

20-mesh zinc (preactivated by treating with concentrated aqueous hydrobromic acid) and 6.85 g. (8.64 mmol.) of  $\alpha$ -III in 70 ml. of absolute ethanol was refluxed for 7 hr. (Remaining chunks of white solid were crushed after 50 min. of refluxing, and all  $\alpha$ -III had dissolved in 90 min.; continued refluxing with zinc is probably responsible for the conversion of IV to bromine-free material and should therefore be avoided.) Isolated as described earlier in detail,<sup>3</sup> the product was distilled (short-path apparatus, at 0.01 $\mu$ ) to give 2.55 g. of oil, b.p. (bath temperature) 80–110°; from analysis of another product prepared in the same way and thus indicated to be contaminated with about 6.5% of bromine-free material, the yield of crude  $\alpha$ -IV is estimated to be about 88%. Assuming the bromine-free contaminant to be heptadecatriene (produced by zinc reduction of IV) and hence more volatile than the desired product, the crude  $\alpha$ -IV was freed of a small fraction, b.p. up to 116° (bath temperature) at 0.03 $\mu$ , and the residue, predominantly all-*cis*-8,11,14-( $\alpha$ )-IV,  $n_D^{25}$  1.4885,  $d_4^{25}$  1.0134, analyzed and used in the preparation of  $\alpha$ -linolenic-1-C<sup>14</sup> acid.

*Anal.* Calcd. for C<sub>17</sub>H<sub>28</sub>Br: C, 65.17; H, 9.33; Br, 25.50. Found: C, 65.87; H, 9.34; Br, 24.80.

Infrared examination of a similar preparation of  $\alpha$ -IV indicated the presence of 12% *trans* olefin (*i.e.*, on the average, one of the three double bonds in 12% of the material has the *trans* configuration), while ultraviolet absorption revealed 1.4% conjugated diene and 0.6% conjugated triene. The extent of double bond isomerization indicated by these analyses is typical of polyenes of this kind submitted to bromination-zinc-debromination.<sup>11</sup>

Similarly, refluxing 6.59 g. (8.31 mmol.) of  $\gamma$ -III with zinc in ethanol for 8.67 hr. (probably overly long—all  $\gamma$ -III had dissolved in 3.17 hr.) gave 2.1 g. of crude  $\gamma$ -IV; b.p. 120–135° (bath temperature) at 0.1 $\mu$ . Analysis of the oil indicated the presence of 11.3% bromine-free material; yield of  $\gamma$ -IV is thus estimated to be 72%. Ultraviolet examination of this predominantly all-*cis*-5,8,11-( $\gamma$ )-IV revealed the presence of 0.75% conjugated diene and 0.025% conjugated triene. Inasmuch as the bromine-free contaminant was expected to be inert in subsequent operations and to be easily and cleanly separable by chromatography from the ultimate fatty acid ester, no further effort was expended on purification of these samples of IV.

Zinc-debromination of a 350-mg. sample of chromatographically purified "isomeric" (oily)  $\gamma$ -III (see above) gave a product (twice distilled, but without fractionation) containing 96%  $\gamma$ -IV (by bromine analysis), possibly reflecting the benefit of a shorter reaction (5.5 hr.). The origin of this non-crystalline  $\gamma$ -III is perhaps most evidently explained on the basis of racemization (during the Borodin reaction) to give *erythro* vicinal dibromide groups which, with zinc, would yield *trans* double-bonds. It is therefore surprising that the sample of  $\gamma$ -IV prepared from this oily  $\gamma$ -III contained but 8–10% *trans* material. Conjugated polyenes were, however, present in comparatively large amounts (0.76% diene, 0.48% triene, and 0.21% tetraene).

In confirmation of the 5,8,11-structure of  $\gamma$ -IV, the material obtained by debromination of the oily  $\gamma$ -III was ozonized and the monocarboxylic acid fraction of the products shown by paper chromatography to consist solely of *n*-hexanoic acid. (The presence of small amounts of *n*-valeric acid would not have been detected under the conditions employed.)

*Linolenic-1-C<sup>14</sup> acids and methyl linolenates-1-C<sup>14</sup>.* Using techniques described in detail before,<sup>3,4</sup> 1.0783 g. (3.34 mmol.) of  $\alpha$ -IV (97.2% by bromine analysis) was converted in 63% yield to the corresponding Grignard reagent, which was treated with 2.90 mmol. of carbon dioxide containing 1.993 mc. of C<sup>14</sup>. By titration of an aliquot of the crude reaction product, formation of a 64% yield (based on Grig-

nard) of acidic material was indicated. The ether-soluble fraction of the product was treated with excess diazomethane and the resulting material chromatographed on silicic acid-Celite (3:1 by weight), using a 3.4 (dia.)  $\times$  14.0 cm. column; successive column volumes of petroleum ether eluted 340 mg., 5 mg., and a trace of very weakly adsorbed material (heptadecatriene present in the  $\alpha$ -IV and C<sub>24</sub> hydrocarbon formed by Wurtz coupling during the formation of the Grignard reagent); 3% ether in petroleum ether eluted 10 mg., 320 mg., 80 mg., 10 mg., and a trace more of the desired ester; negligible amounts of material were eluted by 10% ether in petroleum ether; and acetone (two column volumes) eluted 70 mg. of strongly adsorbed material. The chromatographically pure ester, *methyl  $\alpha$ -linolenate-1-C<sup>14</sup>*, was obtained in 91% yield (based on acid determined by titration of the crude Grignard product) and found by spectroscopic examination to contain 8–12% *trans* material, 3.3% conjugated diene, 0.25% conjugated triene, and 0.5% conjugated tetraene; the ester is thus about 84% all-*cis*-9,12,15-linolenate. A 10.2-mg. sample of the substance was diluted with 849 mg. of corn oil, plated on lens paper, and counted (thin-window G.M. tube) to establish an activity of 2.01 mc./g. of the undiluted ester.

In the same way, 1.0519 g. (2.98 mmol.) of  $\gamma$ -IV (88.7% by bromine analysis) gave a 66% yield of Grignard, 1.83 mmol. of which was treated with 2.56 mmol. of active carbon dioxide (1.945 mc.) to give crude  $\gamma$ -linolenic-1-C<sup>14</sup> acid (about 82% from Grignard by titration of an aliquot of the mixed products), converted with diazomethane in ether to the corresponding *methyl ester* (0.40 g. or 90% based on the acid, assay 3.55 mc./g.).

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## Synthesis and Reactions of *p*-Vinylphenylmagnesium Chloride

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*p*-Chlorostyrene in tetrahydrofuran reacts smoothly with magnesium to form *p*-vinylphenylmagnesium chloride. The absence of polymer in the reaction may be attributed to controlled addition, the relative rapidity of the reaction with magnesium or to the stability of the coordination complex formed with the solvent. Under these conditions, monomer concentration remains low throughout the course of the reaction. The organometallic compound has been found to undergo typical Grignard reactions and thus provides a practical method for introducing the *p*-vinylphenyl group into a great variety of nuclei.

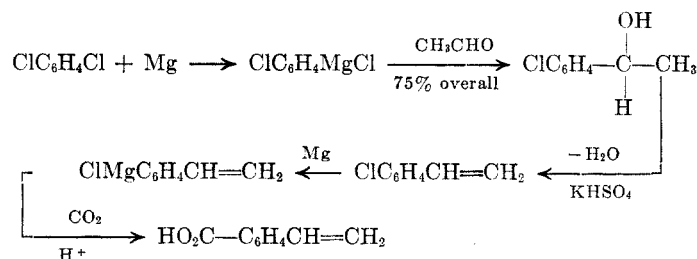
Carbonylation of *p*-vinylphenylmagnesium chloride gave *p*-vinylbenzoic acid in 80% yield. *p*-Vinylbenzoic acid has been prepared from *p*-cyanostyrene<sup>1</sup> and from *p*-bromostyrene.<sup>2</sup> In the latter case, reaction of *p*-bromostyrene with magnesium

(1) C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

(2) G. B. Bachman, C. L. Carlson, and M. Robinson, *J. Am. Chem. Soc.*, **73**, 1964 (1951).

(11) Cf. N. L. Matthews, W. R. Brode, and J. B. Brown, *J. Am. Chem. Soc.*, **63**, 1064 (1941); and J. S. Frankel and J. B. Brown, *J. Am. Chem. Soc.*, **65**, 415 (1943).

in diethyl ether gave *p*-vinylbenzoic acid in 15% yield on carbonation, accompanied by large quantities of polymer. The following reactions were involved in our synthesis:



*p*-Vinylphenyltriphenyltin was obtained in 78% yield by the reaction of *p*-vinylphenylmagnesium chloride with triphenyltin chloride in tetrahydrofuran.

In the reaction of *p*-vinylphenylmagnesium chloride with acetaldehyde, a 43% crude yield of *p*-vinylphenylmethylcarbinol was obtained, accompanied by considerable high-boiling, polymeric residue. Although an inhibitor was present, thermal polymerization apparently occurred during the distillation and molecular flash distillation is indicated.

#### EXPERIMENTAL

*p*-Chlorophenylmagnesium chloride.<sup>3</sup> Two gram atoms (48.6 g.) of magnesium was charged to a 3-necked flask equipped with thermometer, stirrer, addition funnel, and reflux condenser. The system was maintained under nitrogen. The reactor was heated to 35°C. Two moles (294.0 g.) of *p*-dichlorobenzene was dissolved in 500 ml. of tetrahydrofuran<sup>4</sup> and 20 ml. of this solution was added to the reactor. Ethyl bromide (2 ml.) initiated the reaction. The solution was added dropwise over a period of 2 hr., at a rate to maintain gentle reflux. The reaction mixture was then stirred for 2 hr. at reflux temperature. A yield of 90% by titration<sup>5</sup> was obtained.

*p*-Chlorophenylmethylcarbinol. To 2.0 moles of *p*-chlorophenylmagnesium chloride in 500 ml. of tetrahydrofuran at 15° was added 88.1 g. (2.0 moles) of acetaldehyde in 200 ml. of tetrahydrofuran over a period of 1 hr. The reaction mixture was stirred for 1 hr., followed by hydrolysis with dilute sulfuric acid. The organic layer was separated and the aqueous layer was extracted twice with 100-ml. portions of ethyl ether. After the solvent was stripped, the product was distilled *in vacuo*, yielding 235 g. *p*-chlorophenylmethylcarbinol b.p. 102–110°/3 mm., or 75%.

*p*-Chlorostyrene. The procedure described in *Org. Syn.*, **28**, 31 (1948) was employed for the dehydration of *p*-chlorophenylmethylcarbinol.

*p*-Vinylbenzoic acid. After 9.7 g. (0.4 g. atom) of magnesium was charged to a flask under nitrogen, 3 ml. of ethyl bromide in 5 ml. of tetrahydrofuran was added in order

to activate the metal. The temperature rose to 60°. A solution of 27.6 g. (0.2 mole) of *p*-chlorostyrene in 50 ml. of tetrahydrofuran was introduced dropwise over a period of 35 min. at a rate to maintain gentle reflux. The reaction mixture was refluxed for 15 min. and stirred for 45 min. further

without heating. The flask contents were cooled and poured on to crushed Dry Ice.

The carbonated mixture was acidified with dilute sulfuric acid; the layers were separated, and the aqueous layer was extracted with two 100-ml. portions of ethyl ether. The organic layer was added to excess base solution and the solvent boiled off. No appreciable base insoluble polymer was obtained. The basic solution was cooled, filtered, acidified, and filtered. The product was washed with cold water and dried to yield a crude acid melting at 138° (not sharply). Recrystallized from 20% ethanol it gave 23.8 g. of *p*-vinylbenzoic acid (80.4%). A sealed tube melting point showed rapid shrinkage and partial liquefaction at 142° with no clear melt. Its neutral equivalent was 152 (theory 148).

The product decolorized bromine in carbon tetrachloride. Oxidation with permanganate gave terephthalic acid which sublimed at ca. 305°. Microhydrogenation gave a hydrogen number of 153 (theory 148).

*p*-Vinylphenyltriphenyltin. To 0.2 mole of *p*-vinylphenylmagnesium chloride at 50° was added 62.0 g. (0.16 mole) of triphenyltin chloride in 150 ml. of tetrahydrofuran over a period of 45 min. The mixture was stirred for 90 min. during its cooling to room temperature. Then 0.5 g. of *p*-tertbutylcatechol was added to the reaction mixture followed by 200 ml. of 5% hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 100-ml. portions of ethyl ether. The solvents were stripped off *in vacuo*, cold petroleum ether was added to the flask, and the crystalline product was filtered. A crude yield of 57.0 g. (or 78.5%) m.p. 102°, was obtained. The product was recrystallized twice from petroleum ether to m.p. 105.5–108.0°.

*Anal.* Calcd. for C<sub>28</sub>H<sub>22</sub>Sn: Sn, 28.19. Found: Sn, 26.18; % chlorine, negligible.

*p*-Vinylphenylmethylcarbinol. Acetaldehyde (8.8 g., 0.2 mole) in 100 ml. of tetrahydrofuran was added to 0.2 mole of *p*-vinylphenylmagnesium chloride over a period of 30 min. at 10°. The reaction mixture was stirred for 1 hr. further at 10°. *p*-Tertbutylcatechol (0.5 g.) was added to the flask and hydrolysis was effected by cautious addition of 150 ml. of 20% hydrochloric acid, maintaining temperature below 20°. The organic layer was separated and the aqueous layer extracted with a 100-ml. portion of ethyl ether. Solvents were stripped from the combined extracts and the crude product was distilled *in vacuo* to yield a fraction, b.p. 86–88°/1 mm. The yield was 12.8 g. or 43%; residue, 6.1 g., a dark red polymeric material. The product decolorized bromine in carbon tetrachloride rapidly. % Hydroxyl (acetylation), Calcd.: 11.5; Found: 9.8. The product was not purified further.

(3) (a) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); (b) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (c) H. Normant, *Bull. soc. chim. France*, **1957**, 728.

(4) Purity of tetrahydrofuran is important; see ref. (3) (a).

(5) H. Gilman, E. A. Zollner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).