[Contribution from the Converse Memorial Laboratory of Harvard University]

# ORGANOMETALLIC COMPOUNDS OF STYRENE

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This investigation has developed from numerous attempts to obtain the stereoisomers of 1-phenylbutadiene-1,3. The methods employed in this study, as well as those of Muskat and co-workers[1] have failed to differentiate either the *cis* and *trans* phenylbutadienes or the isomeric carbinols from which they are formed. It is probable that Muskat and Herrman had neither isomer of styrylmethylcarbinol in the pure state, because this compound, prepared from methylmagnesium chloride and fractionated cinnamaldehyde by varying the method of Klages,[2] is not a liquid, as they thought, but a solid melting at 31°.[3] Upon dehydration of this purer carbinol, the ordinary phenylbutadiene was obtained and characterized by mercuration;[4] it is possible that the differences in physical constants reported by Muskat and Herrman were caused by varying amounts of the ever-present dimeric analogs.

Since the reported methods of obtaining these isomers proved abortive, the approach *via cis-* and *trans*-styrylmagnesium bromide and acetaldehyde was investigated. This likewise failed; the styrylmethylcarbinol so obtained was a mixture of the geometric isomers. The failure to obtain the pure compound did, however, suggest a study of the cause of such isomerization and of the reaction step wherein it occurred.

Because of the possible catalytic effect, such substances as iodine, iodine-activated magnesium, or Grignard reagents prepared by such catalysts were avoided in starting the reaction between β-bromostyrene and magnesium although this halide is notorious[5] for its sluggishness toward Grignard formation. Nevertheless, by scrupulous attention to purity of reagents[6] it has been found possible to start the reaction spontaneously. A reproducible induction period before reaction set in was characteristic of either the solvent or the halide, but not of the magnesium or the reaction vessel. This was proved by carrying out a second reaction on the excess

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[1] Muskat and Herrman, *J. Am. Chem. Soc.*, **53**, 252 (1931).

[2] Klages, *Ber.*, **39**, 2591 (1906).

[3] Kenyon, Partridge, and Phillips, *J. Chem. Soc.*, **1936**, 86.

[4] Wright, *J. Am. Chem. Soc.*, **57**, 1993 (1935).

[5] Gilman and Kirby, *Rec. trav. chim.*, **54**, 577 (1935).

[6] Gilman, Zoellner, Selby, and Boatner, *ibid.*, **54**, 589 (1935).

of magnesium remaining after a previous preparation; the identical induction period was observed. Incidence of reaction was characterized by the red coloration of the solution in the case of the *trans* isomer, or by the Gilman test with the pale yellow solution obtained from *cis*-bromostyrene.

On the basis of comparative yields, as well as amount of bromostyrene recovered after reaction, the *trans* halide was converted to the magnesium derivative more rapidly than the *cis* modification (Table I). Since a mixture of cinnamic acids resulted upon carbonation of the Grignard reagents from both forms, the apparent difference in reaction rate suggests that such isomerization does not occur in the halide itself. This evidence, in itself insecure, is supported by the fact that the equilibrium mixture (m.p. +2°), which Dufraisse[7] found to consist largely of the *trans* β-bromostyrene, yielded more *cis*- than *trans*- cinnamic acid. In other words the isomerization is away from, rather than toward, the composition of the mixture resulting from either thermal or photochemical equilibration of the geometric isomers. For these reasons it is probable that isomerization does not occur until the Grignard reagent is formed. Another possibility was eliminated by ascertaining that the chloromagnesium cinnamates did not isomerize in aqueous solution.

The isomerization must, then, take place: (*a*) when the Grignard reagent is formed; or (*b*) when it undergoes reaction with itself; or (*c*) when it reacts with another substance. If the distinctive red color of the Grignard solution prepared from *trans*-β-bromostyrene is truly characteristic of *trans*-styrylmagnesium bromide, then the isomerizing step must be (*c*), since the Grignard reagent prepared from *cis*-bromostyrene shows no red color.

$$\begin{tikzcd} \mathrm{PhCH{:}CHBr} \arrow[r, "\mathrm{Mg}", "(a)"'] & \mathrm{PhCH{:}CHMgBr} \arrow[r, "\mathrm{CO_2}", "(c)"'] \arrow[d, shift right] & \mathrm{PhCH{:}CHCOOMgBr} \\ & \mathrm{(PhCH{:}CH)_2Mg + MgBr_2} \arrow[u, shift right, "(b)"'] & \end{tikzcd}$$

If this be true, then it is probable that the extent of isomerization will differ with various reactants. Admittedly poor evidence for this reasoning is offered in the fact that only one styrylmercuric bromide can be detected when styrylmagnesium bromide from the equilibrium mixture of β-bromostyrene is treated with mercuric bromide. This compound, which was prepared in order to ascertain the stability of the hitherto unknown type of vinylmercurial, was found to be much less susceptible to decomposition than certain presumably aromatic types,[8] and it suffered no change over a period of eighteen months.

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[7] Dufraisse, *Compt. rend.*, **172**, 67 (1921).

[8] Gilman and co-workers, *J. Am. Chem. Soc.*, **55**, 3302, 4197 (1933).

Although previous reports[9] have indicated that styryllithium could not be prepared, it was found in the present investigation that either *cis*- or *trans*-bromostyrene reacted immediately with lithium to give a reagent in 50 to 70 per cent. yield which, when carbonated, yielded a 4:1 mixture of *trans*-cinnamic and phenylpropiolic acids. No *cis*-cinnamic acid could be detected from either isomer. The formation of the acetylenic acid is remindful of the conversion of β-bromostyrene to phenylpropiolic acid with sodium and carbon dioxide,[10] but the mechanism of dehydrogenation is not apparent, since no gas is evolved during the reaction. Furthermore the volume increase on adding the solution of styryllithium to cracked ice is insufficient to account for the phenylacetylene formed. A possible oxidation-reduction involving formation of phenylpropionic acid is likewise eliminated by the absence of this saturated acid among the carbonation products.

I wish to thank Professor E. P. Kohler for his advice and perspective, which were so helpful in this research.

## EXPERIMENTAL

Cis- *and* trans-*β-bromostyrene.*—When the powdered equilibrium mixture* was allowed to melt partially on a suction filter at +6° the *trans* isomer was retained. Repetition of this process gave a *trans*-β-bromostyrene (m.p. 6.5°, b.p. 88°/4 mm., $n_D^{20}$ 1.6093), which was considered pure because it showed only a 0.2° drift on a twenty-five minute cooling curve. The melt from the equilibrium mixture was repeatedly fractionated at 4 mm. in a smoked Claisen flask until about one-third of this melt boiled at 63.7–64.5° and melted at −8° to −7.5°, $n_D^{22}$ 1.5990. These are capillary melting points determined in the apparatus of Stolzenberg[11] which was constructed with a vacuum jacket around the bath, thus obviating difficulties due to fogging. This *cis* compound compares closely with that prepared by Dufraisse[12] except in odor, but probably neither is pure. The *cis* halide is odorless, in contrast to the *trans* isomer with its characteristic hyacinth odor. About ten per cent. of the equilibrium mixture was obtained as *cis*-bromostyrene.

*Optimum conditions for reaction.*—The flask illustrated in Fig. 1 has been chosen from a number of designs as satisfactory for preparation of organomagnesium compounds. It is conveniently made from an Erlenmeyer flask; a siphon tube filled with glass wool serves to filter the prepared reagent. The following characteristics recommend this flask. The reaction is started in the constricted base where the volume is small, and hence maximum contact between solution and magnesium is obtained. The narrow base likewise facilitates removal of the prepared reagent by means of the siphon tube. The conical shape obviates "bumping" and, with a properly designed stirrer, no magnesium is thrown out of the zone of reaction. The latter is a troublesome disadvantage of the spherical flask. In the 10-, 25-

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[9] Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

[10] Glaser, *Ann.*, **154**, 140 (1870); Nef, *ibid.*, **308**, 268 (1899).

* Kindly furnished by Mr. A. L. van Amerigen of van Ameringen Haebler, Inc.

[11] Stolzenberg, *Ber.*, **42**, 4323 (1909).

[12] Dufraisse, *Compt. rend.*, **171**, 960 (1920).

and 50-cc. sizes a condenser finger is connected, as illustrated, to the jacket *A* which also is used for introduction of the siphon tube, the while nitrogen is passed into *C*. An auxiliary gas inlet is placed at *B*. For reaction, the magnesium is placed in the flask, which is then swept out with nitrogen, and finally heated gently to remove residual moisture from the metal. Premature heating while oxygen yet remains in the flask may deposit an oxide coating on the magnesium; this should be avoided, since certain halides will not react spontaneously unless unusually pure magnesium is employed. All of the commercially available grades are ineffective for spontaneous reaction[6] unless they be activated. However, the magnesium generously supplied by Professor Gilman and Dr. Zoellner reacted without catalyst after a reproducible induction period of fifteen to twenty minutes when the following conditions were maintained.

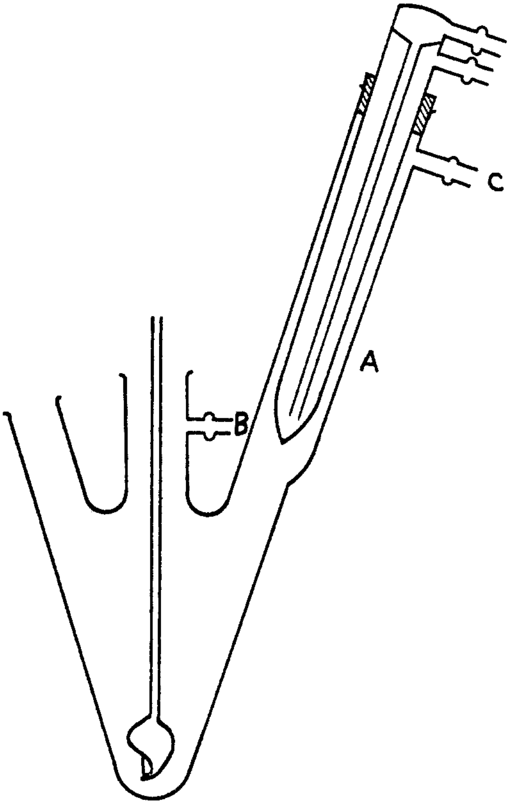

Fig. 1

*Styrylmagnesium bromide.*—The reaction flask was coated with soot to exclude light since the isomeric $\beta$-bromostyrenes are photosensitive. To 2.4 g. (0.1 mole) of 30–80 mesh magnesium was added *ca.* 0.5 cc. of a solution of 5.49 g. (0.03 mole) of freshly distilled $\beta$-bromostyrene in 30 cc. of ether distilled from methylmagnesium iodide. When the reaction started, the remainder of the halide was added over a ninety-minute period. After one-half hour of subsequent stirring, the reaction mixture was siphoned into a flask containing powdered dry ice which had been freed of water ice by violently shaking while evacuating the flask at the water pump. The solution was hydrolyzed with iced, dilute acid and the mixture of *cis*- and *trans*-cinnamic acids removed with dilute alkali and separated by the difference in solubility of their calcium salts.[13] The non-acidic products of the reaction were evidently a complicated mixture; the only constituents thus far identified are *trans*,*trans*-1,4-diphenylbutadiene-1,3 and unchanged β-bromostyrene (in the case of the *cis* halide which reacts more slowly than the *trans* compound).

*Attempted isomerization of cinnamic acids.*—When an ether solution of either *cis*- or *trans*-cinnamic acid was treated dropwise with exactly one equivalent of methylmagnesium bromide and the magnesium salts allowed to stand overnight, the acids were recovered, upon acidification, without isomerization. Likewise, the calcium salt of *trans*-cinnamic acid was converted, after two days, to *trans*-cinnamic acid containing no trace of *cis*-cinnamic acid.

TABLE I

PRODUCTS FROM CARBONATION OF STYRYLMAGNESIUM BROMIDE

| RUN NO. | HALIDE | CRUDE ACIDS | | PURIFIED ACIDS | | | | *trans*, *trans*-DIPHENYLBUTADIENE, YIELD | REMARKS |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *trans*-Cinnamic | | *cis*-Cinnamic | | | |
| | | Yield | M.p. | Yield | M.p. | Yield | M.p. | | |
| | | *per cent.* | °*C.* | *per cent.* | °*C.* | *per cent.* | °*C.* | *per cent.* | |
| 1 | *cis*-Bromostyrene, m.p. −7.5° | 35 | 52 | 9 | 130 | 19 | 48 | 3.0 | Reaction mixture, pale yellow |
| 2 | Equilibrium mixture bromostyrene, m.p. +2° | 48 | 85 | 12 | 130 | 19 | 48 | 4.4 | By acid titration, RMgX, 56%† |
| 3 | *trans*-Bromostyrene, m.p. +6.5° | 62 | 75–80 | 30 | 132 | 20.5 | 53* | 11.0 | Reaction mixture, deep red |

* The yields of *cis*-cinnamic acid are all of equal purity, the 53° sample being a mixture of the polymorphs.

† When the quantities used in Run 2, Table I, were increased tenfold, using a threefold period of addition, the yield was not decreased.

*Styrylmethylcarbinol.*—To the organomagnesium compound prepared from 0.025 moles of β-bromostyrene (m.p. 6.5°) was added 0.025 moles of gaseous acetaldehyde. Hydrolysis with ammonium chloride solution yielded 1.13 g. (30%) of styrylmethyl carbinol; b.p. 94–106°/4 mm. That this was a mixture of stereoisomers, was shown by the fact that the crude phenylurethane melted at 79° whereas the crude phenylurethane from the solid styrylmethylcarbinol melts at 87°. Furthermore, the reaction product would not crystallize at 0° even after seeding with the solid carbinol (m.p. 31°, b.p. 109°/3.5 mm.), $n^{31}$ 1.5700), prepared in 77% yield by adding one mole of cinnamaldehyde (b.p. 137°/20 mm.) to two moles of methylmagnesium chloride. The same styrylmethylcarbinol, identified by mixture melting point, was obtained

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[13] LIEBERMANN, *Ber.*, **23**, 141 (1890).

by repeating Burton's saponification of the acetate prepared from his α-phenylcrotyl alcohol.[14] The latter compound can be prepared in 87% yield by filtering off the magnesium alcoholate prior to hydrolysis.

*Styrylmercuric bromide.*—To the stirred solution prepared from 0.33 moles of β-bromostyrene (equilibrium mixture, m.p. +2°) and one mole of magnesium was added slowly 100 g. (0.28 mole) of mercuric bromide. After eight hours' stirring the reaction was filtered to remove 61 g. (m.p. 198°) of mercurial which was purified by Soxhlet extraction with ethanol to yield 39 g. (36%) of styrylmercuric bromide; m.p. 202–203°. The ethereal filtrate was evaporated and the residue washed with benzene to yield 16.5 g. of impure product melting at 190°. Upon solution in hot acetone and precipitation of this solution into water the melting point was raised to 201°. The mercurial is insoluble in cold ethanol and hot or cold benzene, slightly soluble in chloroform but readily soluble in acetone.

*Anal.* Calc'd for $C_8H_7BrHg$: C, 25.10. Found: 25.31.

The mercurial was characterized by treating a suspension of 3.89 g. (0.01 mole) in 20 cc. of chloroform with a solution of 1.6 g. (0.01 mole) bromine in 5 cc. of chloroform. The 74% yield of β-bromostyrene boiling at 79–81°/4 mm. melted at 2.5°; a mixture melting point with the equilibrium mixture was not lowered.

*β-Iodostyrene.*—When 2.56 g. (0.01 mole) of iodine was added to the shaken suspension of 3.89 g. (0.01 mole) of styrylmercuric bromide in 25 cc. of chloroform the solution became colorless in ten minutes with precipitation of mercuric salt. The latter was filtered off, and the filtrate was distilled under reduced pressure to yield 1.81 g. (79% theoretical) of β-iodostyrene; b.p. 101°/4 mm., $n^{20}$ 1.6621, $n^{25}$ 1.6583.

*Anal.* (by Mr. F. B. Pickett). Calc'd for $C_8H_7I$: I, 55.20. Found: 55.24.

*Styryllithium.*—Following the suggestion of Dr. E. B. Herschberg, 0.7 g. (0.1 mole) of 18-gauge lithium wire (prepared in a sodium press and the required 100 inches folded into a ten-strand bundle) was cut into 1–2 mm. lengths over the mouth of the flask jacket *A* from which nitrogen was streaming. To this metal was added a solution of 5.49 g. (0.03 mole) of β-bromostyrene (m.p. 6.5°) in 30 cc. of Grignard-dried ether. The reaction started immediately and continued over an addition period of seventy-five minutes. By means of a gas burette filled with sulfuric acid and attached to the outlet of the condenser, it was found that no gas was evolved during the reaction. The blood-red solution was added dropwise to a 200-cc. flask containing 100 g. of cracked ice and connected to the gas burette. A volume increase of 25 cc. was detected during the hydrolysis. The vapor pressure of ether at 0° accounts for this augmentation. The hydrolysate was separated and the aqueous layer titrated, being equivalent to 0.021 moles of hydrochloric acid, or 68% of the theoretical yield of R–Li. The ether layer was distilled at 50–60° under 2 mm. pressure into a dry-ice trap, to yield 1.32 g. of product. Upon treatment with ammoniacal cuprous chloride solution this precipitated 0.40 g. of cuprous phenylacetylide, a yield of 8% of the bromostyrene used in the reaction. The styrene remaining after removing the phenylacetylene was identified as the dibromide; m.p. 71–72°. It represented 34% of the theoretical yield.

When the styryllithium from an identical preparation was carbonated with dry ice, a mixture of crude acids melting at 104° was obtained; 1.1–1.3 g. or 25–30% of theoretical. Separation by means of the calcium salts[13] revealed that this was a mixture of *trans*-cinnamic and phenylpropiolic acids in the ratio of 4:1. The purity (m.p. 132–134°) of the phenylpropiolic acid regenerated from its calcium salt

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[14] Burton, *J. Chem. Soc.*, **1929**, 455.

confirms the absence of more than a trace of *cis*-cinnamic acid. Upon brominating the mixture of acids in aqueous suspension, excess of bromine being removed with formic acid, and centrifuging the cold suspension to remove the brominated acids no phenylpropionic acid was found in the remaining aqueous solution.

The non-acidic products from the carbonation reaction were exceedingly complex. The residue from evaporation of the ether solution, weighing 0.95 g., was crystallized from ethanol. It weighed 0.28 g., melted at 144°, and was identified by mixture melting point as *trans*,*trans*-1,4-diphenylbutadiene-1,3.

In a larger preparation (0.25 mole $\beta$-bromostyrene added over a 400-minute period) the yield by acid titration was 61%; the yield of crude acid mixture was 33%. The non-acidic reaction products were fractionated at 2 mm. pressure, yielding a small fraction boiling up to 163°, a second boiling at 167–200° and a resinous third fraction, b.p. 200–230°.

## SUMMARY

The reactions for preparation of *cis*- and *trans*-styrylmagnesium bromide, styrylmercuric bromide and styryllithium have been studied.