TABLE I

MONOALKYL ETHYLENEDIAMINES AND SOLID DERIVATIVES

Base	B. p., °C.	Mm.	Yield,[a] %	Dipicrate M. p., °C., cor.	Dipicrate N, % Calcd.	Dipicrate N, % Kjeld.[b]	Dibenzamide M. p., °C., cor.	Dibenzamide N, % Calcd.	Dibenzamide N, % Kjeld.[b]	Disulfonamide M. p., °C. cor.	Disulfonamide N, % Calcd.	Disulfonamide N, % Kjeld.[b]
$CH_3—C_2H_7N_2$	115–116[c]	757	33	220[d]	21.05	20.98	112	9.93	9.92	94[e]	7.91	7.82
$C_2H_5—C_2H_7N_2$	129–131[f]	759	20	195[g]	20.51	20.36	120	9.46	9.47	126[h]	5.32	5.32
$C_6H_5CH_2—C_2H_7N_2$	100[i]	4	10	222[j]	18.42	18.36	188[k]	7.82	7.86	198[l]	4.76	4.75

[a] Over-all yield from ethylenediamine. [b] Reported analytical results are the averages of two or more determinations none of which differs from the theoretical by more than 0.15%. [c] 115–117°, *Ber.*, **70**, 979 (1937). [d] 220–222° decomp., THIS JOURNAL, **38**, 2135 (1916); 225° decomp., *Z. physiol. Chem.*, **174**, 119 (1928). [e] Dibenzenesulfonamide. [f] "About 130°," German Patent 446,547. [g] Precipitates as a solvate. After drying at 100° over phosphorus pentoxide for several hours, the picrate is distinctly lighter in color, melts higher and gives the correct analysis. [h] Di-*p*-bromobenzenesulfonamide. Recrystallized from absolute ethanol. [i] 162–165° at 20 mm., *Ber.*, **32**, 1829 (1899); 165° at 18 mm., *Rec. trav. chim.*, **54**, 594 (1935). [j] 222° decomp., *Ber.*, **32**, 1829 (1899). [k] 187°, *Rec. trav. chim.*, **54**, 594 (1935). [l] Di-*p*-bromobenzenesulfonamide. Recrystallized from glacial acetic acid.

in dilute ethanol and recrystallized from the same solvent. The amides were made from the appropriate acid chlorides by the Schotten–Baumann technique and were recrystallized from dilute ethanol except when otherwise stated.

The author is indebted to Mr. Samuel M. Raymond for some of the analytical data in this publication. The production of N-alkylated ethylenediamines by the reductive alkylation of monoacetylethylenediamine will be described in a forthcoming paper.

Summary

1. A practical synthesis for pure monoalkyl ethylenediamines has been developed.

2. The amines produced have been thoroughly characterized as solid derivatives.

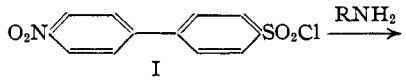
SWARTHMORE, PA. RECEIVED NOVEMBER 26, 1940

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY, MEDICAL SCHOOL OF BUENOS AIRES]

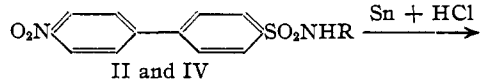
Sulfonamide. II.[1] Diphenyl Derivatives

BY ARMANDO NOVELLI AND J. C. SOMAGLINO[2]

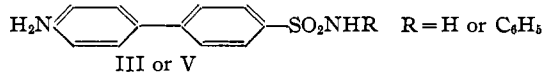
The appearance of a report by Van Meter and co-workers[3] prompts us to advance the publication of our results in the same field. By a method similar to that described by the above authors, we have prepared some derivatives, part of which we report here; we are not publishing details because they coincide along general lines. As we have prepared these compounds by another procedure as well, which also corroborates their structure, this experimental part is reported in detail. The reactions are summarized in the chart; we start from *p*-(*p*-nitrophenyl)-benzenesulfonyl chloride (I) and *p*-(*p*-nitrophenyl)-benzenesulfonamide (II) prepared according to Gabriel and Dambergis.[4]



I



II and IV



III or V

The aim of this work has been to determine whether, when amino and sulfonamide groups, fundamental in the action of sulfonamide as demonstrated by Fourneau and co-workers,[5] are found in different nuclei, they are still capable of maintaining their bactericidal effect. This is also interesting from a chemical point of view, because Le Fèvre and Turner[6] accept that in the molecule of diphenyl both of the nuclei are independent.

Besides the compounds described in this work, the derivatives 2-aminopyridine and 3-methyl-2-aminothiazole are being prepared (patent).

(1) First paper, *Ciencia*, **1**, 260 (1940).

(2) With a grant from the Asociacion Argentina para el Adelanto de las Ciencias.

(3) Van Meter, Bianculli and Lowy, THIS JOURNAL, **62**, 3146 (1940).

(4) Gabriel and Dambergis, *Ber.*, **13**, 1408 (1880).

(5) Fourneau, Tréfouel, Tréfouel, Nitti and Bovet, *Compt. rend. soc. biol.*, **122**, 652 (1936).

(6) Le Fèvre and Turner, *J. Chem. Soc.*, 246 (1928).

Experimental Part

***p*-(*p*-Aminophenyl)-benzenesulfonamide (III).**—To a suspension of 2 g. of *p*-(*p*-nitrophenyl)-benzenesulfonamide (m. p. 228°) in 100 cc. of ethanol are added 100 cc. of a solution of 20% hydrochloric acid and 4 g. of finely divided tin (excess). The mixture is heated on a steam-bath at a temperature not exceeding 55° until it is totally dissolved (approximately two hours). The solution is then poured off from the excess of tin and the clear solution is treated with hydrogen sulfide until the precipitation of tin is complete. It is then filtered and to the filtrate are added small quantities of sodium carbonate solution until the mixture is alkaline. The white precipitate is then gathered on a Buchner funnel, drained and dried. It is purified by crystallization from hot alcohol. The yield is 0.90 g. (51%), of white needles, m. p. 262–263° (dec.). The properties are described by Van Meter.[3] *Anal.* Calcd. for $C_{12}H_{12}N_2O_2S$: N, 11.29. Found: N, 11.30.

***p*-(*p*-Nitrophenyl)-benzenesulfon-N-phenylamide (IV).**—To 2.87 g. (0.0096 mole) of *p*-(*p*-nitrophenyl)-benzenesulfonyl chloride (m. p. 178°), is added 1.86 g. (0.02 mole) of aniline in 20 cc. of alcohol and shaken. The mixture is heated under reflux condenser at 60° for one hour. It is left to settle overnight and the crystalline precipitate which has formed is separated by filtration. The mother liquor is diluted with water and a small additional quantity of anilide is recovered. It is recrystallized from alcohol; yield 3.30 g. (94%); m. p. 182–183°. *Anal.* Calcd. for $C_{18}H_{14}N_2O_4S$: N, 7.90. Found: N, 7.80.

***p*-(*p*-Aminophenyl)-benzenesulfon-N-phenylamide (V).**—3.54 grams of *p*-(*p*-nitrophenyl)-benzenesulfon-N-phenylamide is suspended in 250 cc. of ethyl alcohol in a 500-cc. flask. A mixture of 30 cc. of hydrochloric acid and 45 cc. of water is added, and then 5 g. of finely divided tin. The mixture is heated under reflux at 55° until total solution is obtained (from four to five hours). The clear liquid is poured off from the residue and saturated with hydrogen sulfide. It is then filtered and the filtrate is evaporated on the water-bath at 50° to half volume. It is not convenient to concentrate more because oily drops separate. If this happens before concentration to the above volume the evaporation should be stopped and the oily product redissolved by addition of a small quantity of alcohol. Sodium carbonate is added until no more precipitation takes place. The precipitate is left to settle and is then filtered, washed and dried. The crude product (V) is purified by crystallization from hot alcohol. It crystallizes in slender silky white needles; yield, 1.20 g. (37%); m. p. 182–183°. *Anal.* Calcd. for $C_{18}H_{16}N_2O_2S$: N, 8.64. Found: N, 8.58.

Summary

The preparations of *p*-(*p*-aminophenyl)-benzenesulfonamide, *p*-(*p*-nitrophenyl)-benzenesulfon-N-phenylamide and *p*-(*p*-aminophenyl)-benzenesulfon-N-phenylamide are described.

BUENOS AIRES
REPUBLICA ARGENTINA RECEIVED DECEMBER 24, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

7-Methylcholanthrene and 1',5-Dimethyl-1,2-benzanthracene

BY W. E. BACHMANN AND S. R. SAFIR

In a previous paper[1] we described the preparation of 4- and 5-methylcholanthrene, utilizing the procedure which had been employed successfully in the synthesis of cholanthrene from 5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene.[2] The latter method offers considerable promise as a general procedure for the synthesis of isomeric methylcholanthrenes, and we have now extended it to the synthesis of 7-methylcholanthrene (V),[3] a new monomethyl derivative of the active carcinogen cholanthrene.

This methylcholanthrene, with its alkyl substituent in the 7-position, is particularly interesting because of its structural similarity to the potent carcinogen 3,4-benzpyrene. Both can be regarded as substitution products of the tetracyclic hydrocarbon, 1,2-benzanthracene. From this view 7-methylcholanthrene is a 1',5,10-trisubstitution product and benzpyrene is a 1',9-disubstitution product of the parent hydrocarbon. Thus the new methylcholanthrene contains part of the substitution of benzpyrene in addition to the cholanthrene nucleus. In a subsequent paper with Dr. Marvin Carmack the hydrocarbon 4',5-dimethylene-3,4-benzpyrene will be described which combines the complete structures of both cholanthrene and 3,4-benzpyrene.

The required ketone (I) was obtained recently from 4-methylphenanthrene.[4] This hydrocarbon was found to react with succinic anhydride in the 1- and 6-positions, and from one of the isomeric keto acids the ketone was prepared by the usual method of reduction and cyclization. The cyclic ketone was reduced by means of aluminum isopropoxide to the corresponding secondary alcohol (II), and the latter converted to the chloride by

(1) Bachmann and Chemerda, *J. Org. Chem.*, **6**, 50 (1941).
(2) Bachmann, *ibid.*, **3**, 434 (1938).
(3) The numbering system is that employed in the index of *Chemical Abstracts*.
(4) Bachmann and Edgerton, THIS JOURNAL, **62**, 2550 (1940).