described it as crystallizing from water in the form of platelets, melting point 112–113°. Later, G. Ivánovics and V. Bruckner[2] described this compound and also *p*-nitrobenzoyl-*d*(−)-glutamic acid as having melting points of 170°; since no analyses were given, the purity of these products may be open to question. In each instance, the compounds were prepared by the reaction of *p*-nitrobenzoyl chloride with l(+)- or *d*(−)-glutamic acid, a reaction known to produce racemization. Corresponding amino derivatives were obtained by reduction. No optical properties of these compounds have been reported.

*p*-Nitrobenzoyl-*d*(−)-glutamic acid has been prepared in this Laboratory by resolution of *p*-nitrobenzoyl-*dl*-glutamic acid through repeated recrystallization of the strychnine salt from water. The slightly soluble salt of the *d*(−)-enantiomorph was obtained in good yield. After removal of strychnine, the free acid derivative crystallized from aqueous solution in fine white needles which softened at 77° and melted at 115–116° (*Anal.* Calcd. for $C_{12}H_{12}N_2O_7$: N, 9.46. Found: N, 9.39). This is in good agreement with the melting point of the l(+)-derivative reported by Van der Scheer and Landsteiner.[1] The specific rotation of the aqueous solution containing 2 moles of alkali was −16.02°.

*p*-Aminobenzoyl-*d*(−)-glutamic acid has been prepared in this Laboratory by the reduction of the nitro compound using the method of Van der Scheer and Landsteiner[1] for the preparation of *p*-aminobenzoyl-l(+)-glutamic acid. The compound crystallized from water in clusters of microscopic needles (*Anal.* Calcd. for $C_{12}H_{14}N_2O_5$: N, 10.53. Found: N, 10.50) melting at 166–167°, somewhat lower than that (175°) reported by Ivánovics and Bruckner.[2] Its specific rotation in aqueous solution containing 2 moles of alkali was −27.4°; in 9% hydrochloric acid +15.5°. It is possible that some racemization occurred under the conditions of the reduction.

(2) Ivánovics and Bruckner, *Z. Immunitäts.*, **93**, 119 (1938).

BIOCHEMICAL RESEARCH FOUNDATION
OF THE FRANKLIN INSTITUTE
PHILADELPHIA, PA.

RECEIVED AUGUST 1, 1940

---

## The Preparation of Tetraphenylgermanium

BY DAVID E. WORRALL

Two classical methods for the preparation of organometallic derivatives are those of Grignard and Fittig. Surprising it is, therefore, that both are said to give poor results in the synthesis of tetraarylgermanes.[1] Perhaps that is why most investigators have not reported yields. Morgan and Drew[2] found it necessary to employ 36 molar equivalents of phenylmagnesium bromide, obtaining a 40% yield of tetraphenylgermanium. Kraus and Foster[3] modified the usual procedure by converting the intermediate magnesium compound into diphenylzinc in an atmosphere of nitrogen, subsequently replacing the ether with toluene. Excellent yields are obtainable but the procedure is elaborate and time consuming and a rather large excess of reagent is used.

It has been found in this Laboratory that the presence of zinc compounds or a large excess of the organomagnesium derivative is unnecessary. A good yield of tetraphenylgermanium may be obtained by the usual technique provided only that toluene is substituted for ether. A similar replacement in the Fittig synthesis of the same compound gives fair results.

### Experimental

A solution of phenylmagnesium bromide prepared from 29 g. of monobromobenzene was filtered by decantation mixed with 100 cc. of dry toluene and heated on a water-bath to remove ether. While still warm and connected to a reflux condenser, 10 g. of germanium tetrachloride mixed with 10 cc. of toluene was run in with occasional shaking at such a rate that vigorous boiling took place. The mixture was then heated for two hours on an oil-bath. Following hydrolysis using hydrochloric acid, several hundred cc. of warm toluene was added and the filtered toluene layer concentrated to a small bulk. White needle-like crystals separated from the yellow solution. It was filtered by suction, washed first with a few cc. of cold toluene, then with several volumes of alcohol; yield 14.1 g., m. p. 225–226° (uncor.).

In another experiment a mixture containing 10 g. of germanium tetrachloride, 100 cc. of toluene, 9 g. of granulated sodium and 30 g. of monobromobenzene was heated cautiously under a reflux condenser until the reaction started. Once started the reaction became violent so that outside cooling from time to time was necessary. The mixture was heated for an hour after the spontaneous reaction ceased and worked up while still hot. Although the solution was deeper colored than that obtained by the magnesium method, the product was perfectly white; yield 9.6 g. Longer heating or the replacement of toluene with xylene did not noticeably increase the yield.

PEARSON MEMORIAL LABORATORY
TUFTS COLLEGE
MEDFORD, MASSACHUSETTS

RECEIVED SEPTEMBER 19, 1940

---

(1) Simons, Wagner and Müller, THIS JOURNAL, **55**, 3705 (1933).

(2) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

(3) Kraus and Foster, THIS JOURNAL, **49**, 457 (1927).