atoms, and 6.91, attributed to the methylene hydrogen atoms. The values of 7.74 and 7.98 were attributed to the hydrogen atoms on the methyl groups *para* and *ortho* to the carbonyl functions, respectively. The spectrum peaks were identified by the relative areas under their curves as compared to the number of the hydrogen atoms.

Treatment of duryl o-vinylphenyl ketone[8] *with sodium.* This experiment was performed in the manner just described. The products, however, offered great difficulty in purification. This might be the main reason for the relatively low yields. Duryl *o*-ethylphenyl ketone[8] was obtained in 2.2% yield and the reductive coupling product, colorless crystals from chloroform-ethanol, m.p. 242–244°, in 30.8% yield. The infrared and the nuclear magnetic resonance spectra of 1,4-di(*o*-duroylphenyl)butane (VIIb) were similar to those of its mesityl analog.

Anal. Calcd. for $C_{38}H_{42}O_2$: C, 85.99; H, 7.98. Found: C, 85.55; H, 8.18.

URBANA, ILL.

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(13) The nuclear magnetic resonance spectra were determined by Mr. O. W. Norton at 60 mc. with a Varian Model V-4300 B high-resolution spectrometer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Oxidation of Methyl-*t*-butylcarbinol with Lead Tetraacetate

WILLIAM A. MOSHER, CLIFTON L. KEHR, AND LEON W. WRIGHT

Received March 30, 1960

The oxidation of methyl-*t*-butylcarbinol with lead tetraacetate yields the expected ketone along with *t*-butyl acetate, isobutylene, and acetaldehyde. The relative yields of ketone and cleavage products may be varied by changing the conditions of oxidation with either the ketone or oxidative cleavage products becoming the major product. These products are consistent with an ionic mechanism.

The oxidation of benzpinacolyl alcohol with lead tetraacetate has been reported by Mosher and Neidig[1] to give 70% triphenylcarbinol as a result of oxidative cleavage. Because this represents the highest yield of such a cleavage yet reported, the reaction of the analogous aliphatic alcohol has now been carried out; methyl-*t*-butylcarbinol also yields cleavage products with lead tetraacetate under a variety of conditions.

The results of this study are summarized in Table I. Several individual reactions were carried out under the general conditions reported for the various runs. Carbon dioxide was invariably a product indicating secondary oxidations and considerable unchanged alcohol and its acetate were found. Material balances varied from 60% to nearly theoretical. With a 1:1 molar ratio of alcohol to lead tetraacetate the cleavage was 6% at 50–65° while it was almost 50% at 95–100° working in acetic acid solution. In nitrobenzene solution more esterification occurred and cleavage at 65–75° was 30%. Previous studies with this alcohol and chromic acid yielded 4% cleavage in acetic acid–water at 30°.[2]

EXPERIMENTAL

Preparation of reagents. Methyl-*t*-butylcarbinol was prepared in 31% yield by the reaction of *t*-butylmagnesium chloride and acetaldehyde, and in 68% yield by the reduction of pinacolone with aluminum isopropoxide in isopropyl alcohol. Distillation of the crude alcohol through a Whitmore-Lux[3] total condensation, partial take-off column packed with a single turn glass helices, and equivalent to twenty theoretical plates, resulted in a product boiling at 120–121° at 760 mm., n_D^{20} 1.4152. The procedure used for lead tetraacetate has been previously described.[4]

Oxidation. The data given in Table I indicate the mole quantities of alcohol, oxidizing agent, and solvent used in each experiment. In the usual case, the alcohol and oxidizing agent were mixed at room temperature with the indicated solvent in a 3-l., three-necked, round bottomed flask equipped with a thermometer, a mercury-sealed stirrer, and a reflux condenser to which was attached a Dry Ice trap, two Ascarite tubes, and a gas-collecting bottle. In Runs 1, 4, and 5, Table I, the Dry Ice trap was omitted and the acetaldehyde was absorbed by the Ascarite (with polymerization). In Run No. 2, Table I, the oxidizing agent was added, in small portions, to the stirred acetic acid–alcohol solution at reaction temperature in order to maintain a large excess of alcohol. After tetravalent lead was no longer present (negative potassium iodide test) in the reaction mixture, the product was diluted with water and steam distilled. The combined oil layers were separated, washed with bicarbonate solution, dried over anhydrous potassium carbonate, and fractionated through a column of twenty theoretical plates. In a typical experiment, from the distillation charge of 70.0 g., Run No. 1, Table I, the following cuts were obtained: I. *t*-Butyl acetate (3.8 g., 3.3%), acetanilide derivative by the method of Hardy[5] gave m.p. and mixed m.p. with an authentic sample of acetanilide, 113–115°; the ester was refluxed with hydrochloric acid (6*N*) to give *t*-butyl chloride (b.p. 54–56°, n_D^{20} 1.3850), which then was converted through Grignard reagent and phenyl isocyanate to trimethylacetanilide, m.p. 127–129°. II. Pinacolone (9.2 g., 9.2%), 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 126–128°. III. Unchanged carbinol (46.0 g.; 45.1%). IV. Pinacolyl acetate (5.7 g.; 4.0%), acetanilide derivative obtained by the method of Hardy[5] gave m.p. and mixed m.p. 113–114°; the ester was also hydrolyzed in basic diethylene glycol and the liberated alcohol converted to the 3,5-dinitrobenzoate ester, m.p. and mixed m.p. 105–106°. The pot residue consisted of 2.3 g. of slightly charred

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(1) W. A. Mosher and H. A. Neidig, *J. Am. Chem. Soc.*, **72**, 4452 (1950).

(2) W. A. Mosher and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2544 (1948).

(3) F. C. Whitmore and A. R. Lux, *J. Am. Chem. Soc.*, **54**, 3448 (1932).

(4) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

(5) D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

TABLE I

LEAD TETRAACETATE OXIDATION OF METHYL-*t*-BUTYLCARBINOL

Run No.	1	2	3	4	5	
Solvent	HOAc	HOAc	HOAc	$C_6H_5NO_2$	HOAc	HOAc–Acetone
Moles solvent	3.3	4.1	4.0	4.0	3.3	1 3
Moles $Pb(OAc)_4$	1	1	1	1	1	1
Moles alcohol	1	1	2	1	0.4	1
Temperature	50–60	95–100	95–100	65–75	75–85	45–50
Products (Moles/100 moles alcohol allowed to react)						
Pinacolone	17	3	3	5	13	25
Pinacolyl acetate	8	14	15	31	22	10
t-Butyl acetate	6	31	30	16	8	13
Isobutylene	—	20	22	—	—	—
Acetaldehyde	—	20	18	32	23	10
% cleavage	6	51	52	32	23	13

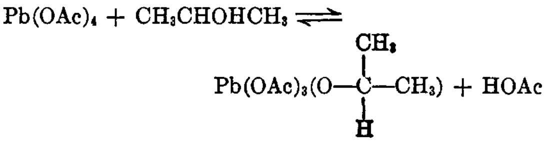
liquid. In Run No. 2, Table I, the isobutylene was characterized by distilling into a series of three cold traps containing pure bromine. A second Dry Ice trap in the series immediately after the bromine traps did not contain any liquid, indicating the absence of isobutane. Hydrolysis of the isobutylene dibromide[6] gave isobutyraldehyde, 2,4-dinitrophenylhydrazone m.p. and mixed m.p., 185–186°.

DISCUSSION

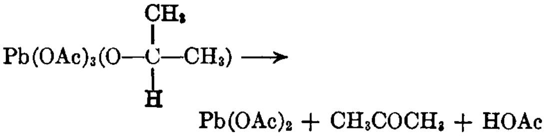
The data in Table I indicate that lead tetraacetate is a very unusual oxidizing agent for methyl-*t*-butylcarbinol because the ratio of normal product, ketone, to cleavage product, *t*-butyl alcohol or isobutylene, may be varied within limits by changing temperature and reactant concentrations. The highest yields of cleavage are obtained when a large excess of alcohol is maintained throughout the reaction. In nitrobenzene solution or in the presence of moderate amounts of acetic acid, lead tetraacetate is an effective acetylating agent.

The ability of lead tetraacetate to cleave glycols discovered and so successfully developed by Criegee[7] is well known and is believed to proceed through an ionic mechanism involving electron transfer between the tetravalent lead atom and the glycol oxygen in a cyclic ester intermediate.[8] This mechanism is considerably strengthened by the work on chromate ester intermediates in chromic acid oxidations by Westheimer and his students.[9]

The formation of cyclic esters is not possible in the present case but the probability of the formation of simple esters is very good. Criegee[8] has isolated from methanol solution such species as $Pb(OAc)_3(OCH_3)$ and $Pb(OAc)_2(OCH_3)(OH)$. These compounds were unstable and decomposed readily to formaldehyde and lead diacetate. Presumably such intermediates are formed in all monohydric alcohol oxidations with lead tetraacetate although we have not been able to isolate such compounds in the present study. Kharasch, *et al.*[10] explain the oxidation of monohydric alcohols by the following scheme:

(1)


$$\mathrm{Pb(OAc)_4 + CH_3CHOHCH_3 \rightleftharpoons Pb(OAc)_3(O{-}\overset{CH_3}{\underset{H}{C}}{-}CH_3) + HOAc}$$

(2)


$$\mathrm{Pb(OAc)_3(O{-}\overset{CH_3}{\underset{H}{C}}{-}CH_3) \longrightarrow Pb(OAc)_2 + CH_3COCH_3 + HOAc}$$

These reactions cannot be the only steps involved, however, for equation 1 illustrates an equilibrium which will probably be initiated when the reagents (in the ratios shown) are mixed in acetic acid as solvent.[8] Yet the reaction mixture can be heated at reflux for many hours until the lead tetraacetate decomposes completely to lead diacetate without even a trace of carbonyl compound being formed. It has been demonstrated,[11] however, that if the alcohol is added in considerable excess over the oxidizing agent, *e.g.* 15:1, the reaction proceeds quite rapidly below 100° C. One can conclude from these observations that a third equilibrium, Equation 3, may be involved before oxidation proceeds:

$$\mathrm{Pb(OAc)_3(OR) + HOR \rightleftharpoons Pb(OAc)_2(OR)_2 + HOAc} \quad (3)$$

$$\mathrm{Pb(OAc)_2(OR)_2 \longrightarrow Pb(OAc)_2 + RO^- + RO^{+}}\text{[12]} \quad (4)$$

Evidence for a reaction such as (4) has been previously presented.[4]

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[6] W. L. Evers, *et al.*, *J. Chem. Soc.*, **55**, 1136 (1933).

[7] R. Criegee, *Ber.*, **64**, 260 (1931).

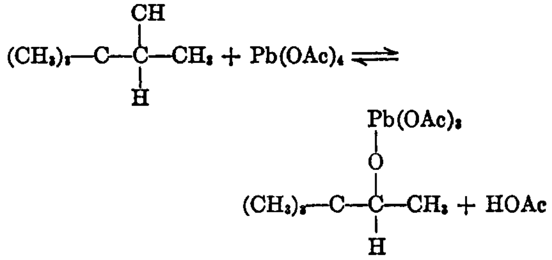
[8] R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 159 (1933).

[9] A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.* **74**, 4383 (1952).

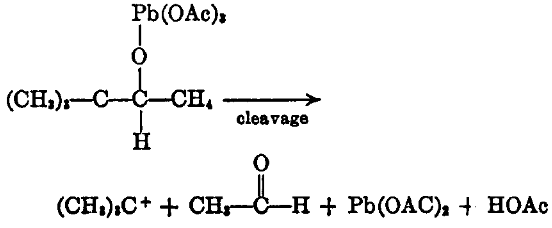
[10] M. S. Kharasch, H. N. Freidlander, and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

[11] C. L. Kehr, Ph.D. Dissertation, University of Delaware (1952).

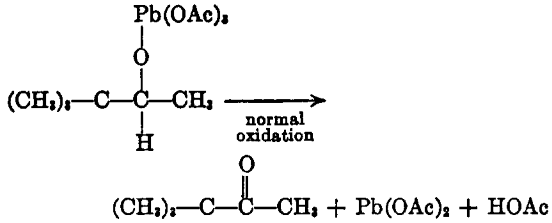
[12] RO^+ will, of course, have only a transitory existence and is probably involved as a polarized part of the $Pb(OAc)_2(OH)_2$ molecule in concerted reactions. The formulation is for simplicity.

(5)


$$(CH_3)_3\text{—C—}\overset{CH}{\underset{H}{C}}\text{—}CH_3 + Pb(OAc)_4 \rightleftharpoons (CH_3)_3\text{—C—}\overset{Pb(OAc)_3 \atop O}{\underset{H}{C}}\text{—}CH_3 + HOAc$$

(6)


$$(CH_3)_3\text{—C—}\overset{Pb(OAc)_3 \atop O}{\underset{H}{C}}\text{—}CH_4 \xrightarrow[\text{cleavage}]{} (CH_3)_3C^+ + CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}H + Pb(OAC)_2 + HOAc$$

(7)


$$(CH_3)_3\text{—C—}\overset{Pb(OAc)_3 \atop O}{\underset{H}{C}}\text{—}CH_3 \xrightarrow[\text{normal oxidation}]{} (CH_3)_3\text{—C—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 + Pb(OAc)_2 + HOAc$$

The formulations used for the decomposition of alkoxy lead triacetate result in the development of positive polarity on the hydroxyl oxygen and are, therefore, essentially equal to our previous formulations with positive character on oxygen atoms in alcohol oxidations.[2]

The high yield of pinacolyl acetate (Run No. 3, Table I) is probably due to the decomposition of the monoester of tetravalent lead, *i.e.* $Pb(OAc)_3(OR)$, *via* Equation 8.

$$(8)\quad Pb(OAc)_3(OR) + HOAc \rightleftharpoons Pb(OAc)_3(OH) + ROAc$$

The resulting tetravalent lead salt equilibrates with the other tetravalent lead compounds or reacts with solvent (acetic acid) to reform lead tetraacetate.

Kharasch, *et al.*[10] have shown that lead tetraacetate reacts, when heated to 120° in acetic acid solution, to give carbon dioxide (42%), methane (30%), acetoxyacetic acid (40%), and methylene diacetate (6%). These workers propose a radical type mechanism involving triacetoxy lead radicals to account for the observed reaction products. Mosher and Kehr[4] reinvestigated and extended the work of Kharasch, *et al.* to a variety of organic acids in an attempt to elucidate the type of mechanism involved. Mosher and Kehr concluded that the decomposition of lead tetraacetate in acetic and similar organic acids occurred *via* an ionic mechanism even at the high temperature (100–135°) used in their study.

The results of the present oxidation study are also best explained by an ionic mechanism. Any attempt to explain the cleavage products by a free radical mechanism falls short because of the absence of isobutane and hexamethylethane in the product mixture. It is known, for example, that *t*-butyl free radicals, when formed in solution at the same temperature employed in this study disproportionate quantitatively to isobutane and isobutene.[13] At low temperatures the *t*-butyl free radical is known to dimerize to give hexamethylethane (in the preparation of branched chain carbinols with *t*-butyl Grignard reagents, some hexamethylethane is always found as a by-product). In the oxidation of methyl-*t*-butylcarbinol, neither isobutane nor hexamethylethane was found in the product mixture.

NEWARK, DEL.

(13) H. C. McBay Ph.D. Dissertation, University of Chicago (1945).

[CONTRIBUTION FROM UNION CARBIDE PLASTICS CO., DIVISION OF UNION CARBIDE CORP.]

Aromatic Aldehydes from Benzyl Alcohols *via* Inorganic Hypochlorite Oxidation[1]

CAL Y. MEYERS[2]

Received June 14, 1960

The action of aqueous inorganic hypochlorite on several benzyl alcohols has been studied. Benzaldehyde and *o*-methoxybenzaldehyde were thus obtained in good yield from their respective alcohols. Under the conditions employed there was no evidence of reaction between the hypochlorite and these aldehydes. *o*-Hydroxybenzyl alcohol, under identical conditions, provided no aromatic aldehyde but was chlorinated in the nucleus with a concurrent elimination of formaldehyde. Possible mechanisms are considered.

The potential stock of variously substituted hydroxybenzyl alcohols is apparent from the recent compilations by Martin[3] and Megson.[4] This particular type of benzyl alcohol is simply prepared from the phenol and formaldehyde and

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(1) Presented before the Meeting-in-Miniature, North Jersey Section, American Chemical Society, Jan. 28, 1957.

(2) Present address and that to which inquiries should be directed: Istituto di Chimica Industriale, Università di Bologna, Viale Risorgimento, 4, Bologna, Italy.