air and the adsorption of the stable argon from air is traced. Approximately 13% of the total argon present in air was found to be adsorbed.

In these studies with radioactive argon it has been found that the use of radioactive tracer for mixed gas adsorption is feasible and gives more consistent results than the conventional method. In cases where the chemical analysis of the gas mixture is difficult by ordinary means, the use of a radioactive tracer, if available, provides a convenient method for studying mixed adsorption. It is recognized that the technique described here using separate samples of silica gel for each experiment does not insure that the adsorbent has exactly the same adsorption properties in each experiment. Experiments in which the only variable was the sample of silica gel used showed this error to be of the order of 3%.

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Summary

1. An apparatus is described suitable for studying binary mixed gas adsorption in which one component is radioactive or contains radioactive atoms as a tracer. The apparatus is also suitable for certain mixed adsorption studies by conventional means. Simple adsorption isotherms were obtained for air, argon and carbon dioxide on silica gel at 25°.

2. Adsorption isotherms for radon in air, in argon and in carbon dioxide on silica gel at 25° were studied. The isotherm in air follows Henry's law and substantiates the Langmuir theory of mixed adsorption as applied to low concentrations. The adsorption of radon is slightly suppressed in carbon dioxide. The studies with radon in argon show that the adsorption of radon is enhanced in the presence of argon even though a very small fraction of the total surface of silica gel is covered by radon.

3. The heat of adsorption of radon in air and in argon was estimated from the data obtained to be of the order of magnitude of 9,000 calories per mole.

4. Methods are described for the use of radioactive argon to follow the adsorption of argon in mixtures with carbon dioxide and with air.

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NOTES

The Reduction of 6-Methyl-8-(4'-diethylamino-1'-methylbutylidene)-aminoquinoline

BY H. J. BARBER, D. H. O. JOHN AND W. R. WRAGG

The recent publication by Elderfield, *et al.*,[1] reporting a study of the synthesis of Plasmochin by the reductive condensation of 1-diethylaminopentanone-4 (I) with 6-methoxy-8-aminoquinoline (II), from which a satisfactory method did not ensue, is of considerable interest to us since we were concerned during the war with a similar process which gave Plasmochin in excellent yield. We wish therefore to record some additional data.

Early in our work we investigated a process revealed by Bergmann[2] for the reductive condensation of 6-methoxy-8-nitroquinoline with (I), following his conditions as closely as practicable (our palladium/barium sulfate catalyst was prepared by the method of Sabalitschka and Moses[3]), but we could not obtain any Plasmochin. A second Bergmann, patent[4] claims, but does not exemplify, the reductive condensation of (I) and (II).

Preparation of the Schiff base, 6-methoxy-8-(4'-diethylamino-1'-methylbutylidene)-aminoquinoline (III), was accomplished by Elderfield, *et al.*,[1] by the interaction of (I) and (II) using ethylbenzene as an entrainer to remove water, but condensation under these conditions was slow and far from complete. The Schiff base may be obtained in almost quantitative yield using the diethyl ketal of (I), instead of (I) itself, (*cf.* van Shelven[5]) by the procedure described[6] for 6-methoxy-8-amino-1,2,3,4-tetrahydroquinoline (IV). The Schiff base, without distillation, could then be reduced in ethyl acetate solution at 60° and 450 lb. hydrogen pressure in the presence of a platinum/charcoal catalyst, but the results were not consistent. Considerable improvement was effected by using an Adams platinum oxide catalyst[7] at the same pressure but at room temperature. Reproducible results were obtained and an 80% over-all yield (calculated on (II)) of distilled Plasmochin base was obtained on a production scale.

In our experience the reduction is very susceptible to minor changes in materials, catalyst or

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[1] Elderfield, Kreysa, Dunn and Humphreys, THIS JOURNAL, **70**, 40 (1948).

[2] British Patent 547,302.

[3] Sabalitschka and Moses, *Ber.*, **60**, 800 (1927).

[4] British Patent 547,301.

[5] British Patent 388,087, Example 32.

[6] Barber and Wragg, *J. Chem. Soc.*, 610 (1946).

[7] John, *J. Soc. Chem. Ind.*, **63**, 256 (1944).

reaction conditions and unless hydrogenation proceeds rapidly and smoothly, by-products are formed. In one explanation of the imidazole formation observed in their reductive condensations of (I) and (II), Elderfield and Kreysa[8] suggest that on reduction of the Schiff base (III), saturation of the pyridine ring occurs before substantial reduction of the azomethine linkage. This clearly requires qualification since under conditions now reported the reverse is the case. However, the more drastic hydrogenation conditions and the different catalyst used by Elderfield, *et al.*, might have caused the reaction to follow the alternative course. That these latter conditions led to extensive nuclear reduction is in accord with our experience since we used similar conditions except for the solvent employed, for making tetrahydro-Plasmochin and (IV), the published yield and analysis[6] of which have been overlooked by Elderfield, *et al.*[8]

It is of interest to note that Andersag also reports a failure to achieve more than a few per cent. yield of Plasmochin by the aminoketone route.[9]

A considerable part of this experimental work was carried out by H. G. Thompson and A. C. Benzie.

[8] Elderfield and Kreysa, THIS JOURNAL, **70**, 44 (1948).

[9] I. G. Elberfeld, *Jahresberichte*, 1940 (B. I. O. S. 116), Appendix 2).

RESEARCH LABORATORIES
MAY & BAKER LTD.
DAGENHAM, ESSEX
ENGLAND

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The Preparation of 1-(*p*-Nitrophenyl)-1,3-butadiene

BY E. C. COYNER AND G. A. ROPP[1]

In the continuation of a study[2] on Diels–Alder reactions with 1-aryl-1,3-dienes, 1-(*p*-nitrophenyl)-1,3-butadiene and its adduct with maleic anhydride have been prepared and characterized.

The diene was synthesized in two steps by a modification of the procedure described in a review[3] of German war-time investigations on extensions of the Meerwein[4] reaction.

$$CH_2{=}CH{-}CH{=}CH_2 + ClN_2C_6H_4NO_2\text{-}p \longrightarrow ClCH_2{-}CH{=}CH{-}CH_2C_6H_4NO_2\text{-}p + N_2$$

$$ClCH_2{-}CH{=}CHCH_2C_6H_4NO_2\text{-}p + KOH \longrightarrow CH_2{=}CH{-}CH{=}CHC_6H_4NO_2\text{-}p + KCl + H_2O$$

The chlorobutene, obtained in the first step, may be distilled successfully in small quantities under high vacuum, but it was found that this operation could be omitted as well as the removal of impurities, chiefly *p*-nitrophenol, from the chlorobutene by steam distillation. Actually, inclusion of these operations, as described in the Germany report, give only very low yields of diene, whereas the abbreviated procedure given in detail below resulted in a yield of 61% of purified product based on *p*-nitroaniline. Furthermore, the product is described in the German report as an oil, but in this work 1-(*p*-nitrophenyl)-1,3-butadiene was found to crystallize in yellow needles, m. p. 78.0–78.8°. It reacts readily with maleic anhydride and has been kept at room temperature in dark bottles for several months with no apparent decomposition.

Studies are now underway on the reactions of 1-(*p*-nitrophenyl)-1,3-butadiene with unsymmetrical dienophiles.

Experimental

1-(*p*-Nitrophenyl)-4-chloro-2-butene.—Technical *p*-nitroaniline was recrystallized once from ethanol and 140 g. (one mole) was dissolved in a hot solution of 240 cc. concentrated hydrochloric acid and 100 cc. of water. The solution was stirred rapidly and cooled in an ice–salt-bath. After 100 g. of ice was added, a solution of 70 g. of sodium nitrite in 120 cc. of water was run in during one hour while the temperature was kept between −4 and +4.5°. Stirring was continued for an additional twenty minutes and the reaction mixture was filtered. The filtrate was kept at 0° while it was added over a period of ninety minutes to a well-stirred mixture of 1 liter of acetone, 80 g. of sodium acetate dissolved in 100 cc. of water, 30 g. of cupric chloride dissolved in 50 cc. of water, and 130 cc. of liquid butadiene. The reaction mixture was maintained at −3 to +5° by means of an ice–salt-bath during the addition and was then allowed to warm to room temperature. Stirring was continued for an additional sixteen hours. One liter of ether was then added to extract the oily product, and the ethereal solution was separated, washed four times with 1-liter portions of water and dried over anhydrous magnesium sulfate. Removal of the solvent on the steam-bath gave 187.5 g. (88.6%) of crude 1-(*p*-nitrophenyl)-4-chloro-2-butene as a dark brown oil.

1-(*p*-Nitrophenyl)-1,3-butadiene.—The crude chlorobutene was dissolved in a solution of 500 cc. of ligroin and 500 cc. of benzene and treated with 5 g. of activated charcoal under reflux for two hours. The charcoal was removed by filtration, the solvents were evaporated on the steam-bath and the residual oil was dissolved in 400 cc. of methanol. This solution was then stirred at 15–33° while a solution of 112 g. of potassium hydroxide in 600 cc. of methanol was added over thirty minutes. Stirring was continued for an additional five minutes and the precipitated light yellow crystalline diene was removed by filtration; it was washed thoroughly with water and dried in a vacuum desiccator to give 76.5 g. of product, m. p. 75.0–76.8. The methanolic filtrate was added to 1200 cc. of water to precipitate 41.5 g. of less pure, dark brown product, which upon recrystallization from 400 cc. of ligroin gave 30 g. of light yellow crystalline diene, m. p. 75.5–76.8°. The total yield of product, m. p. 75.0–76.8° is therefore 106.5 g. (61% based on *p*-nitroaniline). A highly purified sample, m.p. 78.0–78.8°, was prepared by repeated recrystallizations from ligroin and from methanol.

Anal. Calcd. for $C_{10}H_9O_2N$: C, 68.56; H, 5.18. Found: C, 68.44, 68.44; H, 5.07, 4.96.

Adduct with Maleic Anhydride, 3-(*p*-Nitrophenyl)-1,2,3,6-Tetrahydrophthalic Anhydride.—A mixture of one-hundredth mole quantities of 1-(*p*-nitrophenyl)-1,3-butadiene (1.75 g.) and maleic anhydride (0.98 g.) was heated at 70° for fifteen minutes, during which time the melt solidified. The solidified cake was then heated under reflux with 3 cc. of xylene for ten minutes and cooled to room temperature. The solid product was re-

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[1] Research Corporation Fellow.

[2] For a previous publication see Coyner and Ropp, THIS JOURNAL, **69**, 2231 (1947).

[3] Müller, "The Action of Aromatic Diazo Compounds on Aliphatic Unsaturated Compounds," PB 737, Office of Technical Services, Department of Commerce, Washington, D. C.

[4] Meerwein, Buchner and van Emster, *J. prakt. Chem.*, **152**, 237–266 (1939).