(3) **The Preparation of 3,5-Dibromo-1-ethyl-2-pyridone.**—The filtrate obtained in the preceding experiment was treated in exactly the manner described for that obtained in the cleavage of phenacylpyridinium chloride. The final distillation yielded 2 g. of a liquid boiling at 124° (9 mm.). This compound was brominated according to the directions of Decker and Kaufmann for the bromination of 1-methyl-2-pyridone. The product obtained melted at 101–104°, and when recrystallized twice from 50% ethyl alcohol, melted sharply at 109°.

The Preparation of 3,5-Dibromo-1-ethyl-2-pyridone from Pyridine and Diethyl Sulfate.—Following the directions of Decker and Kaufmann[3] but substituting diethyl sulfate for dimethyl sulfate, 1-ethyl-2-pyridone was prepared in 30% yields from 2.7 g. of pyridine. It boiled at 124° (9 mm.); 132° (12 mm.). This was brominated by following the procedure of Decker and Kaufmann for the bromination of 1-methyl-2-pyridone. The 3,5-dibromo-1-ethyl-2-pyridone obtained was recrystallized from 50% ethyl alcohol; it melted at 109°.

Anal. Calcd. for $C_7H_7ONBr_2$: N, 5.0; Br, 56.9. Found: N, 5.0; Br, 56.7.

This compound when mixed with the compound prepared from *p*-bromo-α-methylphenacylpyridinium bromide melted sharply at 109°.

Summary

When phenacylpyridinium chloride and *p*-bromo-α-methylphenacylpyridinium bromide are treated with aqueous alkalies they are cleaved into the corresponding aromatic acids and alkylpyridinium halides. The type of reaction involved is expressed by the equation

$$[ArCOCH(R)NC_5H_5]X + NaOH \longrightarrow ArCO_2Na + [RCH_2NC_5H_5]X$$

The relationship of this reaction to other types of cleavage of carbonyl compounds by alkalies is pointed out.

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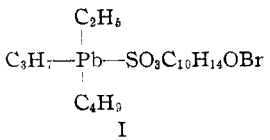
Studies of Organic Lead Compounds. V. Asymmetric Derivatives

BY PAUL R. AUSTIN[1]

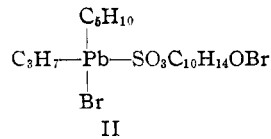
Optically active compounds containing asymmetric silicon, tin and germanium atoms have been known for some time. Analogous lead derivatives have been singularly resistant to resolution, although it seems reasonable to suppose that in organic combination the lead atom possesses a tetrahedral configuration. A large number of mixed lead alkyl-aryls have been prepared[2] and their resolution attempted by means of *d*-bromocamphorsulfonic acid.[3] Ethylpropylisobutyllead *d*-bromocamphorsulfonate (I) was found to be an oil which could not be crystallized. *n*-Propylisoamyllead bromo *d*-bromocamphorsulfonate (II) could be fractionally

(1) National Research Fellow in Chemistry.
(2) Krause and Schlöttig, *Ber.*, **58**, 427 (1925).
(3) Krause, Inaugural Dissertation, Berlin, July 1917, p. 56.

crystallized, but the corresponding halide obtained on decomposition with calcium chloride was optically inactive.



I

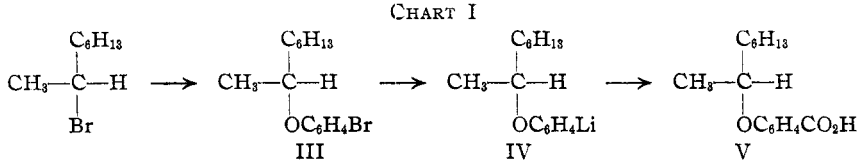


II

For the attempted resolution presented in this paper, a tetra-substituted lead derivative with non-polar valencies only was prepared; such a product should have little tendency to racemize. One of the groups introduced contained an optically active carbon atom, which should produce two diastereoisomers of the tetravalent lead compound if the lead atom is asymmetric. In order to have crystalline products, aromatic derivatives were used as far as possible.

For the introduction of a center of asymmetry in the lead compound, the synthesis of an active *p*-lithiumphenyl-*sec*-octyl ether was performed. Its preparation is shown diagrammatically in Chart I together with the specific rotations of derivatives in the dextro and levo series.

CHART I



	III	IV	V
$[\alpha]_D^{25}$ =	− 37.46°	+ 8.10°	+ 8.4°	+ 9.64°
$[\alpha]_D^{25}$ =	+ 36.36°	− 7.72°	− 9.8°	− 10.42°

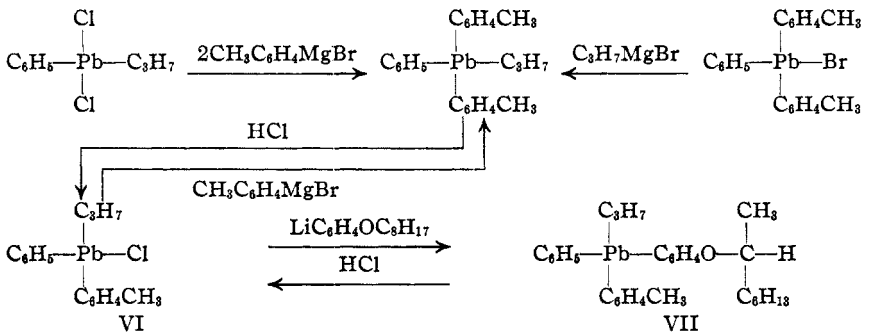
That the lithium aryl (IV) retained optical activity was shown by actual observation of its ether solution and by conversion to the active acids (V) by means of carbon dioxide. The lithium compound is of particular interest in that it makes an optically active organo-metallic reagent available for synthetic purposes. The active bromide (III) was chosen because of its ease of synthesis and because, by analogy with the mercury aryls, ethers of this type should be very readily eliminated from the organo-lead molecule by hydrogen chloride.[4]

The lithium derivative (IV) was next condensed with phenyl-*n*-propyl-*o*-tolyllead chloride (VI) to give the active phenyl-*n*-propyl-*o*-tolyllead *p*-(*sec*-octylphenyl ether) (VII). The synthesis is shown schematically in Chart II. The preparation of intermediates and compounds incidental to this synthesis are described in the Experimental Part.

It is apparent that if the lead were a center of asymmetry, the final product (VII) would exist in two separable forms. All of the intermediate compounds were solids, but the final active derivative (VII) was an oil

(4) Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

CHART II



which, although optically active, could not be separated into its two diastereoisomers. This was not surprising, for unless crystalline products are obtained, the resolution of optically active compounds, even diastereoisomers, invariably has failed. Decomposition of various fractions of (VII) by means of hydrogen chloride resulted in the elimination of the active group, but the final phenyl-*n*-propyl-*o*-tolyllead chloride (VI) was inactive in every case.

Experimental Part

The organo-lead intermediates are summarized in Table I and their preparation is briefly described below.

Triphenyl-*n*-propyllead.—Eighteen grams of triphenyllead chloride was added to an excess of *n*-propylmagnesium bromide in 60 cc. of ether and 100 cc. of benzene. The mixture was stirred and refluxed for two hours and was decomposed with iced ammonium chloride solution. The ether layer was evaporated and the residue was crystallized from alcohol.

Diphenyl-*n*-propyllead Chloride.—Triphenyl-*n*-propyllead (4.8 g.) was dissolved in 200 cc. of chloroform and dry hydrogen chloride was passed in until a precipitate appeared. This was filtered off, the filtrate evaporated and the residue crystallized from alcohol.

Phenyl-*n*-propyllead Dichloride.—In 500 cc. of chloroform there was dissolved 29 g. of triphenyl-*n*-propyllead. This was stirred rapidly and dry hydrogen chloride was introduced at room temperature. The insoluble phenyl-*n*-propyllead dichloride

TABLE I

ORGANIC LEAD DERIVATIVES

Compound	Yield, %	M. p., °C.	Lead, % Calcd.	Lead, % Found	Chlorine, % Calcd.	Chlorine, % Found
$(C_6H_5)_3Pb$-*n*-C_3H_7	95	69–70	43.04	42.91	...	...
$(C_6H_5)_3Pb$-*n*-C_5H_{11}[a]	92	16–17	40.67	40.10	...	...
$(C_6H_5)_2$(*n*-C_3H_7)PbCl	84	141 dec.	47.11	46.59	8.06	8.12
$(C_6H_5)_2$(*n*-C_5H_{11})PbCl[a]	..	123 dec.	44.29	44.22	7.58	7.56
(C_6H_5)(*n*-C_3H_7)$PbCl_2$	93	dec. > 265	...	...	17.81	17.86
(C_6H_5)(*n*-C_3H_7)(*o*-C_7H_7)PbCl	63	103–104	45.66	45.77	7.81	7.83
(C_6H_5)(*n*-C_3H_7)(*o*-C_7H_7)$_2$Pb	94	49–50	40.67	40.69	...	...
(C_6H_5)(*n*-C_3H_7)(*o*-C_7H_7)(*p*-$C_6H_4OC_8H_{17}$)Pb	98	Oil	33.23	32.81	...	...

[a] Prepared as the analogous propyl compound.

was filtered; yield, 22.5 g. The product thus obtained decomposed above 265° and although not analytically pure, was satisfactory for subsequent reactions. No method for its purification could be found.

Phenyl-*n*-propyldi-*o*-tolyllead.—The products obtained by the three methods of preparation illustrated in Chart II were shown to be identical by means of mixed melting points.

(A) To a solution of *n*-propylmagnesium bromide (0.025 mole) in 25 cc. of ether and 50 cc. of benzene there was added 3.7 g. of phenyldi-*o*-tolyllead bromide.[5] The mixture was stirred in the cold for an hour and refluxed for one-half hour. Decomposition was effected by means of iced ammonium chloride solution and the ether layer was separated and evaporated. An oil was obtained which crystallized on cooling in an ice–salt bath; yield, 3.2 g. It was recrystallized alternately from alcohol and from a ligroin-methanol mixture.

(B) Twenty grams of phenyl-*n*-propyllead dichloride was suspended in 250 cc. of ether with rapid stirring, 120 cc. (0.2 mole) of *o*-tolylmagnesium bromide solution was added and the mixture stirred in the cold for three hours. The product was isolated and purified as in (A); yield, 19 g.

(C) To an ether solution of 0.55 g. of phenyl-*n*-propyl-*o*-tolyllead chloride there was added an excess of *o*-tolylmagnesium bromide solution. The mixture was allowed to stand for an hour in the cold and the product was isolated as in (A); yield, 0.45 g.

Phenyl-*n*-propyl-*o*-tolyllead Chloride (VI).—Twenty-three grams of phenyl-*n*-propyldi-*o*-tolyllead in 200 cc. of chloroform was treated with dry hydrogen chloride in the cold until a precipitate appeared. This was filtered off and the chloroform solution was concentrated. The product from two such runs was crystallized from petroleum ether and gave 26 g. of material which was crystallized from aqueous alcohol and then melted at 103–104°. In order to avoid decomposition the melting point was determined by placing the capillary in a bath previously heated to 90°. When crystallized from petroleum ether the compound behaved as though it contained solvent of crystallization. Its melting point varied, the highest obtainable being 122–123°.

Phenyl-*n*-propyl-*o*-tolyllead *p*-(*sec*-octylphenyl ether) (VII).—*p*-Lithiumphenyl-*sec*-octyl ether was prepared from 5.5 g. of *d*-*p*-bromophenyl-*sec*-octyl ether, 0.2 g. of lithium and 60 cc. of ether. Eight grams of phenyl-*n*-propyl-*o*-tolyllead chloride was added and the mixture stirred in the cold for one hour. Decomposition was effected with water and the ether layer after separation and evaporation yielded 11 g. of an oil which resisted all attempts to crystallize it. The oil was dissolved in 30 cc. of alcohol, cooled in an ice–salt bath and the alcohol decanted. Any remaining alcohol was removed in a vacuum; yield, 5 g., $[\alpha]_D^{25}$ +2.4° (chloroform). A second fraction from the mother liquor above gave a similar rotation and no separation could be demonstrated. The third fraction obtained was taken for analysis (Table I).

Starting with *l*-*p*-bromophenyl-*sec*-octyl ether the results were entirely analogous to the above; phenyl-*n*-propyl-*o*-tolyllead *p*-(*sec*-octylphenyl ether) of $[\alpha]_D^{25}$ −3.2° (chloroform) was obtained and no separation of the isomers could be demonstrated. The oil was dissolved in chloroform and treated with dry hydrogen chloride as described for phenyl-*n*-propyl-*o*-tolyllead chloride. The product obtained from the chloroform solution was crystallized from petroleum ether and then from aqueous alcohol and melted at 102–104°. A mixed melting point with an authentic specimen of phenyl-*n*-propyl-*o*-tolyllead chloride showed no depression.

Phenyl-*n*-propyl-*o*-tolyllead chloride obtained by the action of hydrogen chloride on various fractions of active phenyl-*n*-propyl-*o*-tolyllead *p*-(*sec*-octylphenyl ether) was tested for rotation and found to be inactive in every case.

(5) Austin, THIS JOURNAL, **53**, 1551 (1931).

d- **and** *l*-**2-Bromooctane.**[6]—The *l*-2-bromooctane distilled at 80–81° (18 mm.); $[\alpha]_D^{25}$ −37.46°; n_D^{20} 1.4500; yield, 70%. The *d*-2-bromooctane distilled at 78–79° (16 mm.); $[\alpha]_D^{25}$ +36.36°; n_D^{20} 1.4493; yield, 70%.

***p*-Bromophenyl *sec*-Octyl Ether (III).**—Sodium ethylate dissolved in an excess of absolute alcohol was treated with equivalent amounts of *p*-bromophenol and 2-bromooctane and the mixture was refluxed for four to six hours. The time of reflux apparently had no effect on the optical activity of the product. Sixteen grams of *l*-2-bromooctane gave 10 g. of *d*-*p*-bromophenyl-*sec*-octyl ether, b. p. 141–144° (2 mm.); n_D^{25} 1.5121; d_{25}^{25} 1.173; $[\alpha]_D^{25}$ +8.10° (absolute alcohol).

Anal. Calcd. for $C_{14}H_{21}OBr$: Br, 28.05. Found: Br, 27.99.

Thirty-two grams of *d*-2-bromooctane yielded 17 g. of *l*-*p*-bromophenyl *sec*-octyl ether, b. p. 144–147° (3 mm.); n_D^{25} 1.5137; d_{25}^{25} 1.175; $[\alpha]_D^{25}$ −7.72° (absolute alcohol).

Seventy-five grams of *dl*-2-bromooctane gave 52 g. of product which was twice refractionated and then distilled at 127° (1.2 mm.), 141° (2.1 mm.), 150° (3.0 mm.); n_D^{25} 1.5128; d_{25}^{25} 1.172.

Anal. Calcd. for $C_{14}H_{21}OBr$: Br, 28.05. Found: Br, 27.76.

d- **and** *l*-*p*-**Lithiumphenyl *sec*-Octyl Ether (IV).**—The procedure used for the preparation of the lithium derivatives was similar to that recently described.[7] *d*-*p*-Lithiumphenyl-*sec*-octyl ether was prepared in 75 cc. of ether from 13 g. of the corresponding *d*-bromide; yield, 93%; $[\alpha]_D^{25}$ +8.3°. *l*-*p*-Lithiumphenyl-*sec*-octyl ether was prepared from 7 g. of the *l*-bromide in 50 cc. of ether; yield, 90%; $[\alpha]_D^{25}$ −9.8°.

d- **and** *l*-*p*-**Carboxyphenyl *sec*-Octyl Ether (V).**—The above lithium aryls were converted to acids by means of carbon dioxide.[8] From 0.034 mole of *d*-*p*-lithiumphenyl *sec*-octyl ether in 60 cc. of ether there was obtained 3.5 g. of the corresponding acid. This was obtained as an oil which crystallized on chilling and stirring. It was recrystallized from petroleum ether by cooling in an ice–salt mixture and melted at 63–64°; $[\alpha]_D^{25}$ +9.64° (absolute alcohol).

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 71.94; H, 8.87; neut. equiv., 250.2. Found: C, 71.77; H, 8.96; neut. equiv., 256.0.

From 0.015 mole of *l*-*p*-lithiumphenyl *sec*-octyl ether in 35 cc. of ether there was obtained similarly 1.5 g. of the corresponding acid, m. p. 62–63°; $[\alpha]_D^{25}$ −10.42° (absolute alcohol). *Neut. equiv.* Calcd. for $C_{15}H_{22}O_2$: 250.2. Found: 251.7.

The lithium derivative was prepared from 14 g. of the racemic bromide in 75 cc. of ether and after carbonation gave 1.7 g. of solid acid After three recrystallizations it melted at 61–62°.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 71.94; H, 8.87; neut. equiv., 250.2. Found: C, 71.93; H, 8.91; neut. equiv., 255.7.

The author is grateful to Professor C. S. Marvel for many helpful suggestions.

Summary

Optically active *p*-bromophenyl *sec*-octyl ether has been synthesized and converted to the lithium derivative. Optical activity in the lithium aryl was demonstrated by actual observation of its ether solution and by conversion to the corresponding active acid.

By means of active *p*-lithiumphenyl *sec*-octyl ether, optically active phenyl-*n*-propyl-*o*-tolyllead *p*-(*sec*-octylphenyl ether) has been prepared.

(6) Shriner and Young, THIS JOURNAL, **52**, 3337 (1930).

(7) Austin, *ibid.*, **54**, 3726 (1932); Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

(8) Gilman and Van Ess, *ibid.*, **55**, 1258 (1933).

Decomposition of various fractions of the asymmetric lead compound resulted in the elimination of the active group, but yielded only inactive organo-lead products.

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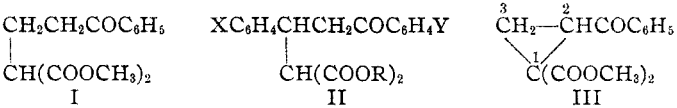
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MCGILL UNIVERSITY]

Addition Reactions of Vinyl Phenyl Ketone. III. Methyl Malonate

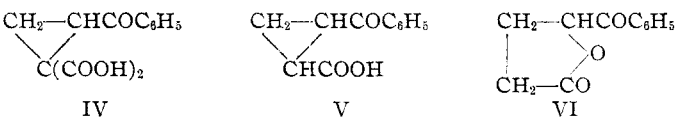
BY C. F. H. ALLEN AND H. W. J. CRESSMAN

In continuation of the investigations described in the earlier papers in this series[1] methyl malonate has been added to vinyl phenyl ketone and the properties of the resulting ketonic ester (I) compared with certain closely related esters (II).[2]



I II III

The addition product was transformed into the cyclopropane ester and acids (III, IV, V).



IV V VI

The cyclic ester (III) was readily hydrolyzed to the dibasic acid (IV). On being heated the latter lost carbon dioxide, giving a deeply colored oil from which three acidic substances were isolated—small amounts of the stereoisomeric monobasic acids (V) and the lactone (VI).

It was of major interest to see if these cyclic substances would react like the other cyclopropane derivatives having one unsubstituted carbon atom[1] when treated with reagents that attack the ring, and be opened only in the 1,2 position. Unfortunately the reactions were not clean-cut and the nature of all the oily by-products formed usually could not be determined, but in every case the greater part of the products were substances that could only have been formed by 1,2 ring opening.

Zinc dust and acetic acid reduced the ester (III) and acids (IV, V) to the open chain substances—*e. g.*, the keto ester (I), dibasic acid (XII) and γ-benzoylbutyric acid; thus the ring was opened in the 1,2 position. None were affected by concentrated sulfuric acid.

(1) (a) Allen and Bridgess, THIS JOURNAL, **51**, 2151 (1929); (b) Allen and Barker, *ibid.*, **54**, 736 (1932).

(2) (a) Kohler, *Am. Chem. J.*, **46**, 474 (1911); (b) Kohler and Conant, THIS JOURNAL, **39**, 1404, 1699 (1917); (c) Kohler, Hill and Bigelow, *ibid.*, **39**, 2405 (1917); (d) Kohler and Steele, *ibid.*, **41**, 1093 (1919).