

placed in a round-bottomed flask and then at room temperature the 50% nickel-50% aluminum alloy was added as rapidly as foaming permitted (one-half to one hour). The alloy was weighed to yield a given amount of nickel upon the assumption of complete removal of the 50% of aluminum. Actually it was found that the aluminum is not completely removed. After completing the addition of the alloy to the alkaline solution, the flask was placed in a glycerol-bath and heated at 115-120° for the desired time interval, after which it was cooled and the nickel washed by decantation an additional five times after the washings first became neutral to litmus. The second procedure differed in that the alloy was added while cooling the alkali in an ice-bath. The flask was then closed with a Bunsen valve and allowed to stand at room temperature for seventy-two hours with occasional shaking. The catalyst was always prepared just prior to use.

Procedure.—The weighed sample of β -methylcinnamic acid was placed in a volumetric flask and known amounts of potassium hydroxide solution added. When the thermostat temperature was reached, the glucose and catalyst, in either order, were added and the flask filled to the mark and shaken. Zero time was taken when the fourth component was added. The reaction mixture was transferred to a specially designed flask to permit vigorous continuous shaking in the thermostat, with provision for sweeping out the air with pure nitrogen and the taking of periodic samples for titration for alkali concentration. The initial alkali concentration was calculated from the amount of acid and base added; completion and rate of the reaction were indicated by the alkali used up.

After completion of the reaction the nickel was filtered off and discarded and the filtrate acidified and extracted with benzene. The benzene layer, after water washing, was filtered through filter paper moistened with benzene, evaporated to constant weight and the residue taken up in 25 ml. of dry benzene for polarimetric observation and titration. To remove any unreduced β -methylcinnamic acid, the benzene solution was extracted by 50 ml. of 0.5 *N*

sodium hydroxide and the alkaline extract neutralized to phenolphthalein. Known amounts of 0.020 *M* potassium permanganate were then added until a small addition gave a color persisting for fifteen minutes; 10 ml. of 1 *N* sodium hydroxide was then added and a benzene extraction made to remove any acetophenone; after this the solution was acidified and the reduced acid recovered as before. In all but three experiments the unreduced acid present, as shown by the permanganate reaction, amounted to less than 0.3%. In these cases the following amounts were present: Expt. 12, 28%; Expt. 17, 15%; Expt. 18, 17%. The rotations reported are for the permanganate-treated acid, although in most cases the activity of the treated and untreated samples was identical within experimental error. Vacuum distillation of one sample did not change the rotation; vacuum distillation of 35 g. of accumulated samples resulted in a product which crystallized on standing, b. p. (10 mm.) 150-156°, uncorr.; yield 34 g.

Summary

The reduction of β -methylcinnamate ion by *d*-glucose in alkaline solution, catalyzed by Raney nickel, has been studied with variations in amount of catalyst, temperature, order of mixing, method of preparation of the catalyst, and relative concentrations of solutes. The optical activity in benzene of the resulting β -phenylbutyric acid varied from $[\alpha]_{5461}^{25} +0.31^\circ$ to -0.42° , corresponding to about 0.5% asymmetric synthesis. The specificity changed with each variable and a tentative explanation of all of the variations has been presented based upon a simple hypothesis of relative rates of adsorption. Attention is called to the analogous behavior of enzyme catalyzed reactions.

BERKELEY, CALIF.

RECEIVED JULY 31, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. IV. Interchange between Triethyllead Chloride and Radioactive Tetraethyllead

BY GEORGE CALINGAERT, HAROLD A. BEATTY AND LEWIS HESS

In the preceding papers of this series¹ it was shown that R_4Pb compounds in general undergo the redistribution reaction in which the intermolecular interchange of R groups leads to the formation of random equilibrium mixtures. Among the effective catalysts for this reaction are the R_3PbX salts, where X is Cl, Br, or I. It is obviously of interest to determine whether these R_3PbX salts also enter directly into this reaction,

(1) Calingaert and Beatty, *THIS JOURNAL*, **61**, 2748 (1939); Calingaert, Beatty and Neal, *ibid.*, 2755; Calingaert and Soroos, *ibid.*, 2758.

and whether both the R and X groups are capable of being interchanged with each other. In the first paper of this series it was indicated that such is the case; the present paper gives the experimental details of the study of the simplest possible reaction of this type, that between R_4Pb and R_3PbX , where all the R groups are identical and no new compounds can be formed; a subsequent paper will describe the more general examples wherein compounds containing different R groups are used.

Study of the present reaction is possible only by the use of some special "tracer" method such as that of radioactive indicators. In the present work, the "tracer" used was lead containing radium D. The β radiation of radium D is so weak that it is desirable to measure instead only the β radiation of its first disintegration product, the bismuth isotope, radium E. The amount of radium E originally present is largely separated from the lead in the course of the chemical reactions used here, but its half-life is short compared with that of radium D. As a result, starting with a preparation containing radium D and no radium E, the concentration of the latter will be within 0.5% of its maximum value after thirty-five days, and will remain so for sixty-five days thereafter.

Procedure.—A solution was made containing equimolecular proportions of radioactive tetraethyllead and inert triethyllead chloride, and was kept at room temperature. Samples were removed at intervals of time from two hours to seven days, and the tetraethyllead and the triethyllead chloride were separated and converted individually to lead sulfate. After the build-up of radium E in each sample was substantially completed, measurements of radioactivity were made.

The data for two duplicate runs given in Table I show that the random distribution of the chlorine atoms between the two lead compounds present takes place rapidly and reaches equilibrium in less than twenty-four hours. Both tetraethyllead and triethyllead chloride are relatively stable compounds under the conditions used, and it is accordingly somewhat surprising to find so rapid an interchange of the chlorine atoms and ethyl radicals.

TABLE I
RADIOACTIVITY OF Et_4Pb AND Et_3PbCl

Time, hr.	Radioactivity, counts per minute			
	Expt. 1		Expt. 2	
	Et_4Pb	Et_3PbCl	Et_4Pb	Et_3PbCl
2	2173	777	2264	953
24	1704	1684	1922	1838
72	1659	1669		
96			1887	1808
168	1673	1679	1887	1703

Experimental.—Lead sulfate which contained about 2×10^{-8} g. of radium D sulfate per g. was reduced to metallic lead by smelting with metallic iron and coke, and this lead was used to prepare the sodium-lead alloy, NaPb , from which radioactive tetraethyllead was synthesized.²

To carry out the redistribution reaction, 0.082 mole each of radioactive tetraethyllead and ordinary triethyllead chloride³ were placed in a small flask under nitrogen, and

diluted with sufficient benzene, 77 ml., to dissolve the salt. The solution was maintained at room temperature for one week, with occasional shaking. The reversible side reaction⁴ of triethyllead chloride in accordance with the equation $2\text{Et}_3\text{PbCl} \rightleftharpoons \text{Et}_2\text{PbCl}_2 + \text{Et}_4\text{Pb}$ was effectively minimized by the low temperature employed, together with the high ratio of ethyl radicals to chlorine. This was evidenced by the very slight precipitation of the nearly insoluble diethyllead dichloride.

Samples were removed for analysis after periods of two hours, and one, three, and seven days, and were treated as follows: most of the benzene was removed by vacuum evaporation at room temperature, 25 ml. of hexane was added to precipitate the triethyllead chloride, the mixture was filtered, and the residue was washed with three 10-ml. portions of hexane, adding the washings to the filtrate. The filtrate and residue were brominated separately with an excess of a solution of bromine in carbon tetrachloride, and the resulting bromides were dissolved in nitric acid and converted to sulfates, which were filtered, washed, dried, and later were measured for radioactivity. The experiment was performed in duplicate.

Measurement of Radioactivity.—The counting system consisted of a scale-of-one counting circuit excited by a Geiger-Müller tube, as described by Duffendack and co-workers.⁵ The tube had a background count of less than 20 per minute. Each sample was measured once only, from thirty-two to forty days after its preparation. Each measurement covered a period of twenty minutes, during which the counter was switched off by a time switch for twelve seconds out of each minute, to provide leisure time for recording the count.

The procedure in general was designed to avoid errors from extraneous sources. However, the counts obtained from a considerable number of presumably identical samples showed variations substantially larger than expected, the reason for which was not evident. Such variations also appear in the data in Table I, but do not affect the general conclusions derived from the experiments.

Acknowledgments.—We are indebted to M. Marcel Pochon of Eldorado Gold Mines, Ltd., for a supply of radioactive lead sulfate, to Dr. Oscar E. Harder of the Battelle Memorial Institute for the smelting of this lead sulfate, and to Professor O. S. Duffendack and Dr. Harold Lifschutz of the University of Michigan for advice and assistance in the measurement of radioactivity.

Summary

Using radium D as an indicator, it is shown that an interchange of chlorine atoms and ethyl radicals between tetraethyllead and triethyllead chloride takes place, and reaches equilibrium in less than one day at room temperature.

DETROIT, MICHIGAN

RECEIVED SEPTEMBER 22, 1939

(4) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 397.

(5) Duffendack, Lifschutz and Slawsky, *Phys. Rev.*, **52**, 1231 (1937); Lifschutz and Duffendack, *ibid.*, **54**, 714 (1938).

(2) Kraus and Callis, U. S. Patent 1,697,245 (1929).

(3) Calingaert, Kurt and Dykstra, to be published.