitative yields of alcohols are obtained without apparent secondary radical reactions such as β scission suggest either concerted cis addition of hydrogen or a very rapid sequential reaction which does not allow the escape of free alkoxy radicals. We now wish to report the induced decomposition of di-*tert*-butyl peroxide in a chlorotris(triphenylphosphine)rhodium(I)/hydrogen homogeneous system.

Hydrogenation of di-*tert*-butyl peroxide using chlorotris(triphenylphosphine)rhodium(I) in benzene solution yielded *tert*-butyl alcohol and acetone. The reaction is first order in catalyst, first order in peroxide (Figure 1), zero order in hydrogen pressure, and inversely proportional to added triphenylphosphine above a 1:1 weight ratio based on catalyst. It can be seen in Table I that only simple phosphine–rhodium (or ruthenium) halide systems are effective. Uncatalyzed reactions under identical conditions (but no catalyst or catalyst but no hydrogen) show only trace (1–3%) peroxide decomposition. Introduction of either radical-stabilizing solvents or effective hydrogen-transfer agents resulted in increased selectivity to *tert*-butyl alcohol (Table II).

TABLE I
EFFECT OF VARIOUS CATALYST SYSTEMS ON SELECTIVITY TO *tert*-BUTYL ALCOHOL[a]

Registry no.	Catalyst[b]	% reacted di-*tert*-butyl peroxide (conversion)	Yield *tert*-butyl alcohol based on reacted peroxide[c] (selectivity)
14694-95-2	L_3RhCl	29	58
14973-89-8	L_3RhBr	53	59
18284-36-1	L_4RhH	2	
13938-94-8	$L_2(CO)RhCl$	1	
20097-11-4	$L_2(NO)RhCl_2$	1	
15529-49-4	L_3RuCl_2	23	61

[a] Data for 0.043 mmol of catalyst, 20 mg of Ph_3P, 5.4 mmol of di-*tert*-butyl peroxide, 30 ml of benzene, 600 psig of hydrogen, 120°, and 1 hr reaction time. [b] L = triphenylphosphine. [c] Remainder was converted to acetone.

TABLE II
EFFECT OF VARIOUS ADDITIVES ON SELECTIVITY TO *tert*-BUTYL ALCOHOL[a]

Additive	g	% reacted di-*tert*-butyl peroxide (conversion)	Yield *tert*-butyl alcohol based on reacted peroxide[b] (selectivity)
Tetralin	1.0	80	94
Phenol	1.0	9	100
m-Cresol	0.5	85	99
Ionol[c]	0.5	57	86

[a] Data for 0.043 mmol of $(Ph_3P)_3RhCl$, 20 mg of Ph_3P, 5.4 mmol of di-*tert*-butyl peroxide, 30 ml of benzene, 600 psig of hydrogen, 120°, and 1 hr reaction time. [b] Remainder converted to acetone. [c] 2,6-Di-*tert*-butyl-4-methylphenol.

Of the additives tested, *m*-cresol appeared to be the best from the standpoint of reaction rate and selectivity. Quantitative measurements indicate that *m*-cresol was not destroyed in the reaction.

A mechanism which involves no induced decomposition and only simple abstraction of rhodium hydrogen seems unlikely because (1) the rate of peroxide decomposition is rapid relative to identical metal-free systems and (2) the rate of disappearance of peroxide is proportional to catalyst concentration, while the selectivity to *tert*-butyl alcohol is independent of catalyst concentration.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot \xrightarrow{MH} (CH_3)_3COH \qquad (2)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (3)$$

$$\text{HRh (complex)} + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + (CH_3)_3CO\cdot + \text{Rh (complex)} \qquad (4)$$

We suggest that a rhodium–hydrogen complex leads to the induced decomposition of peroxide resulting in the formation of free radicals. It should be noted that not all of the rhodium complexes in Table I induce peroxide decomposition. This might be explained by analogy to olefin hydrogenation activity in which these complexes exhibit diverse activity.[2] The inverse dependence on triphenylphosphine might be explained by loss of a triphenylphosphine moiety in the course of reaction; the facility with which the various complexes in Table I could lose a triphenylphosphine moiety is in general agreement with the observed induced decompositions.[2] Indeed, induced decomposition of nonmetallic systems is well known. Induced decomposition of di-*tert*-butyl peroxide has been reported by workers at Shell[3] in explaining increased decomposition rates of neat di-*tert*-butyl peroxide and by

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(1) For discussion and references see P. N. Rylander, "Catalytic Hydrogenation over Platinium Metals," Academic Press, New York, N. Y., 1967, p 489.

(2) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 263 (1972), and references cited therein.

(3) E. R. Bell, F. F. Rust, and W. E. Vanghan, *J. Amer. Chem. Soc.*, **72**, 337 (1950).

Huyser, Bredeweg, and Van Scoy[4,5] in explaining increased decomposition rates of di-*tert*-butyl peroxide in primary and secondary alcohols and amines.

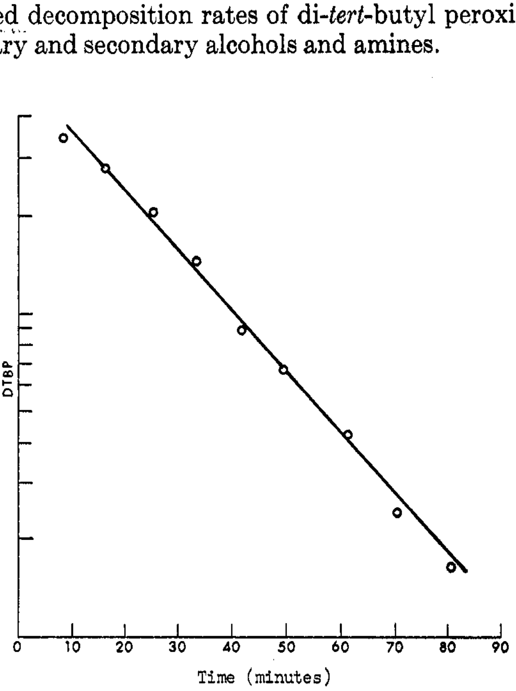

Figure 1.—First-order plot for the decomposition of di-*tert*-*t*-butyl peroxide (DTBP) in benzene with 0.043 mmol of L_3RhCl, 600 psig H_2, 20 mg of Ph_3P, 120°.

Experimental Section

Materials.—Except for the metal systems, commercial materials were used in this work: benzene, triphenylphosphine, tetralin, phenol, *m*-cresol, and Ionol. The following metal complexes were prepared as previously described: $(Ph_3P)_3RhCl$,[6,7] $(Ph_3P)_3RhBr$,[7] $(Ph_3P)_2CORhCl$,[7] $(Ph_3P)_4RhH$,[8] and $(Ph_3P)_3RuCl_2$.[9]

Decomposition of Di-*tert*-butyl Peroxide.—A solution of 0.79 g (5.4 mmol) of di-*tert*-butyl peroxide, 0.020 g (0.076 mmol) of Ph_3P, and 30 ml of benzene was charged in a nitrogen atmosphere to an 80-ml Inconel magnetically stirred autoclave (total free space including system, 126 ml). A pressure of 600 psig hydrogen was charged to the vessel. The temperature (120°) was maintained ±1% by a thermostatically controlled heating mantle. In experiments using metal catalysts, 0.043 mmol of catalyst was also added to the reaction solution. In experiments in which $(Ph_3P)_3RhCl$ concentrations were varied, 0.021, 0.06, and 0.09 mmol of catalyst were employed. The reaction mixture was analyzed by standard glc techniques for di-*tert*-butyl peroxide, *tert*-butyl alcohol, and acetone.

Decomposition of Di-*tert*-butyl Peroxide with Additives.—The above procedure and amounts of reactants were used and 0.5- or 1.0-g amounts of tetralin, phenol, *m*-cresol, or Ionol were also added. Glc analysis showed no loss of *m*-cresol in *m*-cresol experiments.

Registry No.—*tert*-Butyl alcohol, 75-65-0; *tert*-butyl peroxide, 110-05-4.

Acknowledgment.—The authors are grateful to Dr. L. H. Gale and Dr. H. V. Holler for helpful discussions.

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[4] E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

[5] E. S. Huyser, C. J. Bredeweg, and R. M. Van Scoy, *J. Amer. Chem. Soc.*, 4148 (1964).

[6] K. C. Dewhirst, U. S. Patent 3,489,786 (1970), to Shell Oil Co.

[7] J. A. Osborn, F. H. Jardine, J. F. Yonng, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966).

[8] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).

[9] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 1945 (1966).

The Acid-Catalyzed Addition of Acetic Acid to 2-Arylbornenes and 2-Arylapobornenes

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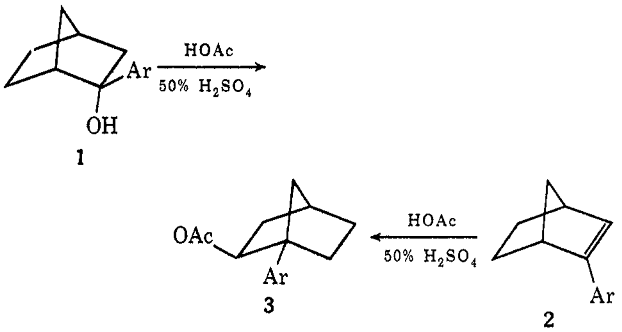
Received January 31, 1973

Ample results from product studies involving arylnorbornyl cationic intermediates have shown that the thermodynamically controlled product is often derived from a rearranged cation. An example that illustrates the above is the rearrangement observed in the interaction of 2-*exo*-aryl-2-*endo*-norbornanols (1) and 2-arylnorbornenes (2) with acetic acid in the presence of sulfuric acid to yield 1-aryl-*exo*-2-norbornyl acetates (3).[1]

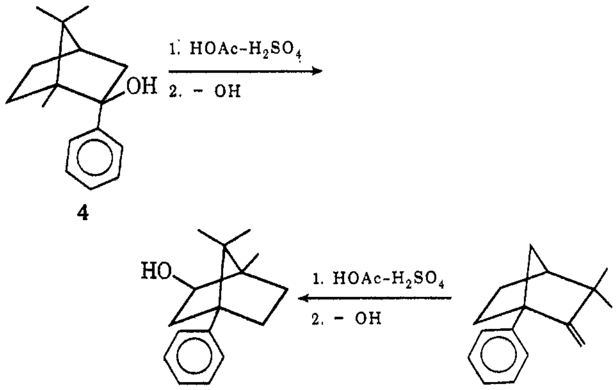


1

3

2

One of the more intriguing results of this type is the reported rearrangement of 2-*endo*-phenyl-2-*exo*-borneol (4) and 1-phenylcamphene (5) to produce 4-phenylisoborneol (6).[2] Obviously a gross structural reorganiza-



4

6

5

tion has taken place, although the final product is again derived from a secondary norbornyl cation.

These earlier observations can be readily confirmed by utilizing nmr structural assignments. Thus, the treatment of 2-*p*-anisylbornene (7) with acetic acid and sulfuric acid under rigorous conditions produced almost exclusively 4-*p*-anisyl-2-*exo*-bornyl acetate (8).

When the reaction was carried out with the same reagent at 25° for 0.5 hr, the only product isolated was

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[1] For an excellent review on these and related rearrangements involving arylnorbornyl cations, see D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.

[2] (a) J. Bredt, *J. Prakt. Chem.*, **98**, 96 (1918); (b) S. Nametkin, A. Kitschkin, and D. Kurssanoff, *ibid.*, **124**, 144 (1930); (c) S. Leduc, *C. R. Acad. Sci.*, **180**, 1502 (1925).