could be identified was a fraction of 0.63 g. (49%) of 1,2-benzanthracene.

B. Preparation from the Ketone *via* Alumina.—A mixture of 1.0 g. of the ketone and 25 g. of alumina was heated at 240–270° under reduced pressure (1.0 mm.) for two hours. The yellow powder was then chromatographed[12] on alumina using a mixture of benzene and petroleum ether (1:4) as the eluent. A yellow fluorescent fraction was collected and rechromatographed on alumina using petroleum ether as the eluent. A colorless, blue fluorescent zone was eluted and concentrated. Crystallization from ethanol gave first colorless prisms, m.p. 193–200°, insoluble in concd. H_2SO_4, which were shown spectroscopically not to be the expected benzanthracene derivative. The analysis corresponds well to a dihydro-9-(2′,6′-dimethylphenyl)-1,2-benzanthracene.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.47; H, 6.56.

The second product of crystallization was colorless plates, m.p. 123.5°, soluble in concd. H_2SO_4 with the formation of a red solution which changed to blue and then to brown. The spectroscopic evidence[7] indicated that this was the expected hydrocarbon.

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.00; H, 6.25.

The remaining fractions could not be identified. The yield of 9-(2′,6′-dimethylphenyl)-1,2-benzanthracene was 6.0%.

Other hydrocarbons, first prepared by acid cyclization[4,6,7] but now prepared by the alumina method, are listed together with the yields.

Compound III	Yield, %	Compound V	Yield, %
R,R′,R″ = H	99	R,R′ = H	74
R = 2′-CH_3; R′,R″ = H	82	R = 2′-CH_3; R′ = H	42
R = 3′-CH_3; R′,R″ = H	92	R = 3′-CH_3; R′ = H	80
R = 4′-CH_3; R′,R″ = H	96	R,R′ = 2′,4′-dimethyl	75
		R,R′ = 2′,5′-dimethyl	46
		R,R′ = 3′,4′-dimethyl	68

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

Reduction and Benzylation by Means of Benzyl Alcohol. II. N-Benzylation. The Preparation of Secondary Aromatic Benzylamines

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A method is described for the monobenzylation of aromatic amines. It consists in heating the amine with benzyl alcohol in the presence of potassium hydroxide and distilling off the water as it is formed. The reaction is accelerated by the addition of benzaldehyde. With bi-primary amines, each amino group is monobenzylated. The method is also suitable for the preparation of benzylaminopyridines.

It has been reported in part I of this series[1] that fluorene and its derivatives are readily benzylated in the 9-position by heating with benzyl alcohol in the presence of potassium hydroxide. The present paper reports the N-benzylation of a variety of primary aromatic amines (Table I) by a modification of this procedure[2] in which equilibrium (1) is forced to the right by distilling off the by-product water as it forms.

$$C_6H_5NH_2 + C_6H_5CHO \rightleftharpoons C_6H_5N{=}CHC_6H_5 + H_2O \quad (1)$$

$$C_6H_5N{=}CHC_6H_5 + C_6H_5CH_2OH \longrightarrow C_6H_5NH{-}CH_2C_6H_5 + C_6H_5CHO \quad (2)$$

Under these conditions it is to be expected that the potassium hydroxide would be converted to potassium benzylate.[3] A closely related procedure using xylene as a solvent and ordinarily employing a U.O.P. nickel catalyst has been published recently,[4] and an earlier paper[5] describes N-alkylation of aniline using dry alkoxides of aliphatic alcohols.

In certain cases (Table I) it is advantageous to accelerate the reaction by adding a small amount of benzaldehyde.[6] This may be correlated with the reported acceleration by benzalaniline and with the interpretation of the function of the U.O.P. nickel.[4] The rate of reaction may also be increased by the use of a higher concentration of potassium hydroxide.

The data of Table I emphasize the variety of primary aromatic amines which are readily benzylated in high yield by this method. It is noteworthy that α-aminopyridines react as readily, although alkylation of these amines by benzyl halides often gives 1-benzyl-2-pyridoneimines.[7]

Experimental

Materials.—All amines used were commercial products, employed without purification, with the exception of the following, which were redistilled *in vacuo:* *o*-toluidine, *m*-toluidine and *m*-phenylenediamine.

Apparatus and Procedure.—The apparatus used consisted of a flask equipped with a separator and a thermometer. As the usual type of trap for separating heavy liquids from water proved inefficient, use was made of the funnel commonly employed for the preparation of alkyl iodides.[8] A "cold finger" passing through its neck and reaching to its bottom served both to condense vapors coming through its side arm and to cool the condensed liquid. To avoid occlusion of water in the narrow depression of the bottom at the beginning of condensation, a few drops of benzyl alcohol were filled into the funnel before reaction was started. The reaction flask was supplemented with a dropping funnel in experiments where benzaldehyde was added during the reaction.

After the reactants had been placed in the flask, the mixture was heated rapidly and kept boiling sufficiently vigorously to enable vapors to condense in the funnel at a moderate rate. The tap of the funnel was opened from time to time to allow the lower layer of the distillate, which consisted of benzyl alcohol, to return to the flask. The benzaldehyde,

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(1) Y. Sprinzak, THIS JOURNAL, **78**, 466 (1956).

(2) Y. Sprinzak, Israeli Pat. 6492 (April 8, 1953); Brit. Pat., 726545 (Jan. 27, 1953).

(3) A. Wacker, French Patent 653818 (May 3, 1928); *Chem. Zentr.*, **100**, **I**, 3036 (1929).

(4) E. F. Pratt and E. J. Frazza, THIS JOURNAL, **76**, 6174 (1954).

(5) J. U. Nef, *Ann.*, **318**, 137 (1901).

(6) *Cf.* reference 1.

(7) A. E. Tschitschibabin, R. A. Konowalowa and A. A. Konowalowa, *Ber.*, **54**, 814 (1921); Th. M. Sharp, *J. Chem. Soc.*, 1855 (1939); J. H. Biel, THIS JOURNAL, **71**, 1306 (1949).

(8) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 285; H. S. King, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 399.

diluted with a sevenfold volume of benzyl alcohol, was added to the boiling mixture in three portions, the first addition made when the temperature of the liquid had risen to a stationary value (about 200° for the monoamines and 225° for the phenylenediamines) after the distillation of some water; the other two portions were added at intervals of about 10 minutes for the monoamines and 7 minutes for the phenylenediamines. Heating was interrupted shortly after water had ceased to appear in the distillate (about 250°), the end temperature varying, somewhat arbitrarily, between 250 and 280°.

With higher-boiling amines, where little benzyl alcohol accompanies the distilling water, the procedure may be modified by replacing the funnel by a Vigreux column and collecting the distillate in the usual manner.

About an equal volume of water was added to the cooled reaction mixture and the crystallized product filtered, washed with water and dried. Liquid products were diluted with ether, separated, washed well with water, dried over sodium sulfate and distilled *in vacuo*.

The results of the benzylation experiments are presented in Table I. No attempt has been made to determine optimum conditions with respect to concentrations, rapidity of distillation and rate of supply of benzaldehyde. Benzyl alcohol was used in 28 to 85% excess[9] of the theoretical amount. Potassium hydroxide was usually used in a concentration of 6 to 8% with regard to benzyl alcohol. To speed up the benzylation of lower-boiling amines, the expedient of adding benzaldehyde was used in preference to that of increasing the hydroxide concentration. (The figures given for benzyl alcohol include the quantity used to dilute the aldehyde). The sixth column of Table I gives the temperature at which reaction was stopped, and the seventh column, the duration of the reaction from the beginning of boiling. The eighth column gives the yields of benzylated products, as obtained by filtering the cooled reaction mixture and washing with water, or, for liquid compounds, by distilling *in vacuo*. The yields recorded for N-benzylaniline include a few per cent. recovered from the filtrate of the reaction mixture. Thus, in the first experiment 87% was obtained by filtering at room temperature and 7% was collected from the ice-cooled filtrate. The degree of purity of the crystalline products was indicated by the fact that the rise in melting point brought about by recrystallization did not exceed two degrees in all but two cases. The per cent. yields of purified products, ordinarily obtained by recrystallization from alcohol, are exemplified by the following typical cases: *o*-benzylaminotoluene, 92; *p*-benzylaminoanisol, 74; *p*-dibenzylaminobenzene, 88; 2-benzylaminodiphenyl, 91; *p*-benzylaminodiphenylamine, 91; *α*-benzylaminonaphthalene, 90; 1,5-dibenzylaminonaphthalene, 96 (from toluene); 2-benzylamino-4-methylpyridine, 93 (from 70% alcohol).

The melting points or boiling points of known compounds agreed satisfactorily with the literature values, with the exception of *p*-benzylaminoanisole, for which Mailhe[10] gives a melting point of 64–65°, as compared with 49.5–50° for our product and 52° recorded by Frohlich and Wedekind.[11] All nitrogen values checked well with the calculated figures.[12]

The following compounds would appear to be new.[13]

o-**Benzylaminobiphenyl**: m.p. 90–91° (from alcohol). *Anal.* Calcd. for $C_{19}H_{17}N$: N, 5.40. Found: N, 5.41.

p-**Benzylaminobiphenyl**: m.p. 94–94.5° (from alcohol). *Anal.* Calcd. for $C_{19}H_{17}N$: N, 5.40. Found. N, 5.37.

p-**Benzylaminodiphenylamine**. m.p. 74–75° (from alcohol). *Anal.* Calcd. for $C_{19}H_{18}N_2$. N, 10.22. Found: N, 10.21. The same structure was attributed by Heucke[14] to a substance of melting point 124°, formed by reduction of *p*-benzalaminodiphenylamine with sodium and alcohol. We were unable to obtain this compound by his method. The identity of our product was checked by comparison with a sample obtained by hydrogenating the benzal derivative (prepared according to Heucke) in alcohol solution and at room temperature in the presence of 2% Pd on $BaSO_4$.

TABLE I

Amine	Amine, g.	Benzyl alcohol, g.	KOH, g.	Benzaldehyde, g.	Final temp., °C.	Time of reac. (min.)	Yield, % of benzylated product
Aniline	46.5	70	4	2	260	46	94
Aniline	46.5	70	12	..	260	55	91
Aniline	46.5	70	4	..	260	138	92
o-Toluidine	53.5	70	5	2.5	265	77	94
m-Toluidine	53.5	70	5	2	250	75	92
p-Toluidine	53.5	70	5	2.5	268	48	89
2,4-Dimethylaniline	40.3	54	12	..	278	53	87
p-Chloroaniline	32.0	50	4	..	235	60	85
p-Anisidine	41.0	45	3	0.7	261	35	82
o-Aminobiphenyl	84.5	80	12	..	279	42	98
p-Aminobiphenyl	28.2	30	2.5	..	271	13	100
p-Aminodiphenylamine	46.0	50	4	..	255	77	95
α-Naphthylamine	35.8	40	3	..	267	15	95
β-Naphthylamine	35.8	40	3	..	264	22	92
m-Phenylenediamine	36.0	95	8	0.7	270	30	97
p-Phenylenediamine	36.0	100	8	1.3	254	37	96
p,p'-Diaminodiphenylmethane	49.5	85	5	..	263	60	99
p,p'-Diaminophenyl ether	50.0	85	5	..	245	110	94
1,5-Diaminonaphthalene	39.5	90	5	..	252	100	98
2-Aminopyridine	31.4	50	3	..	250	14	93
2-Amino-4-methylpyridine	36.0	46	5	..	266	26	97
2,6-Diaminopyridine	36.3	100	5	..	245	47	96

m-**Dibenzylaminobenzene**: m.p. 71.5–72.5° (from alcohol). *Anal.* Calcd. for $C_{20}H_{20}N_2$: N, 9.72. Found: N, 9.80.

p,p'-**Dibenzylaminodiphenylmethane**: m.p. 118–119° (from benzene–heptane 1:1). *Anal.* Calcd. for $C_{27}H_{26}N_2$: N, 7.41. Found: N, 7.37.

p,p'-**Dibenzylaminophenyl ether**: m.p. 99.5–100° (from alcohol). *Anal.* Calcd. for $C_{26}H_{24}N_2O$: N, 7.36. Found: N, 7.39.

1,5-Dibenzylaminonaphthalene: m.p. 186.5–188° (from toluene). *Anal.* Calcd. for $C_{24}H_{22}N_2$: N, 8.28. Found: N, 8.40.

2-Benzylamino-4-methylpyridine: m.p. 97–98° (from 70% alcohol). *Anal.* Calcd. for $C_{13}H_{14}N_2$: N, 14.14. Found: N, 14.01.

2,6-Dibenzylaminopyridine, m.p. 72° (from alcohol). *Anal.* Calcd. for $C_{19}H_{19}N_3$: N, 14.53. Found: N, 14.17.

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[9] Not discounting the amount necessary to form potassium benzylate.

[10] A. Mailhe, *Bull. soc. chim. France*, [4], **29**, 106 (1921).

[11] E. Frohlich and E. Wedekind, *Ber.*, **40**, 1009 (1907).

[12] Most of the analyses were performed by Mr. W. Manser, Federal Institute of Technology, Zurich.

[13] Melting points are corrected.

[14] C. Heucke, *Ann.*, **255**, 189 (1889).