

wise over a period of 15 minutes; the internal temperature was kept below 25°. Stirring was continued for an additional 30 minutes at which time the mixture contained a small amount of gelled material. This was brought into solution by the addition of 60 ml. of water. The resulting solution was then maintained at 0 to +5° and, while stirring, a solution (precooled to 0 to +3°) of 20.5 g. (0.341 mole) of urea dissolved in 102 g. of 20% aqueous acetic acid (0.341 mole acid) was added dropwise over a period of 20 minutes. The two phase system thus produced was extracted with three 25-ml. portions of petroleum ether (b.p. 35–37°) and the extracts were combined and dried over Drierite. Upon distillation there was obtained 18.6 g. (93% yield) of nitrocyclohexane, b.p. 108–109° (40 mm.),  $n_{20}^D$  1.4612; lit. values,<sup>17</sup> b.p. 109° (40 mm.),  $n_{20}^D$  1.4608.

The influence of acidification temperature was studied in the case of nitrocyclohexane. Hydroxylamine hydrochloride at 25° gave a 77% yield (av. of two runs); this is significantly lower than the 89% yield (av. of six runs) obtained at 0°.

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(17) S. Nametkin, *Ber.*, **42**, 1372 (1909).

(18) M. Cenker, Ph.D. Thesis, Purdue University, 1948.

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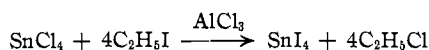
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## The Friedel–Crafts Synthesis of Germanium and Tin Tetraiodides

BY W. H. NEBERGALL AND ROBERT H. WALSH

In connection with investigations<sup>1</sup> concerning the alkylation and arylation of the halides and hydrides of the Group IV elements the conversion of the tetrachlorides of silicon, germanium and tin to their respective iodides was attempted. It is well known that carbon tetraiodide may be prepared by the interaction of carbon tetrachloride and ethyl iodide in the presence of aluminum chloride<sup>2</sup> as a catalyst.

It was found in the present investigation that tin tetrachloride reacts immediately with ethyl iodide in the presence of aluminum chloride to give a quantitative yield of tin tetraiodide.



When aluminum bromide was used as the catalyst the formation of tin tetraiodide was somewhat slower and the crystals were larger; however, the conversion was still quantitative.

Germanium tetrachloride reacted very slowly with ethyl iodide, and after the reaction mixture stood for 48 hours only a 13% yield of germanium tetraiodide was obtained when aluminum chloride was employed as the catalyst. Under similar conditions but with aluminum bromide as the catalyst, a 7% yield of germanium tetraiodide was obtained. Silicon tetrachloride failed to react with ethyl

iodide in the presence of either aluminum chloride or aluminum bromide.

### Experimental

**Tin Tetraiodide from Tin Tetrachloride.**—A 200-ml. erlenmeyer flask was fitted with a cork stopper containing a calcium chloride drying tube to allow the evolution of ethyl chloride but to protect the reaction mixture from the moisture of the air. Into the flask was weighed 10 g. (0.04 mole) of tin tetrachloride, 40 g. (0.16 mole) of redistilled ethyl iodide and 1.6 g. (0.0076 mole) of aluminum chloride. The flask was quickly closed with the stopper and drying tube. An orange color developed immediately in the reaction mixture, and after 30 to 60 seconds ebullition and effervescence began. After one to two minutes orange crystals of tin tetraiodide started to separate. The contents of the flask were swirled occasionally to keep the reactants well mixed and after five to seven minutes the reaction appeared to be complete. The crystals were transferred to a sintered-glass filtering funnel and washed with ice-cold concentrated hydriodic acid to remove the aluminum chloride. The crystalline tin tetraiodide was air-dried, the yield, 25 g., was essentially quantitative, and a sample of the product which was recrystallized from chloroform melted sharply at 141–142°.

The above procedure was repeated using aluminum bromide in place of aluminum chloride as the catalyst. The reaction was somewhat slower, seven to ten minutes being required for completion, and the crystals of tin tetraiodide were considerably larger. The yield again was essentially quantitative.

**Germanium Tetraiodide from Germanium Tetrachloride.**—Germanium tetrachloride (0.04 mole), ethyl iodide (0.16 mole) and aluminum chloride (0.0075 mole) were interacted as described above. Coloration was very slow to appear. After one to one and one-half hours the solution was dark red in color, the aluminum chloride had dissolved, and an oil had separated. The reaction mixture was permitted to stand at room temperature for 48 hours and then it was cooled in an acetone–Dry Ice-bath. After 10 minutes, the crystals of germanium tetraiodide which had formed were collected, washed with cold hydriodic acid and air-dried. The yield was 3 g. (13%); m.p. 140–141°.

When the aluminum chloride was replaced by aluminum bromide as the catalyst, the deep red color appeared almost immediately after the addition of the aluminum bromide, which dissolved in about ten minutes. The oil layer was very slow in appearing and it was not observed until after the reaction mixture had stood for about 48 hours. The product was worked up in the usual manner and the yield of crude germanium tetraiodide was 1.5 g. (7%).

**Attempted Preparation of Silicon Tetraiodide from Silicon Tetrachloride.**—When the procedures outlined above were used in attempts to prepare silicon tetraiodide, there were no indications of any reaction with either aluminum chloride or bromide as the catalyst or with prolonged refluxing. It might be added that when aluminum iodide was employed as the catalyst, the formation of the iodides of carbon, germanium and tin was negligible.

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## Optically Active Phenylmethylcarbiny Ether

BY KURT MISLOW

It was recently pointed out<sup>1</sup> that the usual method of preparation of optically active ethers, by the reaction of an alkyl halide with alkali alcoholate, must, in the case of phenylmethylcarbiny ethers, have led to partially racemized products. The present work describes successful attempts to convert the carbinol to the ether by means of an alkyl iodide–silver oxide mixture. This method has in the past found extensive application in the alkyla-

(1) O. H. Johnson and W. H. Nebergall, *THIS JOURNAL*, **70**, 1706 (1948); O. H. Johnson and W. H. Nebergall, *ibid.*, **71**, 1720 (1949); W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949); W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

(2) J. W. Walker, *J. Chem. Soc.*, **85**, 1090 (1904).

(1) Mislow, *THIS JOURNAL*, **78**, 3954 (1951).