8.51, 8.65, 8.78, 8.91, 9.52, 9.71, 10.00, 10.16, 10.66, 10.91, 11.12, 11.51, 11.74, 12.46, 13.20, 13.80, 14.35 μ.

The *picrate* of I was prepared by adding 0.10 g. of I to 5 ml. of a saturated solution of picric acid in chloroform, heating the mixture to boiling, and allowing it to cool slowly. The precipitate was collected, washed with a little chloroform, and recrystallized from chloroform to give yellow needles melting at 199–200° (dec.).

Anal. Calcd. for $C_{27}H_{20}N_4O_{14}$: C, 51.93; H, 3.23. Found: C, 52.10; H, 3.37.

SWARTHMORE, PA.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORPORATION]

Relative Ease of Hydrogenolysis of Some Organometallic Compounds[1]

H. E. PODALL, H. E. PETREE, AND J. R. ZIETZ

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The hydrogenolysis of diethylmagnesium, triethylaluminum, sodium di- and triisobutylaluminum hydrides, diethylzinc, zinc acetylide, and hexaphenyldilead was investigated. The results of this study confirm and extend the generalization that the ease of hydrogenolysis of the metal-carbon bond (as indicated by the minimum temperature at which hydrogenolysis is observed) parallels its degree of polar or ionic character (measured by Pauling's scale of electronegativity). A unified mechanism involving a trapezoidal transition state is proposed for the hydrogenolysis of alkyl- and aryl-metallic compounds, particularly the ionic ones, which is consistent with available hydrogenolysis information. The appreciably greater ease of hydrogenolysis of the trialkylboron-trialkylamine addition compounds over that predicted from electronegativity considerations is considered to be due to relief of steric strain during hydrogenolysis.

In the course of investigating the direct synthesis of tetraethyllead, triethylaluminum, diethylmagnesium,[2] and diethylzinc, the hydrogenolysis of these and some related compounds was studied. The results on the noncatalytic and catalytic hydrogenolysis of diethylmagnesium, triethylaluminum, diethylzinc, sodium di- and triisobutylaluminum hydrides, zinc acetylide, and hexaphenyldilead are summarized in Table I.[3]

The ease of hydrogenolysis of the ethylmetallics (as indicated by the minimum temperature at which hydrogenolysis is first observed) is $Et_2Mg > Et_3Al > Et_2Zn$. In the case of diethylmagnesium in diethyl ether, hydrogenolysis set in at about 50°, and an essentially quantitative conversion to magnesium hydride was obtained within 10 hours at 75°, 800 p.s.i.g. hydrogen pressure. The hydrogenolysis of triethylaluminum in *n*-hexane was found to set in at 140° at 3000 p.s.i.g. hydrogen pressure and was considerably slower than that of diethylmagnesium. Certain metals such as magnesium, however, were found to catalyze the hydrogenolysis to effect a quantitative conversion of triethylaluminum to diethylaluminum hydride within a few hours at 150°, 3000 p.s.i.g. hydrogen

TABLE I

SUMMARY OF TYPICAL HYDROGENOLYSIS RESULTS

RM	Catalyst	Solvent	Temp., °C.	Pressure, atm.	Time, hr.	Products,[a] % Conversion
Et_2Mg	None	Ether	75	68	21	98% MgH_2[b], C_2H_6
Et_3Al	None	None	140	67	4	12% Et_2AlH, C_2H_6
Et_3Al	Mg	*n*-Hexane	150	194	5.5	99% Et_2AlH, C_2H_6
Et_2Zn[c]	None	None	110	720	1.5	5% Zn, C_2H_6
Et_2Zn	Pd/Al_2O_3	Iso-octane[d]	100	680	16	18% ZnH_2, Zn, C_2H_6
ZnC_2	None	Iso-octane[d]	230	67	14	15% Zn, C_2H_6
ZnC_2	None	Iso-octane[d]	180	740	6	12% Zn, 3%$[Zn(CH{=}CH)]_x$[e]
Na(*i*-Bu_2AlH_2)	PtO_2	*n*-Hexane	150	210	3.5	>97% recovery Na(*i*-Bu_2AlH_2)
Na(*i*-Bu_3AlH)[f]	PtO_2	*n*-Hexane	150	210	3.5	100% Na(*i*-Bu_2AlH_2)
(C_6H_5	Raney Ni	Benzene	100	890	6	50% C_6H_5-C_6H_5[b], Pb
C_6H_5	Copper chromite	Benzene	126	770	6	39% $(C_6H_5)_4Pb$[b], Pb

[a] Based on gas evolution and mass spectral analysis unless otherwise indicated. [b] Isolated. [c] In the presence of zinc metal. [d] 2,4,4-Trimethylpentane. [e] Based on ethylene evolution on hydrolysis. [f] 50% Na[*i*-Bu_3AlH] and 50% Na[*i*-Bu_2AlH_2] by analysis.

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(1) Presented before the Symposium on Organometallic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Sept. 7–12, 1958, Abstracts of Papers, p. 34N.

(2) H. E. Podall and W. E. Foster, *J. Org. Chem.*, **23**, 1848 (1958).

(3) It should be noted that although there was some thermal decomposition of the ethylmetallic compounds here studied, it was negligible relative to the hydrogenolysis reaction. This was evidenced by an uptake of hydrogen rather than an increase in pressure due to thermal decomposition, and by the fact that little or no ethylene was found in the vent gas.

pressure. The hydrogenolysis of diethylzinc was much slower than that of triethylaluminum in the absence of catalysts. The only metallic product produced in the absence of catalysts at elevated temperatures and pressures was metallic zinc. However, in the presence of a palladium-on-alumina catalyst, hydrogenolysis occurred under somewhat milder conditions, thereby permitting the formation of zinc hydride in 18% yield. Zinc hydride, incidentally, was found to be moderately soluble in pyridine at 25°, decomposing at 80–100° with the formation of zinc and hydrogen. The solubility of zinc hydride in pyridine is attributed to the formation of a pyridine–zinc hydride complex.

Correlation of hydrogenolysis results. Consideration of the hydrogenolysis results for the Group IA organometallics and phenylcalcium iodide,[4] tetraalkyllead and tetraphenyllead,[5,6] di-*n*-butylzinc,[5] and diphenylmagnesium,[5] the Group VA organometallics,[6] the trialkylboron-amine addition compounds,[7] and the organometallic compounds here studied reveals an excellent correlation of the ease of the hydrogenolysis of the metal-carbon bond (as indicated by the temperature at which hydrogenolysis is first observed) with its degree of polar or ionic character (measured by Pauling's electronegativity scale for the elements).[8a,8b] This is shown in Table II. The indicated order of reactivity applies to a comparable series of phenyl-, methyl-, or ethylmetallic compounds. In general, as the metallic component becomes more nonmetallic (*i.e.*, approaches carbon in its electronegativity) hydrogenolysis becomes more difficult, boron being the only apparent exception. The result indicated for boron, however, is not strictly comparable with those for the other elements since it pertains to the amine addition compound rather than the free alkylboron compound.

The electronegativity values for zinc, bismuth, and lead were estimated by independent methods as described in the footnotes of Table II. The agreement of these values with the observed order of the relative ease of hydrogenolysis of the respective organometallic compounds suggests that the hydrogenolysis reaction might indeed be used for determining the electronegativity values of various metals. It might be noted that a difference of 0.1 in the electronegativity value corresponds roughly to a factor of 2 in the rate of hydrogenolysis.

TABLE II

CORRELATION OF THE EASE OF HYDROGENOLYSIS[a] WITH PAULING'S ELECTRONEGATIVITY SCALE

Decreasing Ease of Hydrogenolysis	Pauling's Electronegativity Scale	
Cs-C	Cs	0.7
Rb-C	Rb	0.8
K-C	K	0.8
Na-C	Na	0.9
Li-C	Li	1.0
Ca-C	Ca	1.0
Mg-C	Mg	1.2
Al-C	Al	1.5
B-C	(B	2.0)
Zn-C	Zn	1.6[b]
Bi-C	Bi	1.6[c]
Pb-C	Pb	1.6[c]
Sb-C	Sb	1.8
As-C	As	2.0
P-C	P	2.1

[a] Applies to a given series of phenyl or *n*-alkylmetallic compounds. [b] Calculated from the second ionization potential per unit charge, $x = 17.89\,(23.06)/2(130) = 1.6$ (see ref. 8, p. 66). [c] Extrapolated from curves given for other metals of the respective group (see ref. 8, Fig. 11-1, p. 65).

Consideration of the relative stabilities of the metal hydrides indicates that the stability of the metal-hydrogen bond is generally inversely related to that of the corresponding metal-carbon bond. It follows therefore that the order of the relative ease of hydrogenolysis may alternately be correlated in terms of the ionic character or stability of the resulting or potential metal-hydrogen bond; the ease of hydrogenolysis therefore is seen to decrease with a decrease in the ionic character of the potential metal-hydrogen bond. The inverse relationship indicated above may be due, at least in part, to the high lattice energy of the ionic metal hydrides which is lacking or not evident in the corresponding ionic organometallics, and to the tendency of these organometallics to undergo facile decomposition to the corresponding more stable hydrides.

Effect of organic group. Little is known of the effect of different alkyl or aryl groups on the ease of hydrogenolysis of a given organometallic compound. In the case of the organolithium compounds, phenyllithium hydrogenolyzes only slightly more readily than does methyllithium[4] in the case of organolead compounds, tetraethyllead hydrogenolyzes about three times more readily than tetramethyllead which in turn hydrogenolyzes about three times more readily than tetraphenyllead.[6]

Proposed mechanism. Zartman and Adkins[5] proposed a free-radical mechanism for the hydrogenolysis of organometallic compounds such as di-*n*-butylzinc, tetraphenyllead, and diphenylmagnesium. It is difficult, however, to visualize a similar mechanism for the hydrogenolysis of ionic organometallic compounds such as ethylsodium or phenylpotassium. For compounds of this type it appears more reasonable to assume that the hydro-

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(4) H. Gilman, A. L. Jacoby, H. Ludeman, *J. Am. Chem. Soc.*, **60**, 2336 (1938).

(5) W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.*, **54**, 3398 (1932).

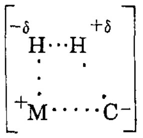
(6) V. N. Ipatieff, G. A. Rasuwajeff, and I. F. Bogdanow, *Ber.* **63**, 335, 1110 (1930).

(7) K. Ziegler (to Studiengesellschaft Kohle m.b.H.) Belgian Patent **558,170**, June 6, 1957.

(8a) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1948, 2nd ed., p. 64.

(8b) E. G. Rochow, D. T. Hurd, and R. N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley & Sons, Inc., New York, 1957, p. 17.

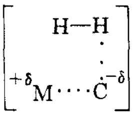
gen reacts at the surface of the solid organometallic compound, and that the rate-determining step involves primarily breakage of the H—H bond. This would be consistent with the fact that the nature of the organic group has apparently little effect upon the ease of hydrogenolysis of an ionic organometallic compound, such as was noted for the organolithium compounds. To account for the relative ease of this reaction despite the strength of the H—H bond, an important feature of this mechanism would appear to involve the participation of the alkyl-or aryl- carbanion and particularly the metal ion in the loosening of the H—H bond in the transition state (Structure I).



$$\left[\begin{array}{ccc} \overset{-\delta}{H} & \cdots & \overset{+\delta}{H} \\ \vdots & & \vdots \\ {}^{+}M & \cdots & C^{-} \end{array}\right]$$

I

The hydrogenolysis of the more covalent organometallic compounds such as diethylmagnesium and possibly triethylaluminum is considered to occur by a similar mechanism, with the degree of bond breaking of the metal-carbon bond and the degree of interaction between the bonded carbon and hydrogen playing more important roles than in the preceding case. For the essentially covalent organometallic compounds such as tetraethyllead and possibly triethylboron, the degree of bond breaking of the metal-carbon is assumed to be of major importance. However, to account for the apparent order of reactivity of different organolead compounds,[6] the slight dependence of the rate of hydrogenolysis upon the hydrogen pressure,[6] and the catalytic effects of certain hydrogenation catalysts upon the hydrogenolysis reaction,[5] it would appear that some interaction of bonded carbon with hydrogen is also present in the transition state (II) of the hydrogenolysis reaction of an essentially covalent organometallic compound.



$$\left[\begin{array}{cc} H- & H \\ & \vdots \\ {}^{+\delta}M\cdots & \overset{-\delta}{C} \end{array}\right]$$

II

Additional information on the structures of the transition states of the hydrogenolysis reactions can be gained from an examination of the energetics of the hydrogenolysis of representative organometallic compounds, such as ethylsodium, triethylaluminum and tetraethyllead, as shown in Fig. 1. It follows from this treatment that the structure of the transition state in the hydrogenolysis of an ionic organometallic, such as ethylsodium, should energetically resemble those of the reactants, whereas the structure of the transition state in the hydrogenolysis of an essentially covalent organometallic, such as tetraethyllead, should resemble more closely those of the theoretically expected products, *viz.* triethyllead hydride and ethane.

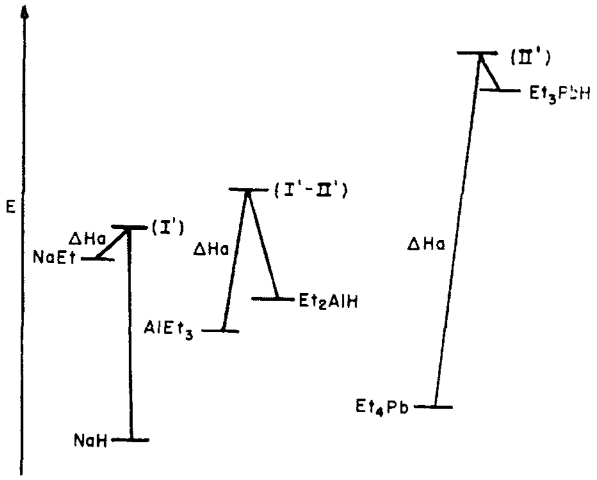
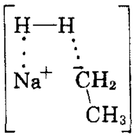


Fig. 1. Energetics of the hydrogenolysis of representative organometallic compounds

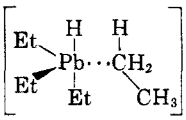
In particular, one would expect that the structure of the transition state in the hydrogenolysis of ethylsodium should be essentially that of ethylsodium loosely bonded to hydrogen, as shown by Structure I′.



$$\left[\begin{array}{cc} H- & H \\ \vdots & \vdots \\ Na^{+} & CH_2 \\ & CH_3 \end{array}\right]$$

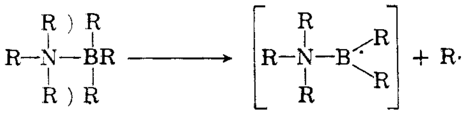
I′

Similarly, one would expect that the transition state in the hydrogenolysis of tetraethyllead should be essentially that of triethyllead hydride containing only a loose metal-carbon bond, such as indicated by Structure II′. In view of the instability of an essentially covalent metal-hydrogen bond, such as the lead-hydrogen bond (indicated in a later section), it is conceivable that the hydrogenolysis of the corresponding organometallic, *viz.* tetraethyllead, follows a different path such as indicated by Structure II, wherein no interaction is assumed to occur between the metal atom and hydrogen. In the absence of further information on the relative stabilities of the covalent hydrides, such as triethyllead hydride, and/or on the heats and entropies of activation for the hydrogenolysis reactions, a decision between these two possibilities is at present best deferred.



II′

The alkylboron anomaly. The appreciably greater reactivity of tri-*n*-alkylboron-trialkylamine addition compounds over that predicted from electronegativity considerations can be explained in terms of a steric acceleration effect, assuming that the rate-determining step involves homolytic cleavage of the alkylcarbon-boron bond. In comparing the hydrogenolysis of the addition compound with that of the free alkylboron compound it is apparent that there would be an appreciable relief of steric strain in going from the addition compound to a dialkylboron-amine transition state, whereas there would be little or no change in the steric strain in going from the free trialkylboron compound to the corresponding dialkylboron transition state, provided the starting trialkylboron compound is essentially strain-free.



Hydrogenolysis of zinc acetylide. The hydrogenolysis of zinc acetylide was found to occur much less readily than that of diethylzinc, with the formation of metallic zinc and *ethane*. At very high hydrogen pressures and moderate temperatures a product was produced which yielded an appreciable quantity of ethylene upon hydrolysis. The presence of ethylene in the gas produced upon hydrolysis suggests the formation and presence of a zinc ethylide compound, $[Zn(CH{=}CH)]_x$, as a possible intermediate in the hydrogenolysis of zinc acetylide.

Hydrogenolysis of complex alkylaluminum hydrides. The sodium alkylaluminum hydrides were found to hydrogenolyze much less readily than the uncomplexed or free trialkylaluminum compounds. The appreciably lower reactivity of these complexes can be explained either simply in terms of steric effects wherein the aluminum atom is considered to be too hindered to permit effective attack by hydrogen at the aluminum-carbon bond, or preferably in terms of an equilibrium reaction wherein it is assumed that hydrogenolysis can occur only *via* the uncomplexed or free alkylaluminum compound. The relative ease of hydrogenolysis of

$$Na^+\ i\text{-}Bu_3AlH^- \rightleftharpoons i\text{-}Bu_3Al + NaH$$
$$i\text{-}Bu_3Al \xrightarrow{H_2} i\text{-}Bu_2AlH + i\text{-}BuH$$
$$Na^+\ i\text{-}Bu_2AlH_2^- \rightleftharpoons i\text{-}Bu_2AlH + NaH$$
$$i\text{-}Bu_2AlH \xrightarrow{H_2} i\text{-}BuAlH_2 + i\text{-}BuH$$

sodium triisobutylaluminum hydride compared with sodium diisobutylaluminum dihydride parallels the relative ease of hydrogenolysis of triethylaluminum compared with diethylaluminum hydride. In each case the more alkylated aluminum compound is more strained and hence may go over more readily to the less strained dialkylaluminum compound. Further hydrogenolysis to the alkylaluminum dihydride may result in no further relief in strain, and consequently hydrogenolysis stops at the monohydride stage. An additional factor contributing to the apparent stability of the monohydride is that it is more dimerized than the starting alkylaluminum compound and hence the aluminum (coordination number 4 in the hydride) resists further attack by hydrogen.

Triphenyllead hydride. In an effort to prepare triphenyllead hydride, hexaphenyldilead was subjected to hydrogenolysis under a variety of conditions. It was found that only in the presence of catalysts such as Raney nickel or copper chromite did appreciable reaction occur at moderate temperatures. However, in the presence of Raney nickel only lead and biphenyl were produced, and in the presence of copper chromite, an apparently milder catalyst for this reaction, only lead and tetraphenyllead were produced. There was no evidence for the presence of triphenyllead hydride in the reaction mixtures.

EXPERIMENTAL

Diethylmagnesium was prepared by the procedure of Wotiz, Hollingsworth, and Dessy.[9]

Triethylaluminum (Ethyl Corp., Orangeburg, S. C.) was 98% pure.

Diethylzinc was prepared by essentially the same method described by Meyer,[10] namely, from zinc powder and ethyl iodide, and was distilled at 45°, 49 mm. under nitrogen (b.p. diethylzinc 118°, 760 mm., lit.[10] 118°, 760 mm.). In this synthesis of diethylzinc *via* ethylzinc iodide, it was found expedient to add a small quantity of diethylzinc at the outset of the reaction to catalyze the formation of ethylzinc iodide.

Zinc acetylide was prepared by a modified version of Durand's[11] procedure, involving reaction of diethylzinc with acetylene in dimethylcarbitol at 140°. The product was a light blue solid analyzing 73% pure zinc acetylide, ZnC_2, based on its acetylene evolution and zinc content. The product is believed to be polymeric in nature due to its insolubility and nonvolatility.

Hexaphenyldilead was prepared in one step in 87% yield by the reaction of excess phenyllithium with lead chloride using essentially the method indicated by Gilman.[12] Temperatures below $-10°$ should be employed for the addition of phenyllithium to lead chloride in order to avoid disproportionation to tetraphenyllead and metallic lead.

Sodium diisobutylaluminum dihydride was prepared by the addition of diisobutylaluminum hydride to an equivalent amount of sodium hydride, followed by recrystallization of the solid product from benzene–petroleum ether (20–40° range). The product was a white crystalline solid, m.p. 160–170°.

Anal. Calcd. for $Na(i\text{-}Bu_2AlH_2)$: Na, 13.8; Al, 16.2; mmole gas/g., 24.1; $n\text{-}C_4H_{10}/H_2$, 1.0. Found: Na, 12.9; Al, 16.0; mmole gas/g., 22.4; $n\text{-}C_4H_{10}/H_2$, 0.7.

Sodium triisobutylaluminum hydride was similarly prepared by reaction of triisobutylaluminum with an equivalent amount of sodium hydride.

General procedure. Magne-Dash (100 ml.) and rocking autoclaves (40 ml.) were employed for carrying out the hydrogenolysis reactions. The desired organometallic compound and solvent were added to an appropriate bomb in the dry box port. Automatic temperature and pressure regulating and recording devices were employed for control and monitoring of the reactions. The autoclave was

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(9) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.*, **78**, 1221 (1956).

(10) M. Meyer, *Chem. News*, **131**, 1 (1925).

(11) J. F. Durand, *Compt. rend.*, **176**, 992 (1923).

(12) H. Gilman, L. Summers, and R. W. Leeper, *J. Org. Chem.*, **17**, 630, (1932).

purged twice with 600 p.s.i.g. of hydrogen and pressurized with hydrogen to the desired pressure. The autoclave was then heated slowly to a temperature where hydrogen uptake occurred (as evidenced by a pressure drop due to the greater solubility of the displaced ethane or other hydrocarbon over that of hydrogen in the solvent used). This temperature was maintained until no further hydrogen uptake was evident. After the autoclave had been cooled to room temperature and a vent gas sample taken, the autoclave was disassembled and the contents of the bomb were transferred to appropriate glassware in the dry box. The reaction mixture was then carefully quenched with isopropyl alcohol-benzene, water, and aqueous hydrochloric acid or aqueous sodium hydroxide in succession in a gas evolution apparatus equipped for measuring the volume of gas evolved and for the withdrawal of a sample for mass spectral analysis.

Acknowledgment. The authors wish to thank S. Henderson, J. Mitchen, and J. B. Chidester for their assistance in the analytical work.

BATON ROUGE, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WHITMORE LABORATORY, THE PENNSYLVANIA STATE UNIVERSITY]

Osmium and Ruthenium Tetroxide–Catalyzed Oxidations of Pyrene[1]

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Received February 19, 1959

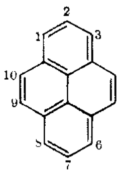
The oxidation of pyrene (I) has been studied as a possible route to precursors of 4,5-dialkylphenanthrenes. The oxidant systems were osmium tetroxide–hydrogen peroxide, osmium tetroxide–sodium periodate, and ruthenium dioxide–sodium periodate. The osmium tetroxide–periodate system produced oxidation exclusively at the 4,5-bond of pyrene, the bond of lowest bond localization energy, to yield pyrene-4,5-quinone (IV) and the lactol of 4-formylphenanthrene-5-carboxylic acid (III). In contrast the ruthenium dioxide–periodate system oxidized pyrene at the atoms of greatest electron density as well as at the 4,5-bond. Although the yields of the desired 4,5-quinone and lactol from the osmium tetroxide–catalyzed oxidation were only 23 and 24%, respectively, this appears to be equal or superior to any other available reaction sequence for the synthesis of 4,5-dialkylphenanthrenes.

Introduction. In recent years interest has developed in the oxidation of pyrene (I) at the 4,5-bond, the bond of lowest bond localization energy,[2] as a route to sterically hindered 4,5-dialkylphenanthrenes. Ozone and osmium tetroxide are the only known reagents which oxidize the 4,5-bond of pyrene.[3-6] Oxidizing agents which do not proceed through cyclic intermediates with double bonds attack the 1,3,6, or 8 positions of pyrene, the atoms of greatest electron density.[7]

Oxidative procedures involving ozone and osmium tetroxide are somewhat hazardous when applied to large amounts of material. The success of osmium tetroxide–catalyzed oxidation of olefinic bonds with hydrogen peroxide[8-10] and periodate[11] suggested that such systems might be suitable for the oxidation of complex aromatic molecules. Therefore we have studied the oxidation of pyrene in aqueous acetone with (a) osmium tetroxide plus sodium meta-periodate, (b) osmium tetroxide plus hydrogen peroxide, and (c) ruthenium dioxide plus sodium meta-periodate in an attempt to obtain selective oxidation at the 4,5-bond of this molecule.

Ruthenium dioxide, a readily available, nontoxic reagent, was studied to see if it would act as a "double-bond attacking" reagent. Periodate readily oxidizes ruthenium from its lower valence state to ruthenium tetroxide which, it was postulated, would then follow the same mechanistic path as osmium tetroxide.

Since aqueous acetone solutions of pyrene and periodate or pyrene and peroxide were shown to be stable, the initial step in the oxidation is believed to be the formation of the osmate ester of the hydrocarbon. Water is necessary to effect hydrolysis of the ester to 4,5-dihydroxy-4,5-dihydropyrene (II) so that the catalyst may be regenerated by the oxidant. Sodium meta-periodate was also expected to cleave this α-glycol.



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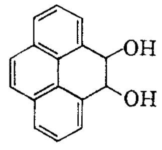
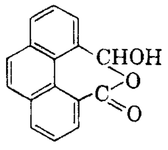


II



III

Results and Discussion. The osmium tetroxide–catalyzed periodate oxidation of pyrene resulted

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[1] This investigation was performed as part of American Petroleum Institute Research Project 42, "The Synthesis and Properties of High Molecular Weight Hydrocarbons," given in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April 1959.

(2) P. S. Bailey, *Chem. and Ind.* (*London*), 1148 (1957).

(3) H. Vollmann, et al., *Ann.*, **531**, 1 (1937).

(4) M. S. Newman and H. W. Whitehouse, *J. Am. Chem. Soc.*, **71**, 3664 (1949).

(5) G. M. Badger, et al., *J. Chem. Soc.*, 2326 (1950).

(6) *J. Cook and R. Schoental, J. Chem. Soc.*, 170 (1948).

(7) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

(8) N. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936).

(9) M. Mugdan and D. Young, *J. Chem. Soc.*, 2988 (1949).

(10) J. Cook and R. Schoental, *J. Chem. Soc.*, 47 (1950).

(11) R. Pappo, et al., *J. Org. Chem.*, **21**, 478 (1956).