

clear solution resulted from which the brucine salt precipitated when the side of the beaker was rubbed with a stirring rod. The mixture was cooled and filtered, yielding 12.8 g. of salt which gave $[\alpha]_D -37^\circ$. On concentrating the filtrate, 10 g. of salt of $[\alpha]_D +12^\circ$ was obtained. The first fraction was recrystallized from 200 cc. of absolute alcohol to constant rotation. The more soluble fraction was recrystallized from ethyl acetate.

l-Salt.—0.1137 g. made up to 15 cc. with chloroform at 20° gave $\alpha_D -0.68^\circ$; $l = 2$; $[\alpha]_D^{20} -44.9^\circ$; m. p. 231–232° (dec.).

Anal. Calcd. for $C_{37}H_{39}O_3N_3$ (monobrucine salt): C, 67.96; H, 6.0. Found: C, 67.74; H, 6.1.

d-Salt.—0.1551 g. made up to 15 cc. with chloroform at 20° gave $\alpha_D +0.28^\circ$; $l = 2$; $[\alpha]_D^{20} +13.5^\circ$; m. p. 175–180° (dec.).

Anal. Calcd. for $C_{37}H_{39}O_3N_3$: C, 67.96; H, 6.0. Found: C, 67.71; H, 6.1.

d- and *l*-N-2-Carboxyphenyl-2,5-dimethyl-3-carboxypyrroles.—The salts were decomposed by shaking in a separatory funnel with dilute hydrochloric acid and ether. The acid went into the ether layer and was obtained by evaporating to dryness. The acids were crystallized from ethyl acetate to constant rotation.

l-Acid.—0.1349 g. made up to 15 cc. with absolute alcohol at 20° gave $\alpha_D -0.49^\circ$; $l = 2$; $[\alpha]_D^{20} -27.2^\circ$; m. p. 203–204°.

d-Acid.—0.1753 g. made up to 15 cc. with absolute alcohol at 20° gave $\alpha_D +0.63^\circ$; $l = 2$; $[\alpha]_D^{20} +27.0^\circ$; m. p. 202–204°.

Racemization Experiments.—About 0.3 g. of *l*-compound in 50 cc. of absolute alcohol was boiled for eight hours. No change in initial rotation took place. In boiling glacial acetic acid, the rotation dropped to nearly zero in one hour but there was obviously decomposition occurring which probably accounted for this. Only a gram could be recovered from the heated solution.

A solution of 0.2107 g. of *l*-acid in 25 cc. of 0.1 *N* sodium hydroxide gave an initial rotation of $\alpha_D -0.39^\circ$ ($[\alpha]_D^{20} -23.1$). After eighteen hours' standing at room temperature, no change occurred. Upon boiling for twenty-four hours, the rotations were as follows: 1 hr., $\alpha_D -0.39^\circ$; 4 hrs., $\alpha_D -0.31^\circ$; 8 hrs., $\alpha_D -0.26^\circ$; 24 hrs., $\alpha_D -0.03^\circ$. Upon acidification racemic acid was obtained, m. p. 224–225°.

Summary

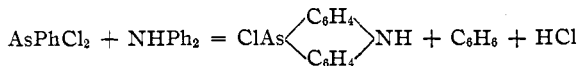
The preparation and resolution of N-2-carboxyphenyl-2,5-dimethyl-3-carboxypyrrole has been described.

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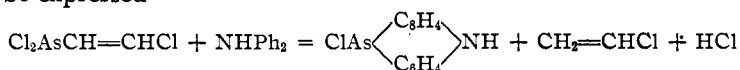
NOTES

The Reaction between Dichloro-arsines and Secondary Aromatic Amines.—Lewis and Stiegler [THIS JOURNAL, 52, 4164 (1930)] appear to have overlooked work already published on this subject.

Burton and Gibson [J. Chem. Soc., 464 (1926)] having shown that the reaction between phenyldichloro-arsine and diphenylamine did not yield 10-phenyl-5,10-dihydrophenarsazine but 10-chloro-5,10-dihydrophenarsazine according to the equation



were led to compare the analogous reaction using β -chlorovinyl-dichloro-arsine as described by Lewis and Stiegler [THIS JOURNAL, 47, 2546 (1925)]. They found (*loc. cit.*, p. 466) that not only is 10-chloro-5,10-dihydrophenarsazine and not "6-chlorovinylphenarsazine" formed by the action of β -chlorovinyl-dichloro-arsine on diphenylamine, but, by proving the production of vinyl chloride in the reaction, showed that the course of the latter may be expressed



Burton and Gibson also proved that the reaction between phenyldichloro-arsine and other substituted diphenylamines and of β -chlorovinyl-dichloro-arsine and phenyl- α -naphthylamine proceeds analogously. These results have since then been fully verified by Seide and Gorski [*Ber.*, 62, 2186 (1929)]. Scherlin and Epstein [*Ber.*, 61, 1823 (1928)] have also shown that the reaction between β -chloro-ethyl-dichloro-arsine and diphenylamine yields 10-chloro-5,10-dihydrophenarsazine, the reaction being quite similar.

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Phenylmagnesium Fluoride.—The relative reactivities of RX compounds with magnesium in ether is in the order RI > RBr > RCl > RF. Actually, only one RMgF compound (*n*-amylmagnesium fluoride) has been prepared, and this synthesis was effected by unusually extensive refluxing with a large quantity of iodine.

In connection with studies concerned with improved catalysts for the formation of organomagnesium halides, it was observed that none of the highly active catalysts induced a reaction between fluorobenzene and magnesium in ether. There has been described recently a satisfactory method for the preparation of phenylmagnesium chloride in the absence of a solvent, and this method is distinctly superior to the very slow formation of this compound when ether is used with varying quantities of iodine and with the magnesium-copper alloy.¹ In this study involving no solvent and a sealed tube it was shown that when fluorobenzene was heated with magnesium at 300° for about 200 hours, a small quantity of diphenyl formed. The formation of diphenyl is almost certain evidence for the intermediate formation of phenylmagnesium fluoride,² and the statement was made that this Grignard reagent would probably be prepared by heating at a lower (as yet undetermined) temperature for a longer time.

¹ Gilman and St. John, *Rec. trav. chim.*, 49, 717-723 (1930).

² Gilman and Brown, THIS JOURNAL, 52, 5045 (1930).