



Fig. 1.

pressures varying from 2–3 mm. up to 150–200 mm. can be obtained quickly and maintained indefinitely without perceptible variation.

The same device may be used for regulation of a partial vacuum by adding a side-arm at the site of the air vent, connecting this to the apparatus, and leaving the opening below the ball free for the entrance of air.

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An Improved Method for the Preparation of Aromatic Diazoketones

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Common practice in the preparation of diazoketones involves the treatment of an acid chloride with two moles of diazomethane, one being destroyed by the hydrogen chloride produced.¹

(1) Bachmann and Struve, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. I, 1942, p. 39.

Since this is wasteful of diazomethane, we have investigated the use of tertiary amines to remove the hydrogen chloride.

When benzoyl chloride was added to an ether solution containing one equivalent each of diazomethane and triethylamine, the diazoketone was produced in excellent yield. The reaction worked as well with anisoyl chloride. In the case of *n*-caproyl chloride, nitrogen was evolved during the addition and a mixture of products was formed. Indirect evidence for the presence of a considerable proportion of diazoketone in this mixture was obtained but it was not isolated. With the thought that the evolution of nitrogen during addition of caproyl chloride to the mixture of diazomethane and triethylamine might have been due to the α -hydrogen, we repeated the experiment with trimethylacetyl chloride. The evolution of nitrogen during addition was less but still appreciable. The results when pyridine was used in place of triethylamine were not encouraging.

It thus appears that, at least with aromatic acid chlorides, diazomethyl ketones can be produced in excellent yield with the consumption of only one equivalent of diazomethane.

Experimental

Ethereal solutions of diazomethane were prepared from *N*-nitrosomethylurea and were standardized.² The triethylamine was dried over barium oxide.

Diazoacetophenone.—A solution of 14.1 g. (0.1 mole) of benzoyl chloride in 25 cc. of ether was added during twenty minutes to a well-stirred cooled (ice-salt-bath) solution of 4.2 g. (0.1 mole) of diazomethane and 10.1 g. (0.1 mole) of triethylamine in 235 cc. of dry ether. A crystalline precipitate of triethylamine hydrochloride separated. After stirring in the cold for twelve hours, the hydrochloride, 11.8 g. (86%), was collected and washed with dry ether. The solvent was removed under reduced pressure from the combined filtrate and washings to yield 15.2 g. (104%) of crude crystalline diazoketone. An assay of this crude diazoketone by acid decomposition resulted in the collection of 93.6% of the theoretical amount of nitrogen. Recrystallization from low boiling petroleum ether (Skellysolve F) yielded the pure diazoketone, m. p. 47.8–48.4°, with little loss. Experiments using pyridine in place of triethylamine were unpromising.

***p*-Methoxy- α -diazacetophenone.**—In a similar way, anisoyl chloride was converted into crude diazoketone in high yield. Recrystallization from benzene and petroleum ether, b. p. 60–70°, yielded pure diazoketone, m. p. 86–89° dec., in 73% yield.

Reaction of Caproyl Chloride with Diazomethane.—When a solution of 9.9 g. (0.064 mole) of caproyl chloride in 30 cc. of ether was added as above described during forty-five minutes to an ethereal solution containing equivalents of triethylamine and diazomethane 0.0224 mole (35%) of nitrogen was evolved. No further nitrogen was obtained after the mixture stood for twelve hours in the cold. Triethylamine hydrochloride was isolated in 91% yield, and from the filtrate and washings 9.7 g. (69%) of a crude diazoketone fraction which yielded only 58% of the theoretical amount of nitrogen on acid decomposition.

It was shown that triethylamine hydrochloride does not react with diazomethane under the conditions of this experiment. Hence we are unable to offer an explanation

(2) F. Arndt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 165.

(3) Wolff, *Ann.*, **325**, 142 (1902).

for the gas observed with caproyl chloride but not with benzoyl or anisoyl chlorides.

Reaction of Trimethylacetyl Chloride with Diazomethane.—A solution of 24.1 g. (0.2 mole) of this acid chloride in 50 cc. of ether was added during eighty-five minutes to a cold solution of 20.4 g. (0.2 mole) of triethylamine and 8.5 g. of diazomethane in 275 cc. of ether. During the addition 0.022 mole (11%) of nitrogen was evolved, but on standing for twelve hours in the cold, no more nitrogen was liberated. The amine hydrochloride (96%) and crude diazoketone (98%) were isolated as described above. On treatment with acid, the crude diazoketone yielded 90% of nitrogen.

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Reduction of Anthracene and Phenanthrene with Lithium Aluminum Hydride

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Nystrom and Brown¹ have found lithium aluminum hydride a useful reagent for a number of organic reductions. No work has been reported on the reduction of aromatic or condensed ring nuclei with this reagent. Preliminary attempts to reduce naphthalene and anthracene in ether and dioxane solutions were unsuccessful, but when the solid lithium aluminum hydride was shaken with molten anthracene and phenanthrene, reduction did take place, the former giving as high as 60% yields of tetrahydroanthracene, and the latter 22% of dihydrophenanthrene. These reductions take place even though the decomposition point of lithium aluminum hydride has been reported at 125–150°. In all our reductions at high temperatures we mixed the powdered reagent thoroughly with the organic substances, and then employed vigorous shaking of the molten materials to ensure intimate mixing.

Method of Reduction.—A series of experiments is reported in which the temperature, the time and the ratio of reducing agent to anthracene and phenanthrene are varied. The experiments were run in a 200-ml. round-bottom flask, fitted with a calcium chloride tube, Bunsen valve and thermometer. The flask is heated with a Gyco heating jacket placed on a shaking machine. In each experiment 0.05 mole of the organic molecule was used. The molten material was shaken for the first two hours of each run, and then for fifteen minutes out of every thirty minutes; at the end of the time specified the hydride is decomposed by the slow addition of water. The reaction is vigorous and often flashes of fire were seen in the flask, but none of the reactions has gotten out of hand to date. After filtering and drying, the anthracene and its reduced form were extracted from the lithium and aluminum compounds with 200 ml. of hot chloroform and the phenanthrene with 200 ml. of ether or 95% alcohol. The unreduced hydrocarbons are less soluble than the hydrogenated products in the solvents used for the extractions, thus providing an effective method of separation. The tetrahydroanthracene was identified by a mixed melting point with a sample prepared by reduction of anthracene with Raney nickel (m. p. 103–104°). The dihydro-

(1) Nystrom and Brown, *THIS JOURNAL*, **69**, 1197, 2548 (1947); **70**, 441 (1948).

(2) Finholt, Bond and Schlesinger, *ibid.*, **69**, 1199–1203 (1947).

phenanthrene and its picrate were identical with those prepared by Schmidt.³

Results of Reduction.—A 60% yield of tetrahydroanthracene was obtained by heating 0.05 mole of anthracene at 220–230° for six hours with 8 g. of lithium aluminum hydride; a 45% yield was obtained by cutting the hydride to one-half. Increasing the temperature to 240–270° or lengthening the time of heating also reduced the yield. A 22% yield of dihydrophenanthrene was obtained by heating 0.05 mole of phenanthrene at 220–230° for six hours with 8 g. of lithium aluminum hydroxide. Reducing the temperature to 180–200° and the quantity of hydride, reduced the yield to 10–17%.

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(3) Schmidt, *Ber.*, **40**, 4240–4257 (1907).

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Electroreparation of Technetium from Rhenium and Molybdenum

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Heretofore, technetium has been plated from acidic solutions^{2,3,4} under nearly the same conditions used for the deposition of rhenium. It seems quite likely, therefore, that the separation from rhenium would be poor. During the course of a polarographic study of technetium with G. E. Boyd⁵ it was found that distinct reduction waves were found for pertechnetate in 2 *M* sodium hydroxide whereas perrhenate and molybdate did not reduce, at the platinum electrode, up to the potential at which hydrogen was evolved rapidly.

The brown-black precipitate which appeared on the electrode was soluble in a mixture of ammonia and hydrogen peroxide indicating that a lower oxide of technetium was formed since technetium metal is insoluble.⁶ The height of the diffusion current confirmed the idea that the reduction step involved several electrons. Since the polarographic diffusion current reached a constant value at about -0.9 v. vs. the saturated calomel electrode (S.C.E.) and since the rapid evolution of hydrogen did not begin until about -1.2 v., the intermediate region of potential represented a promising one for the separation of technetium.

Experimental Results

A 100- μ l. sample of 2 *M* sodium hydroxide containing 0.2 mg. of technetium ($Tc^{99} - 9 \times 10^5$ years) as TcO_4^- plus a somewhat larger amount of molybdenum and a smaller amount of rhenium was placed upon a flat platinum foil used for the cathode. The anode was a large

(1) Present address: Massachusetts Institute of Technology, Cambridge 39, Mass.

(2) C. Perrier and E. Segrè, *J. Chem. Phys.*, **7**, 155 (1939).

(3) J. F. Flagg and W. E. Bleidner, *J. Chem. Phys.*, **13**, 269 (1945).

(4) E. E. Motta, Q. V. Larson and G. E. Boyd, Plutonium Project Record, MonC-99, April, 1947.

(5) G. E. Boyd and L. B. Rogers, reported by G. E. Boyd at the Symposium of the Division of Physical and Inorganic Chemistry at Syracuse, N. Y., June 28–30, 1948.

(6) G. E. Boyd, private communication.