nitro-group, and represents a certain loss of the desired product.

Proof of the structure was obtained by reduction to 2-amino-3,4-xylenol, m.p. 138–139°. The previously reported value for this aminophenol, prepared by reducing 6-hydroxy-2,3-dimethylazobenzene, was 126°.[3] Repetition of this earlier work gave a compound, m.p. 138–139°, identical with that obtained from the nitrophenol.

Experimental

2-Nitro-3,4-xylenol.—Purified 3,4-xylenol, 122 g. (1.0 mole) was dissolved in 122 ml. of concentrated sulfuric acid and the solution warmed on the steam-bath until reaction was under way and the temperature had risen to 60–70°. Heating was then discontinued and the mixture stirred until crystallization occurred, and to the cooled mixture 600 ml. of water and 240 ml. of concentrated sulfuric acid were added. Nitration was accomplished by adding 70 ml. of nitric acid, sp. gr. 1.42 (1.1 moles), diluted with 100 ml. of water, dropwise, with stirring at 0–5° and allowing the temperature to remain thus for an hour after addition was complete. The mixture was poured into 1200 ml. of ice-water and filtered from the precipitated nitroxylenols. Sodium chloride added to the clear filtrate salted out 2-nitro-3,4-xylenol-6-sulfonic acid as a thick, orange precipitate. The latter was collected, the filtrate saturated with salt and a second crop of sulfonic acid collected after cooling for several hours. The crude nitrosulfonic acid was steam distilled at 130–140° from an initial volume of 1050 ml. of 70% sulfuric acid. After the initial distillate, mainly 3,4-xylenol, 2-nitro-3,4-xylenol, crystallizing in the condenser as an orange solid, was collected. After separating and drying this, it was recrystallized once from petroleum ether (b. p. 60–90°) yielding 68 g. (41%) of a slightly impure product, m. p. 67–70°. After recrystallizing six times from the same solvent it melted at 71.5–72.0°.

Anal. Calcd. for $C_8H_9O_3N$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.46, 57.58; H, 5.21, 5.25; N, 8.51, 8.61.

Nitration in glacial acetic acid and at lower and higher temperatures proved less satisfactory. Also, the amount of nitric acid proved to be critical. For example, 0.25-mole quantities of the xylenol in corresponding amounts of water and sulfuric acid were sulfonated and then nitrated at 0–5° with 40-ml. quantities of nitric acid in varying concentrations:

Moles of HNO_3 in 50 ml. of solution	Yield of crystallized 2-nitro-3,4-xylenol Grams	%	Crude precipitated nitroxylenols, g.
0.22	10.6	25	2.6
.28	16.7	40	4.0
.34	13.9	33	7.1
.40	6.0	14	9.0

The crude nitroxylenols, precipitating on dilution of the nitrated mixture, when dried and treated with petroleum ether separated into a soluble portion, crystallizing on cooling, m. p. 67–68°, and an insoluble fraction which was recrystallized from alcohol. The latter was 2,6-dinitro-3,4-xylenol, m. p. 122.5–124.0°. The low-melting material was not identical with 2-nitro-3,4-xylenol and could be made to yield the 2,6-dinitro-compound on crystallization from alcohol. An equimolecular mixture of the 2-nitro- and 2,6-dinitroxylenols melted at 67–68° and did not depress the m. p. of the above material.

2,4-Dinitrophenyl 2-Nitro-3,4-Xylyl Ether.—This derivative was prepared by the procedure of Bost and Nicholson,[4] and recrystallized three times from ethyl alcohol; m. p. 157.0–157.5°.

Anal. Calcd. for $C_{14}H_{11}O_7N_3$: C, 50.45; H, 3.33; N, 12.61. Found: C, 50.41, 50.35; H, 3.15, 3.25; N, 12.38, 12.14.

2-Amino-3,4-xylenol.—Reduction of 2 g. of the nitrophenol with 10 g. of sodium hydrosulfite, 5 g. of sodium bicarbonate and 33 ml. of water[5] gave a solid which darkened readily. This was decolorized in alcoholic solution, the solvent removed *in vacuo* and the buff-colored residue recrystallized from benzene. The m. p. was 138–139°.

Catalytic reduction in absolute alcohol at 50 p. s. i. over palladium-on-charcoal catalyst[6] gave the identical compound in 98% yield.

Anal. Calcd. for $C_8H_{11}ON$: C, 70.05; H, 8.06; N, 10.21. Found: C, 70.15, 70.12; H, 7.82, 7.89; N, 10.10, 10.16.

6-Hydroxy-2,3-dimethylazobenzene was prepared and purified as described by King.[7] It was reduced to 2-amino-3,4-xylenol in accordance with the previously published procedure[3] and the product purified. The m. p. and mixed m. p.'s with samples prepared by the above methods were all 138–139°.

2-Acetamino-3,4-xylenol.—The aminophenol, 0.5 g., was treated with 2 ml. of acetic anhydride, the resulting solid dissolved in 10% potassium hydroxide and the desired derivative precipitated with dilute acid; yield 0.35 g., m. p. 159–160° after four recrystallizations from benzene.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.81. Found: C, 67.05, 66.94; H, 7.11, 7.09; N, 7.77.

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[3] Hinkel, Ayling and Bevan, *J. Chem. Soc.*, 2529 (1928).

[4] Bost and Nicholson, *ibid.*, **57**, 2368 (1935).

[5] Hodgson and Beard, *J. Chem. Soc.*, **127**, 498 (1925).

[6] Hartung, This Journal, **50**, 3370 (1928).

[7] King, *J. Chem. Soc.*, 1157 (1939).

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RECEIVED NOVEMBER 8, 1948

A Simple Device for Regulating Pressure or Vacuum

BY J. HOWARD MUELLER

In certain experimental procedures it is often necessary to apply moderate air pressure to a piece of apparatus over a considerable period of time. The increasing use of chromatographic columns for various purposes is a case in point. A simple device which may readily be constructed at little expense has proved extraordinarily useful for this purpose and possibly merits brief description. A compressed air supply is essential to its use, but this is almost universally available.

The principle employed is to form a valve between a stainless steel ball and a narrow "seat" turned in the end of a hole drilled through a lucite or metal rod. By applying more or less pressure on top of the ball, a slow stream of air passing upward through the hole is impeded, and variable pressures are obtained in a closed system of which this valve forms the outlet. The drawing illustrates the manner in which this may be accomplished. The stem of the regulator passes through a stopper inserted into a small filter flask, which is connected to the system. A very slow stream of air is admitted by slight opening of an ordinary valve on the supply line, and the pressure is set where desired by regulating the tension on the spring by means of the knurled headed screw. The air escapes through a small vent drilled in the wall of the cylinder just above the ball. In this way,

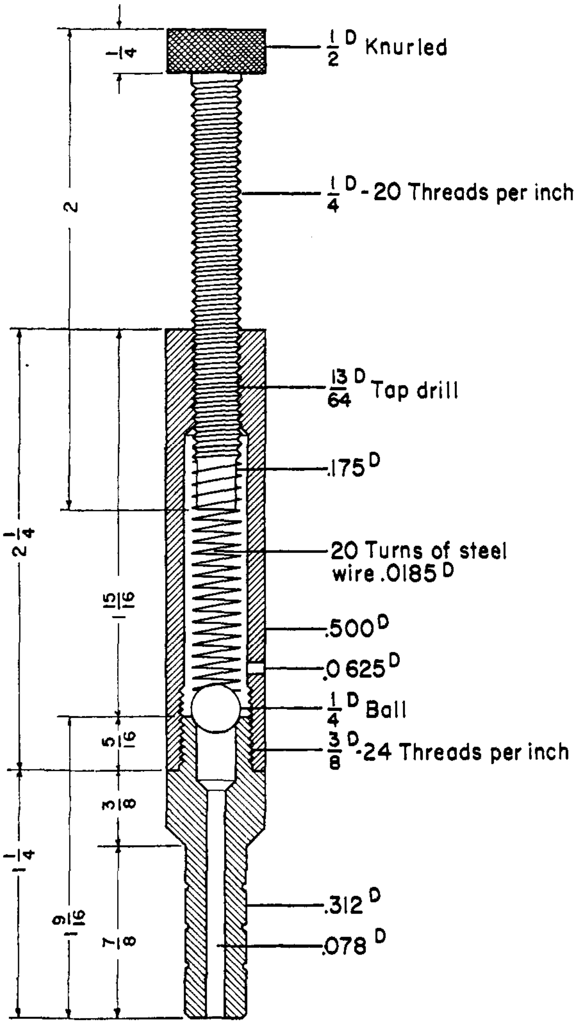

Fig. 1.

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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RECEIVED JANUARY 6, 1949

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] 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°,[3] with little loss. Experiments using pyridine in place of triethylamine were unpromising.

***p*-Methoxy-α-diazoacetophenone.**—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

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

(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).