

coefficient are both much greater than for a diffusion controlled current. A mechanism is proposed for this wave which is based on the catalysis

of hydrogen discharge by the  $\text{Re}^{-1}\text{-Re}^{+1}$  couple.

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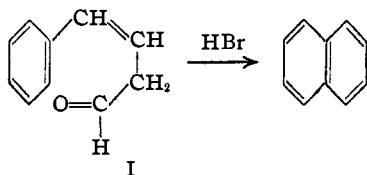
RECEIVED DECEMBER 27, 1941

## NOTES

### Cyclization of $\beta$ -Styrylacetaldehyde

BY CHARLES K. BRADSHER<sup>1</sup>

It has been reported by Rinkes<sup>2</sup> that  $\beta$ -styrylacetaldehyde (I) may be cyclized to give naphthalene. Inasmuch as he failed to report either the



yield or the method employed in this cyclization, we have undertaken to reinvestigate this matter.

The required aldehyde (I) was prepared by the more convenient method of Meyer,<sup>3</sup> involving the pyrolysis of  $\alpha$ -methoxycinnamylacetic acid. When refluxed with hydrobromic and acetic acids, the aldehyde gave naphthalene in 25% yield.

While this is the simplest case of aromatic cyclodehydration to give a naphthalene nucleus, there are a number of other instances in which a cyclization of this type is believed or known to take place.<sup>4</sup>

### Experimental

**Naphthalene.**— $\beta$ -Styrylacetaldehyde was prepared in 25% yield by the method of Meyer.<sup>3</sup> This aldehyde (0.65 g.) was dissolved in acetic acid (13 cc.) and added dropwise to boiling 34% hydrobromic acid (6.5 cc.), the addition requiring about five hours. Refluxing was allowed to continue for a total of forty-eight hours. The mixture was then diluted with water and extracted with ether. The ethereal extract was washed, dried, concentrated and the residue sublimed *in vacuo*. The sublimate consisted of small white plates; m. p. 80–81°; yield, 0.14 g. (25%). This material showed no depression of melting point when mixed with an authentic sample of naphthalene.

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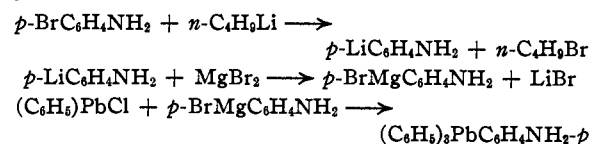
- (1) National Research Fellow (participating basis).
- (2) Rinkes, *Rec. trav. chim.*, **39**, 200 (1920).
- (3) Meyer, *Compt. rend.*, **204**, 508 (1937).
- (4) E. g. Zincke, *Ann.*, **240**, 137 (1887); Erlenmeyer and Kunlin, *Ber.*, **35**, 384 (1902); Haworth and Sheldrick, *J. Chem. Soc.*, 636, 1576 (1935); Omaki, *J. Pharm. Soc. Japan*, **58**, 4 (1938).

### Diazotization of an Aminoaryllead Compound<sup>1</sup>

BY HENRY GILMAN AND C. G. STUCKWISCH

*p*-Aminophenyllithium has been used for the introduction of the *p*-aminophenyl group into organoarsenic and organophosphorus compounds.<sup>2</sup> In attempts to effect a related transformation between triphenyllead chloride and *p*-aminophenyllithium, complex mixtures were obtained. The difficulty probably resides in the metal-metal interconversion reactions between organolead and organolithium compounds.<sup>3</sup>

However, because M–M interconversions only occur to a highly subordinated extent between Grignard reagents and organolead compounds, we first converted the RLi compound to the corresponding RMgBr compound by means of magnesium bromide.<sup>4</sup> The following sequence of reactions illustrates the preparation of triphenyl-*p*-aminophenyllead, which was obtained in a 66% yield.



The *p*-aminophenyllead compound was diazotized by conventional procedures, despite the presence in the molecule of a supposed labilizing aminoaryl group. The diazonium compound was coupled with  $\beta$ -naphthol to give an azo-lead compound which was red in acid solution and green in basic solution. The general reactions described now provide the essential means for the resolution of some RM compounds, and the introduction of water-solubilizing groups to vary the lipid-water distribution of the less chemically reactive RM compounds.

- (1) Paper XLIV in the series "Relative Reactivities of Organo-metallic Compounds"; the preceding paper is in THIS JOURNAL, **63**, 2844 (1941).
- (2) Gilman and Stuckwisch, *ibid.*, **63**, 2844 (1941).
- (3) Gilman and Moore, *ibid.*, **62**, 3206 (1940).
- (4) Gilman and Kirby, *ibid.*, **63**, 2046 (1941).

### Experimental

**Triphenyl-*p*-aminophenyllead.**—To 0.128 mole of *n*-butyllithium in 200 ml. of ether was added dropwise 6.9 g. (0.04 mole) of *p*-bromoaniline in 50 ml. of ether. After addition was completed, the solution was stirred at room temperature for thirty minutes. The low temperature ( $-60^{\circ}$ ) reported previously<sup>2</sup> for the preparation of *p*-aminophenyllithium is not necessary. A slight excess of an ether solution of anhydrous magnesium bromide, prepared by adding bromine dropwise to magnesium suspended in ether, was then added to the reaction mixture. The Grignard reagent thus formed was allowed to react with 18.4 g. (0.04 mole) of triphenyllead chloride for two hours at room temperature, and then hydrolyzed with iced ammonium chloride solution.

The ether layer was extracted with dilute hydrochloric acid. From the hydrochloric acid extract was isolated 3.5 g. of *p*-bromoaniline. The residual ether layer was dried and then evaporated under reduced pressure. The solid residue yielded, after several crystallizations from petroleum ether (b. p. 60–68°), 2.2 g. of a white crystalline solid, m. p. 166–167°.

The ether insoluble material obtained from the reaction was extracted with three 200-ml. portions of petroleum ether (b. p. 60–68°). The extractions yielded 4.8 g. of material melting at 166–167° and identical with the substance obtained from the ether soluble portion. The total yield was 7.0 g. or 66%, assuming that the unrecovered *p*-bromoaniline was converted to *p*-aminophenyllithium.

*Anal.* Calcd. for  $C_{24}H_{21}NPb$ : Pb, 39.01. Found: Pb, 39.45.

**Triphenyl-1-(2-hydroxynaphthyl)-azophenyl-4-lead.**—One gram of triphenyl-*p*-aminophenyllead was diazotized and coupled with  $\beta$ -naphthol in the usual manner. The coupling product, crystallized from dilute ethanol, decomposed at 135°, and was red in acid solution and green in the presence of base.

*Anal.* Calcd. for  $C_{34}H_{26}ON_2Pb$ : Pb, 30.02. Found: Pb, 29.65.

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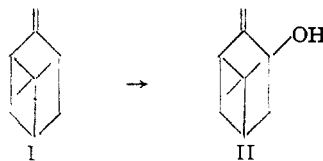
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### The Oxidation of $\beta$ -Pinene with Selenium Dioxide

BY LLOYD M. JOSHEL AND S. PALKIN

The oxidation of  $\beta$ -pinene (I) with selenium dioxide<sup>1,2</sup> has been recently reinvestigated by Stallcup and Hawkins,<sup>3</sup> who reported that no pinocarveol (II) or other alcohol could be found in the oxidation mixture. In order to make available a ready means for the preparation of pinocarveol from  $\beta$ -pinene and in view of the possible bearing on the mechanism of selenium dioxide oxidation, we are prompted to report the results of

some experiments made some time ago in this Laboratory.



Both the French workers<sup>1</sup> and Stallcup and Hawkins<sup>3</sup> used one mole (two equivalents) of selenium dioxide per mole of  $\beta$ -pinene. We found that when somewhat less than one-half a mole of selenium dioxide is used per mole of  $\beta$ -pinene, pinocarveol is readily obtained. Zacharewicz,<sup>2</sup> who used an even smaller ratio of selenium dioxide to  $\beta$ -pinene, also obtained pinocarveol but in less than one-half the yield reported below.

We are indebted to Messrs. Hawkins and Stallcup for their kindness in trying out the oxidation procedure described below. In a private communication Dr. Hawkins has informed us that they have confirmed our findings with regard to the main product, pinocarveol, and the small amount of carvopinone formed under these conditions.

### Experimental

A solution of 21 g. (0.16 mole) of c. p. selenious acid in 40 ml. of absolute ethanol was added dropwise during one-half hour, with mechanical stirring, to 54 g. (0.40 mole) of  $\beta$ -pinene. During the addition the solution became warm and turned yellow in color. After stirring another half-hour at room temperature, the solution was refluxed for four hours. The solution, which was red at this point, was then steam-distilled and the oil in the distillate was taken up in ether, washed, dried and distilled under nitrogen, furnishing, along with other fractions, 21 g. (42%) of a colorless liquid, b. p. 101.5–103° (25 mm.). The physical constants and active hydrogen determination indicated that this material was pinocarveol of about 85–90% purity. It could be further purified by conversion to the borate. The alcohol was heated with an equal volume of ethyl borate at 100–125° for one-half hour and the volatile contaminants removed by reducing the pressure gradually to 2 mm. while the bath was raised to 150°. The residual ester was then simultaneously hydrolyzed and steam distilled and the oil in the distillate taken up in ether, washed, dried, and distilled under nitrogen. In this way a colorless liquid, b. p. 101–102° (20 mm.), was obtained in 69% yield from the crude alcohol, or 29% over-all yield;  $n_D^{20}$  1.4995,  $d_4^{20}$  0.9798,  $\alpha_D^{20}$  +67.48°,  $\alpha_D^{20}$  +71.57°,  $\alpha_D^{20}$  +83.37°. Active hydrogen determination (semimicro) with methylmagnesium iodide showed 11.55% hydroxyl; calcd., 11.17%. The phenylurethan melted at 84–86°. This compares favorably with the m. p. of this derivative as usually reported,<sup>3,4</sup> although Schmidt<sup>5</sup> reported that on

(1) Dupont, Allard and Dulou, *Bull. soc. chim.*, [4] **63**, 599 (1933).

(2) Zacharewicz, *Roczniki Chem.*, **17**, 630 (1937).

(3) Stallcup and Hawkins, *THIS JOURNAL*, **63**, 3339 (1941).

(4) Schmidt, *Ber.*, **62**, 2945 (1929).

(5) Schmidt, *ibid.*, **63**, 1129 (1930).

rigorous purification the m. p. can be raised to 88–89°. On catalytic hydrogenation the alcohol absorbs 0.9–1.0 mole of hydrogen.<sup>6</sup>

Three grams of a non-alcoholic liquid were recovered from the volatile fraction obtained during the above ethyl borate treatment. The substance polymerized very rapidly on heating and this property, together with the rotation, refractive index, and method of preparation, indicates that it was probably impure carvopinone.<sup>3</sup>

(6) Joshei, Hall and Palkin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 447 (1941).

BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON, D. C. RECEIVED OCTOBER 27, 1941

### The Separation of Ytterbium from Accompanying Rare Earths by Means of its Amalgam

BY HERBERT N. MCCOY AND R. PHILIP HAMMOND

The preparation of ytterbium amalgam by the electrolytic method described earlier<sup>1</sup> has been repeated, using a larger amount (4 g. of oxide) of the same starting material. The electrolyses were carried to the point where no further amalgam formation took place. The rare earths from amalgams and from residual electrolytes were then extracted as chlorides called I and II, respectively. Chloride I formed much the larger part of the material; chloride II amounted to about 0.1 g.

From chlorides I and II spectrograms were made using a replica grating of 15,000 lines per inch (5906 lines per cm.) and a graphite arc source. These spectrograms for the region 2500 to 4600 Å., accompanied by that of iron, were enlarged photographically to give prints with a dispersion of one Å. per mm. The enlarged prints were examined with the aid of Massachusetts Institute of Technology wave length tables<sup>2</sup> and more than 250 of the strong lines identified.

The spectrogram of chloride I was that of ytterbium containing a much smaller proportion of europium. No lines of other rare earths could be found on this spectrogram. That of chloride II showed in addition to some remaining ytterbium and europium, the presence of gadolinium, terbium, dysprosium, yttrium, erbium, thulium and lutecium. The presence of holmium was probable but could not be established with certainty because its strong lines were masked by those of other elements present.

(1) McCoy, *THIS JOURNAL*, **68**, 1622, 3432 (1941).

(2) "Massachusetts Institute of Technology Wave Length Tables," George W. Harrison, John Wiley and Sons, Inc., New York, N. Y., 1939.

This work shows that of the rare earths contained in the starting material only ytterbium and europium form amalgams by the method used. If the small proportion of europium present had first been removed, as might easily have been done by fractional crystallization as dimethyl phosphates,<sup>3</sup> bromates<sup>4</sup> or ethyl sulfates<sup>5</sup> the separation of ytterbium from the rare earths that usually accompany it would have been complete.

(3) Morgan and James, *THIS JOURNAL*, **36**, 10 (1914).

(4) James and Bissel, *ibid.*, **36**, 2060 (1914).

(5) Urbain, *Compt. rend.*, **126**, 835 (1898).

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RECEIVED JANUARY 2, 1942

### The Purification of Thorium Chloride Octahydrate

BY CHESTER B. KREMER

In connection with previous researches on thorium compounds as well as in recent work in the production of thorium dioxide catalysts, the necessity of obtaining pure thorium chloride octahydrate arose. Thorium chloride "c. p." as purchased on the market contains appreciable amounts of iron and silica. Purification by simple recrystallization is difficult because of the tenacity with which iron compounds are retained by the salt and the formation of concentrated solutions, sirupy in nature, which will not deposit crystals. However, it is possible to obtain pure  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$  by a method which in part is based upon a slight modification of the Gooch and Havens method for the determination of aluminum.

Specially prepared asbestos for the following operations is obtained by boiling a high grade variety repeatedly with concentrated hydrochloric acid until free of detectable iron and then washing thoroughly with distilled water.

Two hundred grams of the "c. p." salt is dissolved in just enough 6 *M* hydrochloric acid for complete solution, filtered through asbestos and then extracted twice with ethyl ether,<sup>1</sup> this operation removing practically all of the iron.<sup>2</sup> The solution is then evaporated to small volume on a hot plate. Excess silica precipitates out and is filtered off through asbestos. The filtrate is cooled to 0° and dry hydrogen chloride bubbled in until the solution is saturated with the gas. An equal volume of ethyl ether is

(1) Isopropyl ether may be employed; see Dodson, Forney and Swift, *THIS JOURNAL*, **68**, 2573 (1936).

(2) Langmuir, *ibid.*, **22**, 102 (1900).

added and the mixture agitated with hydrogen chloride gas until it becomes homogeneous. From this solution thorium chloride octahydrate precipitates as pure white crystals, which are filtered off, washed with ether and dried. A sample of the salt when dissolved in water gives a negative thiocyanate test for iron.

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### The Action of Monoethanolamine on Ethyl Bromomalonate

BY CHESTER B. KREMER, M. MELTSNER AND H. HINDIN

In the course of work being carried out in these Laboratories dealing with the synthesis of diureides, the condensation of monoethanolamine with ethyl bromomalonate was attempted. As ordinarily carried out, we find condensation does not result; rather the bromine atom in the ester is replaced by hydrogen. This reaction is analogous to the action of alkaline reagents and halogen acids on similar compounds containing active halogen atoms.

The ethyl bromomalonate was prepared by the action of bromine on ethyl malonate dissolved in carbon tetrachloride. The product was carefully purified by several distillations through a column under reduced pressure. The fraction boiling at 126–127° under 18 mm. pressure was used.

Forty-six grams of monoethanolamine (0.752 mole) and 90 g. of the ethyl bromomalonate (0.376 mole) were refluxed together for six hours. On cooling, the mixture separated into two layers, the lower one eventually solidifying. The solid material was identified as monoethanolamine hydrobromide. The liquid upper layer was extracted with diethyl ether, thus effecting separation from any excess monoethanolamine, and the ether extract dried over anhydrous magnesium sulfate. The ether was distilled off and the resulting liquid fractionated. A low-boiling fraction, b. p. 58–60° (2 mm.), was shown to be ethyl malonate by its refractive index ( $n_D^{20}$  1.4144) and density ( $d_4^{20}$  1.055). The yield was 11 g. A higher boiling fraction (36 g.), b. p. 92–93° (2 mm.), was identified by its boiling point and density ( $d_4^{20}$  1.426) as unchanged ethyl bromomalonate.

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### The Mutarotation of $\alpha$ -D-Glucose in Dioxane-Water Mixtures at 25°

BY H. H. ROWLEY<sup>1</sup> AND WARD N. HUBBARD

The mutarotation of  $\alpha$ -D-glucose has been an object of study for many years by numerous investigators. Though the majority of the experiments concerned this phenomenon in aqueous solution both with and without catalysts, a few have been studied in mixed aqueous solvents. Worley and Andrews<sup>2</sup> studied the mutarotation in methanol-water mixtures; Richards, Faulkner and Lowry<sup>3</sup> in both methanol-water mixtures and ethanol-water mixtures; Lowry and Faulkner<sup>4</sup> in pyridine-water mixtures; and more recently Rowley<sup>5</sup> in ethanol-water mixtures at 25°. The mutarotation of glucose in solution is believed by many to be catalyzed by acids and bases and since water is a complete catalyst, having both acidic and basic properties, the reaction is fairly rapid in pure water. Absolute methanol is amphiprotic and apparently a complete catalyst but much inferior to pure water<sup>6</sup> as is absolute ethanol.<sup>5</sup> On the other hand, pyridine is not amphiprotic but is a fairly strong base so mixtures of this solvent and water should be a fair catalyst for the mutarotation.

In continuing the studies of the mutarotation of  $\alpha$ -D-glucose in mixed aqueous solvents, it was decided to use an inert organic solvent which probably does not itself catalyze the reaction. Unlike the alcohols, which have been used in previous studies, dioxane has no apparent acid group and its basic properties are probably relatively weak. Thus it might be assumed that its catalytic effect on the mutarotation will be exceedingly small. This appears to be justified by subsequent experimental work. Since  $\alpha$ -D-glucose is fairly soluble in mixtures up to ninety weight per cent. of dioxane, the mutarotation of this sugar was studied in dioxane-water mixtures at 25°.

### Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous  $\alpha$ -D-glucose in dioxane-water mixtures of known composition. The concentration ranged from 4.0 g. of sugar/

(1) Present address: Department of Chemistry, Lawrence College, Appleton, Wisconsin.

(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 1880 (1927).

(3) Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1733 (1927).

(4) Lowry and Faulkner, *ibid.*, **127**, 2883 (1925).

(5) Rowley, *THIS JOURNAL*, **62**, 2563 (1940).

(6) Rowley and Bailey, *ibid.*, **62**, 2562 (1940).

100 ml. of solution to 0.6 g. of sugar/100 ml. of solution, decreasing as the solubility in the dioxane-water mixtures decreased. In all cases unsaturated solutions were used. The mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a light source.

Dioxane, of histological grade, was dried by refluxing with sodium and then fractionally distilled in an all glass apparatus. The product boiled at 100.8° and gave a refractive index  $n_D^{25}$  1.41836. No special precautions were taken to remove peroxides since freshly distilled samples and those which had been standing for some time gave identical results. Thus the peroxides, which are known to form readily in dioxane, apparently do not influence the mutarotation of glucose.

A summary of the values for the initial specific rotation, the equilibrium specific rotation and the velocity constants ( $k_1 + k_2$ ), expressed in common logarithms with the time expressed in minutes, is given in Table I.

TABLE I

SUMMARY OF RESULTS			
Wt. % dioxane	Init. rotn. [ $\alpha$ ] $^{25}_D$	Equil. rotn. [ $\alpha$ ] $^{25}_D$	( $k_1 + k_2$ ) $\times 10^4$
0.0	110.5	52.6	105
20.6	111.0	54.2	63.7
40.9	111.1	55.4	36.4
50.8	111.3	56.3	25.9
60.8	111.6	57.1	16.8
70.7		58.0	11.8
80.6	111.7	59.1	7.3
85.4		59.7	5.5
90.3		60.7	3.6
95.3		63.0	1.5
100		(67.0)	(0.5)

The initial specific rotation was obtained by extrapolating to zero time the plot of  $\log(\alpha_t - \alpha_\infty)$  against time. With the more dilute dioxane solutions, the extrapolation could be carried out with reasonable precision. However, above concentrations of 50% dioxane, the rate of solution of the glucose is rather slow so the reported extrapolated values are only approximations. A plot of the initial specific rotation against weight per cent. dioxane shows a slight but definite increase as the amount of dioxane increases. Due to experi-

mental difficulties it was impossible to determine whether a sharp rise occurs above 80% dioxane as was found in ethanol-water solutions.<sup>5</sup>

The equilibrium specific rotation increases as the per cent. of dioxane increases as was found in the case of ethanol-water.<sup>5</sup> The dioxane curve is slightly higher than the ethanol curve and above 80% dioxane the rise becomes more rapid, giving an extrapolated value of about +67° in pure dioxane. Since the solubility of glucose in this solvent is so slight, it is doubtful if this could be checked directly. It is interesting to note that the apparent equilibrium specific rotation value in three pure organic solvents is very close: methanol +66.5°,<sup>6</sup> ethanol +65.5°,<sup>5</sup> dioxane +67°.

Since the mutarotation of  $\alpha$ -D-glucose is known to be a first order reaction, the velocity constant ( $k_1 + k_2$ ) was calculated from the slope of the straight line obtained when  $\log(\alpha_t - \alpha_\infty)$  is plotted against the time. When the velocity constants are plotted against weight per cent. of dioxane, the last four points lie on a straight line allowing extrapolation to the value in the pure solvent.

It is seen from the table that the addition of small amounts of dioxane to water has a much greater effect in reducing the rate of mutarotation than the addition of water to dioxane has in increasing the rate. This is in agreement with the results obtained for methanol-water mixtures<sup>2</sup> and ethanol-water mixtures.<sup>5</sup> For mixed aqueous solvents containing less than 30% by weight of methanol, ethanol or dioxane, the rate constant is practically the same for a given concentration of the organic solvent. Above this concentration the catalytic effect of the organic solvent itself is possibly effective for the values for dioxane-water are lower than for either methanol-water or ethanol-water mixtures of equal weight concentration. The extrapolated velocity constant for pure dioxane is less than 0.00005, which is lower than the values found in either pure methanol, 0.00018,<sup>6</sup> or ethanol, 0.0001.<sup>5</sup>

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