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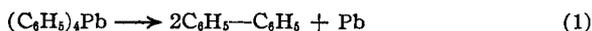
## REARRANGEMENT AND HYDROGENATION OF CERTAIN METAL ALKYL

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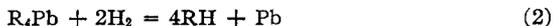
During the course of the study of another problem, catalytically active nickel was found to exert a profound influence upon the decomposition under hydrogen of tetra alkyl and aryl lead compounds. For example, diphenyl was formed almost quantitatively (reaction 1) when tetraphenyllead was heated at 200° with a nickel catalyst for six hours under a pressure of 100 atmospheres of hydrogen. The reaction proceeded so smoothly that the product obtained directly from the reaction had practically the same melting point as purest diphenyl. Both a catalyst and hydrogen are essential for the



rearrangement indicated above, since tetraphenyllead was quite stable under 100 atmospheres of nitrogen or hydrogen at 200°, or under 100 atmospheres of nitrogen and in the presence of nickel.<sup>1</sup>

Tetra-*p*-tolyllead underwent a similar transformation and was converted almost quantitatively into 4,4'-dimethyldiphenyl. The reaction is not limited to tetraaryllead compounds but is also manifested by tetra-*n*-heptyllead. However, in this case the conversion was not as high, for a yield of only 62% of the theoretical amount of *n*-tetradecane was obtained. (The real yield was probably higher as mechanical losses were relatively large in this experiment.) A small amount (6%) of heptene, as determined by a bromine titration of the solvent methylcycloheptane, and presumably some *n*-heptane were produced. There was no evidence of any product boiling higher than tetradecane.

The behavior of the tetra alkyl and aryl lead compounds in the presence of catalytically active nickel is in marked contrast to that of similar compounds observed by Ipatiev, Razuvaev and Bogdanov,<sup>1</sup> who studied the action of hydrogen in the absence of a catalyst. These investigators found that tetramethyl-, tetraethyl- and tetraphenyllead were converted into lead and the hydrocarbon corresponding to the alkyl group as indicated in equation 2.



<sup>1</sup> The data presented in Table I would indicate that tetraphenyllead, for example, is stable at somewhat higher temperatures than would be concluded from the results obtained by Ipatiev, Razuvaev and Bogdanov [*Ber.*, **63B**, 335 (1930), and preceding papers in the *J. Russ. Phys.-Chem. Soc.*]. However, the discrepancy may well be due to the fact that we used a copper and not a glass reaction vessel, and to other differences in equipment, temperature control and purity of materials.

TABLE I  
SUMMARY OF EXPERIMENTAL RESULTS<sup>a</sup>

Substance	Milli- moles	Time, min.	Temp., °C.	125 atm. of	Catalyst, g.	Solvent, ml.	Products	Constants
Tetraphenyllead <sup>a</sup>	33	360	200	H <sub>2</sub>	4(Ni) <sup>n</sup>	100 <sup>o</sup>	Diphenyl	M. p. 69-70°
Tetraphenyllead	1.95	390	200	H <sub>2</sub>	None	25 <sup>o</sup>	Tetraphenyllead	M. p. 227-227.5°
Tetraphenyllead	1.95	330	200	N <sub>2</sub>	1(Ni)	25 <sup>o</sup>	Tetraphenyllead	M. p. 224-226°
Tetraphenyllead	1.95	450	200	N <sub>2</sub>	None	25 <sup>o</sup>	Tetraphenyllead	M. p. 225-226°
Tetra- <i>p</i> -tolyllead <sup>b</sup>	26	360	200	H <sub>2</sub>	4(Ni)	100 <sup>o</sup>	4,4'-Dimethyldiphenyl <sup>l</sup>	M. p. 120-121°
Tetra- <i>n</i> -heptyllead	25	360	200	H <sub>2</sub>	4(Ni)	100 <sup>o</sup>	<i>n</i> -Tetradecane, 62% <sup>j</sup> <i>n</i> -Heptane <sup>k</sup> <i>n</i> -Heptene, 6% <sup>k</sup>	B. p. 245-9° (736 mm.)
Di- <i>n</i> -butyl zinc <sup>c</sup>	187	120	200	H <sub>2</sub>	4(Ni)	None	Butane, octane, 4% <sup>o</sup>	B. p. 120-125°
Di- <i>n</i> -butyl zinc	257	960	160	H <sub>2</sub>	4(Ni)	None	Butane, octane, 3% <sup>o</sup>	B. p. 120-125°
Di- <i>n</i> -butyl zinc	140	540	160	H <sub>2</sub>	2(Ni)	75 <sup>h</sup>	Butane, octane, 3% <sup>o</sup>	B. p. 120-125°
Di- <i>n</i> -butyl zinc	112	630	160	H <sub>2</sub>	2(Cu-Cr) <sup>o</sup>	75 <sup>h</sup>	Butane	
Di- <i>n</i> -butyl zinc	128	600	130	H <sub>2</sub>	2(Ni)	75 <sup>h</sup>	Di- <i>n</i> -butyl zinc	
Di- <i>n</i> -butyl zinc	165	510	160	N <sub>2</sub>	2(Ni)	75 <sup>h</sup>	Di- <i>n</i> -butyl zinc	
Diphenylmagnesium <sup>d</sup>	119	480	200	H <sub>2</sub>	4(Ni)	100 <sup>l</sup>	Benzene, 94% <sup>a</sup> Diphenylmagnesium, 6% <sup>m</sup>	
Triphenylstibene <sup>e</sup>	71	450	200	H <sub>2</sub>	4(Ni)	100 <sup>o</sup>	Triphenylstibene	M. p. 56°

<sup>a</sup> M. p. 225-226°. Gilman and Robinson, *THIS JOURNAL*, **49**, 2315 (1927). <sup>b</sup> M. p. 239-240°. The method was analogous to that used for preparation of tetraphenyllead, except that *p*-bromotoluene was used in place of bromobenzene and toluene in place of benzene. <sup>c</sup> B. p. 70-72° (8 mm.). Noller, *THIS JOURNAL*, **51**, 594 (1929). <sup>d</sup> Noller, *ibid.*, **53**, 635 (1931). The analysis for the amount of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Mg in solution was made by means of titration with standard acid. <sup>e</sup> M. p. 56°. "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 80. <sup>f</sup> Unless otherwise noted the reaction proceeded almost quantitatively. <sup>g</sup> Methylcyclohexane. <sup>h</sup> Absolute ethyl ether. <sup>i</sup> M. p. 121°. Zincke, *Ber.*, **4**, 396 (1871). <sup>j</sup> B. p. 252° (760 mm.). Krafft, *ibid.*, **15**, 1700 (1882). <sup>k</sup> Heptane and heptene have approximately the same boiling points as the solvent, so that the amount of heptane could not be determined, while the heptene was determined by titration of the methylcyclohexane solution with bromine. <sup>l</sup> Ether containing 15 to 20% dioxane. <sup>m</sup> Amount determined by titration with standard acid. <sup>n</sup> Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931). <sup>o</sup> Adkins and Connor, *THIS JOURNAL*, **53**, 1091 (1931). <sup>p</sup> Experimental methods and apparatus were essentially the same as previously reported. Adkins and Cramer, *ibid.*, **52**, 4349 (1930). <sup>q</sup> The hydrogen absorption in each of two hydrogenations was approximately 400 millimoles and no cyclohexane was formed. This indicates that a compound of magnesium and hydrogen was formed. This magnesium compound was exceedingly reactive with air and water.

However, in the present work it was found that di-*n*-butyl zinc in the presence of nickel and hydrogen reacted almost entirely in the sense of equation 2, *i. e.*, zinc and butane were formed. There was only a 3 or 4% yield of octane. Di-*n*-butyl zinc reacted at a somewhat lower temperature than did tetraheptyl lead. It was stable at 130° in the presence of nickel and hydrogen but reacted rapidly at 160°.

Diphenylmagnesium behaved similarly to dibutyl zinc, that is, it was converted into benzene and what was apparently magnesium hydride. Triphenylstibene, on the contrary, was recovered unchanged after it had been subjected to the action of hydrogen and active nickel for seven and one-half hours at 200°.

It seems worth noting that the order of increasing stability of the metallic alkyls toward hydrogen in the presence of catalytically active nickel, appears to be magnesium, zinc, lead and antimony, which is the order of decreasing metallic character. With regard to the mechanism of the reaction attention should be called to the observations of Paneth and co-workers,<sup>2</sup> who believe that they have demonstrated that tetraethyllead decomposes into lead and ethyl radicals. The formation of diphenyl from tetraphenyllead and of benzene from diphenylmagnesium could be explained as involving in the one case the addition of two phenyl radicals and in the second case of a phenyl radical and a hydrogen atom. However, there is no apparent reason why a difference in the metal from which the phenyl radical has separated should determine the subsequent manner of combination of the radicals. There seems no justification for going beyond the conception that hydrogen and metal alkyl were in combination with the metal surface and there suffered rearrangement. A summary of the experimental results is given in Table I.

The authors are indebted to Dr. George Calingaert of the Ethyl Gasoline Corporation for the tetraheptyllead used in this investigation. Dr. Calingaert in a private communication has informed the authors that several years ago he obtained a 40% yield of *n*-butane (accompanied by ethylene and ethane) as the result of passing tetraethyllead over heated pumice. Taylor and Jones reported that when tetraethyllead is decomposed at 250–300° in the presence of hydrogen and ethylene there were produced unsaturated gaseous and liquid hydrocarbons.<sup>3</sup>

### Summary

Nickel catalyzes a synthetic reaction whereby tetraphenyllead is converted quantitatively into diphenyl. A similar reaction occurs with tetra-*p*-tolyl- and tetraheptyllead and to a very limited extent with dibutyl

<sup>2</sup> Paneth and Hofeditz, *Ber.*, **62B**, 1335 (1929); Paneth and Lautsch, *ibid.*, **64B**, 2702 (1931).

<sup>3</sup> Taylor and Jones, *THIS JOURNAL*, **52**, 1111 (1930).

zinc. This type of reaction represents a novel characteristic of this well-known catalyst. Nickel also catalyzes the cleavage of dibutyl zinc and diphenylmagnesium with the formation of butane and benzene, respectively.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## SOME ANALYTICAL REACTIONS OF ALKYL SULFIDES IN BENZENE AND PURIFIED NAPHTHA SOLUTIONS<sup>1</sup>

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In a study of possible agents for the removal of alkyl sulfides from hydrocarbons either by adsorption or by a chemical reaction an analytical method for the determination of sulfides, either alone or mixed with other sulfur compounds,<sup>4</sup> was required. Reliability and rapidity were of more importance than extreme accuracy. As the most of our work on sulfur compounds has been done, for the sake of reproducibility, in benzene this hydrocarbon was used as the solvent in this investigation. The method devised has been found to be applicable to solutions in a naphtha such as purified "Skellysolve" but, unfortunately, cannot be used when unsaturates are present.

Alkyl sulfides have usually been estimated by precipitation with mercury salts. Mabery and Smith<sup>5</sup> separated sulfides from Ohio petroleum by agitation of the naphtha with aqueous or alcoholic mercuric chloride. Thierry<sup>6</sup> used the same method to identify several sulfides from Persian oil. Faragher, Morrell and Monroe<sup>7</sup> recommend "normal" mercurous nitrate,  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , to precipitate sulfides quantitatively from naphtha solutions.

<sup>1</sup> Presented in part before the Petroleum Division at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931 under the title, The Analysis of Mixtures of Sulfides, Disulfides and Mercaptans. This paper contains results obtained in an investigation of "Reactions of a Number of Selected Sulfur Compounds" listed as Project 28 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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<sup>4</sup> The limitations of the method in the presence of mercaptans and disulfides will be presented in a later communication on the estimation of mixtures of mercaptans, sulfides and disulfides in benzene solution.

<sup>5</sup> Mabery and Smith, *Am. Chem. J.*, **13**, 233 (1891).

<sup>6</sup> Thierry, *J. Chem. Soc.*, **127**, 2756 (1925).

<sup>7</sup> Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**, 1281 (1927).