formation of a heavy precipitate. After refluxing in ether for 24 hours, benzene was added, and solvent was distilled until the reaction temperature was about 50°. After refluxing at this temperature for three hours, Color Test I[5] was negative. The reaction mixture was hydrolyzed with water, and the organic layer was separated and dried over sodium sulfate. Removal of solvent yielded 6.4 g. (45.3%) of crystals, m.p. 133.5–137°. Two recrystallizations from a benzene-ethyl acetate mixture gave white needles, m.p. 137–137.5°.

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Synthesis of 2,5-Diaminoethylbenzene and Some Hazards Involved Therein

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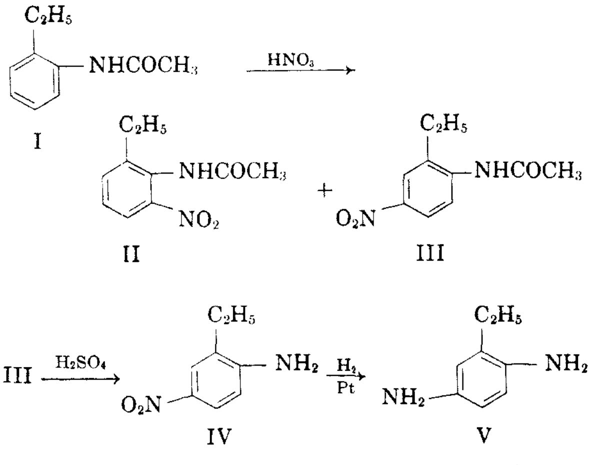
For the preparation of a sizable quantity of 2,5-diaminoethylbenzene, heretofore uncharacterized, the following scheme appeared practicable:



Hansch[1] has reported that the nitration of I (100 g.) gives a mixture of II and III from which, after hydrolysis, the free amines can be separated by tedious steam distillation (40 liters of distillate). 2-Amino-3-nitroethylbenzene (17.6 g.) appears in the distillate with a small quantity of IV from which it is purified by chromatography and the 5-isomer (IV) appears (26.5 g.) in the residue contaminated with some tar. In our attempts to scale up this preparation, certain hazards were encountered and improvements in the purification of the 5-isomer were achieved.

When 250 g. of I was nitrated according to the procedure of Hansch, by dropwise addition of fuming nitric acid to an acetic acid solution of I, at 50–55°, the reaction got out of control and the solution erupted out of the flask spewing acid out in all directions. The size of the charge was reduced to 100 g. of I and although more than a dozen successful runs were made, the reaction got out of control in one experiment even though the temperature was being carefully regulated. The reaction should be run with good stirring and the dropwise addition of the 150 ml. of fuming nitric should take about 0.5 hour and should be only fast enough to keep the temperature in the desired range without appreciable external cooling. Suitable isolation and shielding of the reaction system should, of course, be employed.

After sulfuric acid hydrolysis of the nitrated mixture, the dark red solution was decanted from a black tar and the solution was allowed to cool, whereupon a brown solid separated. This precipitate was separated, air-dried, extracted with ether, and suspended in sodium bicarbonate solution. The precipitate then was filtered and found to be essentially pure 2-amino-5-nitroethylbenzene.

Since our isolation procedure gave pure IV and the previous work indicated almost as much isomeric 2-amino-3-nitroethylbenzene might be present, the decanted tar secured above was investigated in an attempt to isolate the 2,3-isomer. The tar was transferred to a distilling flask and an *in vacuo* distillation attempted. After a few drops of distillate had been secured, the tar erupted, thrusting the thermometer out of the flask and filling the room with copious dense brown fumes. No further investigation was made of the tar.

Platinum oxide-catalyzed reduction of an ethanol solution of IV gave 2,5-diaminoethylbenzene, the only diaminoethylbenzene which has not been previously characterized.

EXPERIMENTAL

Nitration of 2-acetylaminoethylbenzene (I). A solution of 100 g. of I in 180 ml. of glacial acetic acid and 40 ml. of fuming nitric acid (*d.* 1.50) in a three-necked flask containing an unsealed stirrer, dropping-funnel, and thermometer was warmed to 50° with stirring. There then was added 150 ml. of fuming nitric acid, dropwise, at such a rate that the temperature was kept at 50–55° while the flask was occasionally cooled with a shallow ice-water bath. The rate of addition cannot be too slow, otherwise the temperature falls and too much unreacted nitric acid accumulates. On the other hand, too rapid addition also leads to difficulties, already described above. The addition should take about 0.5 hour. After the addition of all the nitric acid, the mixture was kept at 50–55° for 1.5 hours and then poured into 1 l. of ice-water. After 1 hour, the precipitate was filtered off, suspended in a sodium bicarbonate solution, and stirred for 15 minutes. The bicarbonate suspension was filtered and the precipitate was air-dried, leaving 72 g. (56.5 percent) of mixed acetylaminonitroethylbenzenes.

2-Amino-5-nitroethylbenzene (IV). A mixture of 100 g. of the crude nitrated product described above, 80 ml. of con-

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(1) C. Hansch, *J. Org. Chem.*, 20, 1026 (1955).

centrated sulfuric acid, and 250 ml. of water was refluxed for 2 hours. The dark-red solution was decanted from a black tar and the solution was cooled to room temperature. The brown solid which precipitated on cooling was filtered and air-dried. The solid was suspended in 250 ml. of ether, filtered, and the wash treatment repeated. To a beaker containing the washed amine sulfate there then was added a saturated solution of sodium bicarbonate until excess bicarbonate was present (no more evolution of gas). The solid remaining was filtered, washed with a small portion of water, and air-dried, giving 25 g. (31.4 percent) of 2-amino-5-nitroethylbenzene, m.p. 87°.

Attempted distillation of the decanted tar lead to its violent decomposition as described above.

2,5-Diaminoethylbenzene. A solution of 206 g. of 2-amino-5-nitroethylbenzene (IV), in 1600 ml. of absolute ethanol distilled from Raney nickel, was reduced in 400-ml. batches, with platinum oxide and hydrogen at room temperature and 30–50 p.s.i. The ethanol was removed under nitrogen and reduced pressure, and the resulting deep-red solution was distilled at 9 mm. pressure, (b.p. 141–144°) to give 150 g. (88.8%) of a light-yellow liquid which solidified on cooling.

Anal. Calc'd for $C_8H_{12}N_2$: C, 70.56; H, 8.88; N, 20.56. Found:[2] C, 70.6; H, 8.9; N, 20.3.

The diamine is very sensitive to air and quickly turns black on standing. This sensitivity is probably an oxidative phenomenon facilitated by the *para* relationship of the amino groups. Metals appear to catalyze the decomposition. A crude melting point gave a value of about 33°. The diacetylamino derivative was prepared by mixing 1 g. of the diamine and 20 ml. of acetic anhydride at room temperature. After shaking for one minute, the mixture was poured into water and the suspension was filtered. Two crystallizations from ethanol-water gave colorless needles, m.p. 219°.

Anal. Calc'd for $C_{12}H_{16}N_2O_2$: C, 65.50; H, 7.27. Found:[2] C, 65.5; H, 7.4.

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[2] Geller Laboratories, Hackensack, N. J.

4-Methoxy-1-naphthalenemethanol

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In connection with our research 4-methoxy-1-naphthalenemethanol was desired. This compound had been described by Madinaveitia and Puyal[2] as a solid, m.p. 35°, obtained from the Cannizzaro reaction of 4-methoxy-1-naphthaldehyde (I). Careful repetition of this procedure as well as of the modified procedure given by Shoesmith and Rubli[3] yielded only unreacted I. Under more vigorous conditions 4-methoxy-1-naphthoic acid was obtained, but no carbinol could be isolated.

Reduction of I with lithium aluminum hydride gave a solid (II), m.p. 76–77°, from which an acetate and a phenylurethan could be prepared. These compounds all gave analyses agreeing with the theory for a methoxy-naphthalenemethanol and its derivatives. Oxidation of II with alkaline potassium permanganate gave an acid which did not depress the melting point of authentic 4-methoxy-1-naphthoic acid. The method of preparation, the analyses and the oxidation experiment indicates that II is 4-methoxy-1-naphthalenemethanol. Therefore the compound described by Madinaveitia,[2] for which he reported no analyses, is not the carbinol, and from our work as well as from the m.p., which is identical with that of I, it appears that their product was unreacted I. The reported phenylurethan, for which the author likewise gave no analysis (m.p. 240°),[2] might have been diphenylurea (m.p. 240°).

Attempts were made to obtain II directly from 1-methoxynaphthalene by hydroxymethylation with paraformaldehyde in acidic medium. However, only di-(4-methoxy-1-naphthyl)methane (III) was obtained, oxidation of which gave the corresponding dinaphthyl ketone.

EXPERIMENTAL[4]

Reduction of 4-methoxy-1-naphthaldehyde (I). Compound I, prepared by the procedure of Brady and Goldstein,[5] was reduced with lithium aluminum hydride in ether solution in the usual manner[6] to give *4-methoxy-1-naphthalenemethanol* (II), m.p. 76–77° after recrystallization from ether-petroleum ether.

Anal. Calc'd for $C_{12}H_{12}O_2$: C, 76.58; H, 6.43. Found: C, 76.22; H, 6.35.

The *acetate*, m.p. 63–64° after recrystallization from aqueous methanol, was prepared by refluxing II with acetic anhydride.

Anal. Calc'd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.12. Found: C, 72.99; H, 6.35.

The *phenylurethan*, m. p. 103–105°, was prepared in the usual manner.

Anal. Calc'd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57. Found: C, 74.50; H, 5.46.

Oxidation of II with alkaline potassium permanganate gave *4-methoxy-1-naphthoic acid*, m.p. 233° (reported, 234°),[7] the mixture melting point of which with an authentic sample showed no depression.

Reaction of 1-methoxynaphthalene with paraformaldehyde. Paraformaldehyde (9 g., 0.3 mole) and 30% sulfuric acid (50 ml.) were stirred with 1-methoxynaphthalene (40 g., 0.25 mole) overnight. The white solid (20 g., 40%) which

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[2] A. Madinaveitia and J. Puyal, *Anales real soc. espan. fis. quim.*, **17**, 125 (1919).

[3] J. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

[4] All melting points are uncorrected.

[5] O. L. Brady and R. Goldstein, *J. Chem. Soc.*, 1962 (1927).

[6] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

[7] L. Ruzicka, *Helv. Chim. Acta*, **15**, 907 (1932).