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.), $n^{20}\mathrm{D}$ 1.4612; lit. values,[17] b.p. 109° (40 mm.), $n^{20}\mathrm{D}$ 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°.

Acknowledgment.—Our sincere thanks go to Mr. Bernard Taub of this Department for furnishing most of the nitroparaffins employed in this study and to Dr. M. Cenker who carried out several preliminary experiments with hydroxylamine hydrochloride.[18] Financial support from the Research Corporation is gratefully acknowledged.

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

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

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RECEIVED MARCH 23, 1951

The Friedel–Crafts Synthesis of Germanium and Tin Tetraiodides

BY W. H. NEBERGALL AND ROBERT H. WALSH

In connection with investigations[1] 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[2] 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.

$$\mathrm{SnCl_4 + 4C_2H_5I \xrightarrow{AlCl_3} SnI_4 + 4C_2H_5Cl}$$

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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RECEIVED MARCH 17, 1951

(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).

Optically Active Phenylmethylcarbinyl Ethers

BY KURT MISLOW

It was recently pointed out[1] 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 phenylmethylcarbinyl 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) Mislow, THIS JOURNAL, **73**, 3954 (1951).

tion of α-hydroxy acids and sugars.[2] Lander[3] successfully employed it in the alkylation of amides, phenols, acetoacetic ester, and borneol.

When (+)-phenylmethylcarbinol of 92.8% optical purity was refluxed with ethyl iodide in the presence of silver oxide, the resulting ethyl ether had $[\alpha]^{28}_{\mathrm{D}}$ + 88.0°, or +94.8° for the optically pure ether. The ether prepared from ethyl bromide and the potassium salt of (−)-phenylmethylcarbinol has $[\alpha]_{\mathrm{D}}$ −80.7°,[4] corresponding, therefore, to only 85% optical purity. The methyl ether was also prepared from 92.8% optically pure (+)-phenylmethylcarbinol, methyl iodide and silver oxide, and had $[\alpha]^{28}_{\mathrm{D}}$ +119.1°, or +128.3° for the optically pure ether. The highest rotation reported for this product, prepared from methyl iodide and the sodium salt of (+)-phenylmethylcarbinol, is $[\alpha]_{\mathrm{D}}$ +68°,[5] corresponding, therefore, to only 53% optical purity. The very extensive racemization which accompanied the older preparations of phenylmethylcarbinyl ethers is not surprising, in view of the well-known stereochemical equilibration of alcohols in the presence of alkali alcoholates and traces of oxidizing agents,[6] and the lability of the α-hydrogen in the particular system under investigation. While it seems possible that optically pure ethers might also be prepared by the conventional method under conditions strictly exclusive of oxidants, the silver oxide method has the advantage of great simplicity, no special precautions being needed to avoid the possibility of racemization. Whether or not a very small amount of racemization took place during the silver oxide reaction could not be ascertained conclusively. Although the cleavage of the ethyl ether with anhydrous hydrogen bromide resulted principally in styrene and phenylmethylcarbinyl bromide, and not in phenylmethylcarbinol, the unreacted carbinol isolated from the etherification mixture had retained its original rotation, and the rotation of the ethyl ether remained unchanged when the ether was refluxed with ethyl iodide in the presence of silver oxide. Furthermore, consistent results were obtained on successive alkylations. In view of these results it is highly probable that the optical purity of the ethers is the same as that of the starting carbinol.

Experimental

Ethyl α-Methylbenzyl Ether.—Phenylmethylcarbinol was resolved through its brucine salt.[7] A mixture of 5.5 g. of carbinol, $[\alpha]^{25}_{\mathrm{D}}$ +40.4° (no solvent), 28.2 g. of ethyl iodide and 10.5 g. of freshly precipitated, dry silver oxide was refluxed for one hour. The same quantities of ethyl iodide and silver oxide were then added and refluxing was continued overnight. The mixture was filtered and the excess ethyl iodide was distilled off. The residual oil was heated with phthalic anhydride and pyridine on the steam-bath for two hours, the resulting mixture poured into dilute hydrochloric acid and extracted with ether. The ether layer was washed with dilute, cold sodium hydroxide, dried and distilled to yield 3.6 g. (53%) of the desired product, b.p. 89° (31 mm.), n^{25}_{D} 1.4846, d^{25}_{4} 0.9187, $[\alpha]^{28}_{\mathrm{D}}$ +88.0° (no solvent). The product was refluxed for one day with the same quantities of ethyl iodide and silver oxide which were employed in its preparation; filtration and distillation afforded the ether with unchanged rotation.

Methyl α-Methylbenzyl Ether.—A mixture of 14.0 g. of phenylmethylcarbinol, $[\alpha]^{25}_{\mathrm{D}}$ +40.4° (no solvent), 65.2 g. of methyl iodide and 26.6 g. of silver oxide was refluxed and worked up as described for the preparation of the ethyl ether, to yield 6.0 g. (38%) of the desired product, b.p. 88° (47 mm.), n^{25}_{D} 1.4905, d^{25}_{4} 0.9353, $[\alpha]^{28}_{\mathrm{D}}$ +119.1° (no solvent). A mixture of 21.6 g. of phenylmethylcarbinol, $[\alpha]^{25}_{\mathrm{D}}$ −40.2° (no solvent), 100 g. of methyl iodide and 41 g. of silver oxide afforded 7.7 g. (32%) of product, $[\alpha]^{28}_{\mathrm{D}}$ −118.2°. The sodium hydroxide washings from this reaction were heated at 100° for three minutes, the liberated oil extracted with ether and distilled, affording 9.0 g. of phenylmethylcarbinol, n^{25}_{D} 1.5272, $[\alpha]^{25}_{\mathrm{D}}$ −40.2° (no solvent).

Cleavage of Ethyl α-Methylbenzyl Ether.—A mixture of 7.6 g. (0.05 mole) of (±)-ethyl α-methylbenzyl ether and 4.1 g. (0.05 mole) of anhydrous hydrogen bromide, sealed in a tube, was heated at 100° for one hour. The water which had separated was pipetted off; the organic layer, after neutralization and drying with potassium carbonate, weighed 10.6 g. Fractionation yielded diethyl ether, ethyl bromide, ethanol, styrene and phenylmethylcarbinyl bromide. While the residual dark colored oil might have contained some phenylmethylcarbinol, the amount was too small to make further distillation profitable.

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RECEIVED MARCH 20, 1951

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[2] Purdie, *et al.*, *J. Chem. Soc.*, 157, 485 (1899); *ibid.*, 1021, 1037 (1903); McKenzie, *ibid.*, 754 (1899).

[3] Lander, *ibid.*, 729 (1900); *ibid.*, 690 (1901); *ibid.*, 414 (1903).

[4] Extrapolated from values reported by Kenyon and Phillips, *ibid.*, 1676 (1930).

[5] From values reported by Hughes, Ingold and Scott, *ibid.*, 1201 (1937).

[6] Doering and Aschner, THIS JOURNAL, **71**, 838 (1949).

[7] Downer and Kenyon, *J. Chem. Soc.*, 1156 (1939).

Diphenates. I. Preparation of Diphenic Acid

BY WILLIAM F. O'CONNOR AND EMIL J. MORICONI

Recorded instances of the peroxide oxidation of phenanthrene appear only scattered in the literature. Using 30% hydrogen peroxide, the primary oxidation product, 9,10-phenanthrenequinone, has been obtained in unrecorded yields.[1] Furthermore, the quinone, as a reactant, has been converted to diphenic acid *via* the same oxidizing medium,[2] and by treating its reduction product, 9,10-phenanthrenediol, with sodium peroxide in an alkaline medium.[3]

The one-step oxidation of phenanthrene to diphenic acid has been effected with 30% hydrogen peroxide in 29% yield and accompanied by a considerable proportion of resins.[4] The most recent work, using 20% hydrogen peroxide and an osmium tetroxide catalyst, gave a 16% yield of the quinone and a negligible yield of diphenic acid.[5] Both reactions involve long contact time.

We have found that recently available 50% hydrogen peroxide[6] in glacial acetic acid oxidizes phenanthrene to high-purity diphenic acid with minimum by-product formation, short contact time and in 65–70% yields.

Using the same peroxide/phenanthrene molar ratio and identical reaction conditions, 90% hydrogen peroxide[6] gave lower yields and a more difficultly purified diphenic acid.

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[1] Henderson and Boyd, *J. Chem. Soc.*, **97**, 1661 (1910); Milas, British Patent 508,526.

[2] Perkins, *Proc. Chem. Soc.*, **23**, 166 (1907); Holleman, *Rec. trav. chim.*, **23**, 171 (1924); Charrier and Moggi, *Gazz. chim. ital.*, **54**, 988 (1924); Linstead and Walpole, *J. Chem. Soc.*, 855 (1939).

[3] Williams, U. S. Patent 1,423,980.

[4] Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1927).

[5] Cook and Shoental, *J. Chem. Soc.*, 47 (1950).

[6] Research sample supplied by Buffalo Electro-Chemical Co., Inc., Buffalo 7, N. Y.