IODINE AS A CATALYST IN REACTIONS INVOLVING ELIMINATION OF HYDROGEN HALIDES.

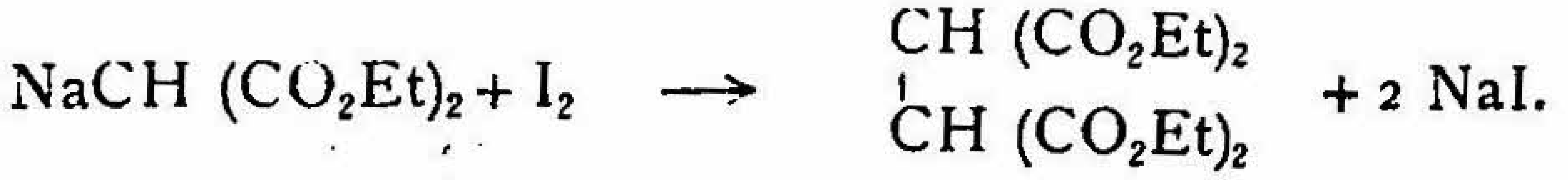
By R. D. Desai.

Iodine is used as a condensing agent either for removing hydrogen or metals in the form of their compounds with iodine, or as a purely catalytic agent when only small amounts are required.

Well-known examples of the first type of reaction are :—

(*a*) The condensation of benzyl cyanide to dicyanostilbene ; $C_6H_5{\cdot}CH_2{\cdot}CN + 4I \longrightarrow C_6H_5{\cdot}C\,(CN) : C\,(CN){\cdot}C_6H_5 + 4HI.$

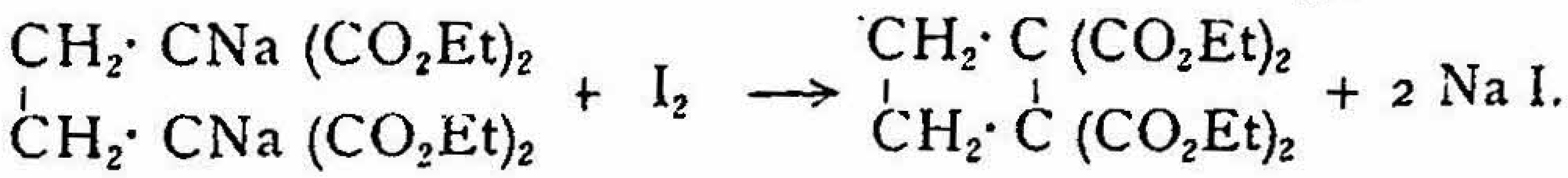
(*b*) The condensation of ethyl sodio-malonate to ethyl ethanetetracarboxylate :



$$NaCH\,(CO_2Et)_2 + I_2 \longrightarrow \begin{array}{l} CH\,(CO_2Et)_2 \\ | \\ CH\,(CO_2Et)_2 \end{array} + 2\,NaI.$$

(*c*) The formation of ethyl diacetylsuccinate from ethyl sodio-acetoacetate :

(*d*) The production of *cyclo*paraffin carboxylic esters by the action of iodine on disodio-derivatives of certain esters,[1] e.g.,



$$\begin{array}{l} CH_2{\cdot}\,CNa\,(CO_2Et)_2 \\ | \\ CH_2{\cdot}\,CNa\,(CO_2Et)_2 \end{array} + I_2 \longrightarrow \begin{array}{l} CH_2{\cdot}\,C\,(CO_2Et)_2 \\ |\quad\;\;| \\ CH_2{\cdot}\,C\,(CO_2Et)_2 \end{array} + 2\,Na\,I.$$

Its use as a catalytic agent was apparently first demonstrated by Hugo Müller,[2] who was able to show that it acts as an excellent halogen carrier in the halogenation of organic compounds, and its usefulness in this direction has been proved by many subsequent workers.[3]

Its use technically as a catalyst in the preparation of carbon tetrachloride from carbon disulphide has been patented.[4]

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[1] Perkin, *Ber.*, 1886, 19, 2041.

[2] *J. Chem. Soc.*, 1862, 15, 41.

[3] Beilstein and Geitner, *Annalen*, 1866, 139, 326 ; Limpricht, *ibid.*, 326 ; Hubuer and Majert, *Ber.*, 1873, 6, 790 ; Krafft and Merz, 1875, 8, 1296 ; Ruoff, 1876, 9, 1483 ; Krafft, 1877, 10, 801 ; Krüger, 1885, 18, 1755 ; Kluge, 1885, 18, 2099 ; Koch, 1890, 23, 2319 ; Wohlrath, *Zeit. Chem.*, 1866, 488 ; Kade, *J. Pr. Chem.*, 1879, [11], 19, 462.

[4] Eng. Pat., 18890 of 1899, cf. also Helfrich and Reid, *J. Amer. Chem. Soc.*, 1921, 43, 593.

In 1914 Knoevenagel[1] drew attention to its value as a catalyst in condensations in which water, hydrogen sulphide or ammonia is evolved, e.g.,

$$C_6H_5{\cdot}NH_2 + CH_3{\cdot}OH \longrightarrow C_6H_5{\cdot}NH{\cdot}CH_3 + H_2O.$$

$$C_6H_5{\cdot}NH_2 + CO\,(C_6H_5)_2 \longrightarrow C_6H_5{\cdot}N:\ C\,(C_6H_5)_2 + H_2O.$$

$$C_6H_5{\cdot}NH{\cdot}C_6H_5 + S \longrightarrow C_6H_4\left\langle\begin{matrix}NH\\S\end{matrix}\right\rangle C_6H_4 + H_2S.$$

$$C_6H_5{\cdot}NH_2 + C_{10}H_7{\cdot}NH_2 \longrightarrow C_6H_5{\cdot}NH{\cdot}C_{10}H_7 + NH_3.$$

A year later Hibbert[2] showed that it is a most efficient catalyst in promoting the dehydration of hydroxy-compounds and studied its use in the conversion of alcohols into unsaturated hydrocarbons and of ketonic alcohols into unsaturated ketones; also its use in the conversion of glycols and glycerols into polyglycols and polyglycerols and in the condensation of aldehydes with polyhydric alcohols.

According to Heinemann[3] it acts catalytically in promoting the sulphonation of benzene. Concentrated acid in the presence of a little iodine appears to have much the same effect as fuming acid. This reaction has been studied in detail by Rây and Dey[4] and they state that iodine acts as a positive catalyst in the sulphonation of aromatic compounds and the reaction proceeds smoothly when hydroxy-, amino-, chloro-, bromo-, or carboxy-groups are contained in the molecule, but not in the presence of nitro or sulphonic constituents. These results, however, have not been confirmed by subsequent workers.[5]

Yanagisawa and Kondô[6] state that a 70 per cent. yield of coumarin can be obtained from salicylaldehyde, acetic anhydride and sodium acetate in the presence of about 2 per cent. of iodine (calculated on the weight of aldehyde) whereas in the absence of iodine the yield is only 27 per cent.

When diphenylamine and carbon tetrachloride were heated on the water bath with a trace of iodine, the formation of a dark blue precipitate was noticed and this was shown to be triphenylpararosaniline hydrochloride or aniline-blue. In the absence of iodine no trace of colouring matter was formed thus proving the catalytic effect of the halogen. As this reaction pointed to the activation of the reaction between aliphatic halogen derivatives and amines by means

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[1] *J. Pr. Chem.*, 1914, [ii] 89, 1, cf. *This Journal*, 1922, 5, 29; Delacre, *Bull. Acad. Roy. Belg.*, 1900, 64, 68.

[2] *J. Amer. Chem. Soc.*, 1915, 37, 1748.

[3] Eng. Pat. 12260 of 1915; *J. Soc. Chem. Ind.*, 1916, 35, 1008.

[4] *J. Chem. Soc.*, 1920, 117, 1405.

[5] Auger and Vary, *Compt. rend.*, 1921, 173, 239.

[6] *J. Pharm. Soc. Japan*, 1921, No. 472, 498.

of iodine, an examination was made of the literature, but no reference to the use of iodine in similar reactions could be found and hence a systematic study of this type of reaction was begun.

The reactions so far studied are :—

I. Formation of monobenzylaniline from aniline and benzyl chloride.

II. Formation of dibenzylaniline.

III. Action of benzyl chloride on diphenylamine.

IV. Action of carbon tetrachloride on diphenylamine.

V. Action of benzyl chloride on diethyl- and dimethyl-aniline.

VI. Action of chloro-, bromo- and iodo-benzene on aniline.

EXPERIMENTAL.

I. Formation of Monobenzylaniline.

Several experiments were made under the following conditions :— Two molecules of aniline (9·3 grams) were heated with 1 molecule of benzyl chloride, at a given temperature and for a specified time, in a small round-bottom flask. In one set of experiments no iodine was added and in the other set iodine equal to 1 per cent. of the weight of the aniline was used. At the end of the given time 50 cc. of water and 15 cc. of concentrated hydrochloric acid were added and the solution cooled to 15-20° when the great bulk of the benzylaniline hydrochloride separated and was removed, washed with 10-15 cc. of water, dried and weighed.

The filtrate was extracted with ether to remove unaltered benzyl chloride and then made alkaline and again extracted with ether to remove aniline and small amounts of benzylaniline. After drying and removal of the ether, both the benzyl chloride and recovered bases were weighed and distilled. The greater portion of the base was aniline boiling at 180-182° under 686 mm. pressure, but a small amount of residue—usually about 0·14 gram—was obtained and this was taken as benzylaniline and included with that obtained from the sparingly soluble hydrochloride.

The results of four pairs of experiments are given in Table I.

TABLE I.

Formation of Monobenzylaniline.

a = 1·0 per cent. of iodine. *b* = no iodine.

Experiment No.	Time in minutes	Temperature deg. cent.	Grams of benzylaniline	Percentage yield of theoretical
1 *a*	10	50	5·36	49
1 *b*	10	50	2·97	27
2 *a*	10	50	4·62	42
2 *b*	10	50	2·40	22
3 *a*	30	30	3·05	28
3 *b*	30	30	2·04	19
5 *a*	30	30	3·15	29
5 *b*	30	30	2·34	21

The results indicate that iodine has a slight catalytic activity in promoting the formation of benzylaniline from benzyl chloride and aniline. The positive effect, however, is not nearly so marked as in some other reactions which have been studied.

II. Formation of Dibenzylaniline.

The method of procedure was similar to that already described with the exception that the aniline and benzyl chloride were used in molecular proportions. The crystalline hydrochloride obtained was usually a mixture of the salts of mono-and di-benzylanilines and the estimation of the percentages of each was necessary. A good separation can be effected by crystallisation of the mixed free bases from 70 per cent. (by volume) alcohol, as the monobenzyl derivative is readily soluble in the cold solvent and most of the dibenzylated base crystallises on cooling in slender needles melting at 66·8–67°. A more accurate method is that due to Noelting,[1] and consists in dissolving a known weight of the mixed hydrochlorides in hydrochloric acid and alcohol, adding sodium nitrite at 0–3° until excess of nitrous acid is indicated by potassium iodide-starch paper and extracting the nitrosamine derived from the secondary base by means of ether and weighing it.

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[1] *Ber.*, 1877, 10, 795.

TABLE II.

Formation of Dibenzylaniline.

No. of Experiment	Time in hours	Temp. in degrees centigrade	Percentage of iodine on weight of aniline	Grams of anhydrous sodium acetate	Grams of Aniline	Grams of Benzyl chloride	Benzyl chloride recovered	Weight of mixture of bases obtained		Percentage of dibenzyl-aniline
							in grams	*Mono-*	*Dibenzyl.*	
1*a*	6	97	1·0	8·5	8·93	6·55	0·38	0·56	12·93	95·0
1*b*	6	97	1·0	0	8·64	6·45	1·65	4·49	6·4	47·0
1*c*	6	97	0	0	8·78	6.52	2·92	8·35	1·49	11·0
2*a*	6	97	1·0	8·5	9·24	6·34	0·24	0·15	13·37	98·4
2*b*	6	97	1·0	0	9·28	6·32	1·59	4·79	6·54	48·2
2*c*	6	97	0	0	9·20	6·32	2·86	8·11	1·47	10·9
3*a*	3	97	1·0	9·5	6·09	17·0	0·20	0	17·80	99·0
3*b*	3	97	1·0	9·5	5·86	16·80	0	0	17·10	99·0
4*a*	2	97	1·0	9·0	5·25	16·60	2·60	1·31	11·83	71·7
4*b*	2	97	1·0	9·0	5·66	14·30	1·55	2·26	12·80	70·6
5*a*	2	97	0·5	9·0	4·24	10·10	1·62	2·08	8·65	70·1
5*b*	2	97	0·5	9·0	4·27	12·90	2·01	1·70	8·78	69·8
6*a*	2	97	0·4	8·8	4·64	12·60	3·14	5·53	6·01	44·0
6*b*	2	97	0·4	8·8	4·60	12·60	3·21	5·63	5·86	43·1
7*a*	3	97	0·5	8·5	4·61	12·70	0	0·11	13·38	98·3
7*b*	3	97	0·5	0*	4·66	12·64	4·75	5·44	3·42	25·0
7*c*	3	97	0	8·5	4·65	12·66	3·15	4·56	6·84	50·5
8*a*	6	97	0	8·3	4·62	12·63	1·34	1·61	11·78	86·9
8*b*	6	97	0	8·5	4·60	12·61	1·30	1·67	11·63	86·0
9*a*	7	97	0	8·5	4·62	12·62	0·35	0·16	13·34	98·4
9*b*	7	97	0	8·5	4·61	12·60	0·30	0·16	13·32	98·3

* 9·7 Grams of Sodium Carbonate.

The amounts of monobenzylaniline in the mixture of salts given in Table II were all determined by this method.

In the course of the experiments it was found that the addition of sodium acetate to a mixture of benzyl chloride and aniline facilitated the formation of the tertiary base and that the addition of a small amount of iodine to such a mixture was very marked.

The results of the experiments are recorded in Table II.

The results show :—

(*a*) That 1·0 per cent. of iodine has a distinct positive catalytic effect on the dibenzylation of aniline. Compare experiments 1 *b* and 1 *c*, 2 *b* and 2 *c*.

(*b*) That anhydrous sodium acetate has a marked effect in increasing the yield of tertiary base. Compare experiments 1 *a* and 1 *c*, 2 *a* and 2 *c*, 1 *c* and 7 *c*. The sodium acetate cannot be replaced by alkalis such as sodium or potassium carbonate.

(*c*) That the best results are obtained with 2 molecular proportions of anhydrous sodium acetate and 0·5 per cent. of iodine. When such a mixture is heated at 97° for 3 hours a quantitative yield of dibenzylaniline is obtained.

This is interesting when compared with the older methods given in the literature. Matzudaira,[1] who was the first to prepare the tertiary base, recommends heating for several weeks on the water-bath a mixture of aniline and benzyl chloride with powdered sodium hydroxide and a subsequent method[2] consists in heating aniline (1 mol.) benzyl chloride (2 mols.) and sodamide (2 mols.) on the water-bath until ammonia ceases to be evolved, but does not specify the time required.

III. Formation of Benzyldiphenylamine.

The tertiary base, benzyldiphenylamine, $C_6H_5{\cdot}CH_2{\cdot}N(C_6H_5)_2$, was first prepared by Bernthsen and Trompetter[3] by the reduction of diphenylthiobenzamide with zinc dust and hydrochloric acid :

$$C_6H_5{\cdot}CS{\cdot}N(C_6H_5)_2 + 4H \longrightarrow C_6H_5{\cdot}CH_2{\cdot}N(C_6H_5)_2 + H_2S$$

They give the melting point as 86·5–87°. More recently Meunier and Desparmet[4] have prepared it by heating equimolecular quantities of diphenylamine and benzyl chloride in the presence of sodamide.

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[1] *Ber.*, 1887, 20, 1611.

[2] D. R. P. 301, 450 and 301, 832.

[3] *Ber.*, 1878, 11, 1761.

[4] *Compt. rend.*, 1907, 144, 273.

The results of a series of experiments on the condensation of diphenylamine and benzyl chloride in the presence of anhydrous sodium acetate and a small amount of iodine are given in Table III.

TABLE III.

Formation of Benzyldiphenylamine.

Temperature 105—110°

No. of Experiment	Time in hours	Percentage of iodine on the weight of diphenylamine taken	Grams of anhydrous sodium acetate	Grams of diphenyl-amine	Grams of benzyl chloride	Grams of benzyl-diphenyl-amine	Percentage yield of benzyl-diphenyl-amine
1*a*	3	0·5	2·1	4·29	3·04	2·62	40·0
1*b*	3	0·5	0	4·11	3·12	1·76	28·0
1*c*	3	0	0	4·04	3·10	0·75	12·1
2*a*	6	0·5	2·1	4·25	3·20	4·54	70·0
2*b*	6	0·5	2·1	4·30	3·15	4·55	69·1
2*c*	6	0	0	4·28	3·10	1·52	23·2
3*a*	8	0·5	2·1	4·22	3·12	5·81	90·0
3*b*	8	0·5	2·1	4·20	3·15	5·76	89·5
3*c*	8	0	0	4·15	3·20	1·94	30·5
4*a*	10	0·5	17·0	33·8	25·3	48·57	93·5
4*b*	10	0·5	16·8	32·5	25·0	46·20	94·0

The general method of procedure was as follows. Equimolecular quantities of diphenylamine and benzyl chloride were heated at 105–110° for a given time, with or without addition of anhydrous sodium acetate and iodine; the mass was then poured into hydrochloric acid (1:4) and the solution cooled with ice and allowed to stand for 2 hours. The condensation product and excess of diphenylamine were removed by suction on a Büchner funnel and washed with 70 per cent. alcohol to remove the secondary base. The tertiary base was obtained pure by one crystallisation from hot 70 per cent. alcohol. In one experiment starting with 33·8 grams of diphenylamine, 48·5 grams of condensation product were obtained after washing with 25 cc. of cold 70 per cent. alcohol and after crystallisation from 125 cc. of hot 70 per cent. alcohol two crops of crystals weighing 45·8 grams and melting at 86·5–87° were obtained and a third crop melting at 82–86° and weighing 1·6 grams.

The results show that at 105–110° benzyl chloride and diphenylamine react slowly, but even after 8 hours the yield of tertiary base is only 30 per cent. of the theoretical. The addition of 0·5 per cent. of iodine, as shown by a comparison of experiments 1 *b* and 1 *c*, increases the yield and the addition of both anhydrous sodium acetate (1 mol.) and iodine (0·5 per cent.) produces marked acceleration, so that at the end of 8 to 10 hours the yield is 90–94 per cent. of the theoretical.

Benzyldiphenylamine crystallises from alcohol in slender, colourless needles melting at 88·0–88·5°, and is readily soluble in ether, benzene, acetone and light petroleum, but only sparingly soluble in cold alcohol or glacial acetic acid. The base gradually turns green in contact with the air. It is characterised by giving an intense blood-red coloration with concentrated sulphuric acid and a drop of nitric or nitrous acid (C = 87·9, H = 6·85 and N = 5·61 ; $C_{19}H_{17}N$ requires C = 88·0, H = 6·56 and N = 5·41 per cent.).

As no derivatives of the base appear to be mentioned in the literature the following have been prepared.

Hydrochloride, $C_{19}H_{17}N$, HCl, is obtained in the form of small colourless needles by passing hydrogen chloride into a solution of the base in light petroleum. It is hygroscopic, has no definite melting point and the hydrogen chloride can be estimated directly by titration with standard sodium hydroxide using phenol-phthalein as indicator (HCl = 12·37 ; theory requires 12·36 per cent.).

Platinichloride, $2C_{19}H_{17}N$, H_2PtCl6, separates from alcoholic solution is a fine, orange-yellow precipitate which turns green when kept. It has no definite melting point (Pt = 20·7 ; theory requires 21·1 per cent.).

Definite compounds with *s*-trinitrobenzene or picric acid could not be obtained.

Nitrobenzyldiphenylamine, $NO_2 \cdot C_{19}H_{16}N$.—After several trial experiments, the following process was found to give a 60 per cent. yield of the mono-nitro-derivative. 5 grams of benzyldiphenylamine are dissolved in 150 grams of glacial acetic acid, the solution cooled to 15° and 1·5 grams of fuming nitric acid (D = 1·52) diluted with 20 grams of glacial acetic acid are run in drop by drop from a separating funnel. In order to obtain a good yield and avoid the formation of tarry matter, it is necessary to keep the mixture well stirred and to maintain the temperature below 20°. At the end of 1·5 hours the reaction is complete as shown by adding a drop of the mixture to water, when the product settles as a yellow mass and the water becomes intensely yellow. The mass is then poured into water, filtered, dried and ground in a mortar. The dry powder is extracted three times with 5 grams of acetone, in order to remove resin. After each treatment the acetone layer is removed by suction and a residue of 3·62 grams of crude nitro-derivative melting at 153–157° is obtained. The pure compound melting at 163° is isolated in the form of yellow prismatic needles after one crystallisation from warm acetone.

0·2556 gram gave 24·1 cc. of nitrogen at 26·5 and 666 mm. N = 9·47 : $C_{19}H_{16}O_2N_2$ requires 9·21 per cent.

Matzudaira[1] has already shown that when dibenzylaniline is nitrated the nitro-group enters the phenyl radical attached to nitrogen and not one of those attached to carbon, and also that the position taken up is the one *para* to the nitrogen atom. In all probability, therefore, the mono-nitro-derivative of benzyldiphenylamine is a *para*-nitro-compound with the nitro-group in one of the phenyl groups attached to nitrogen. That this view is correct is proved by the following considerations :

1. *p*-Nitrobenzyldiphenylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(C_6H_5)_2$, prepared by condensing *p*-nitrobenzyl chloride with diphenylamine is quite different from the product obtained by nitrating benzyldiphenylamine.

2. As a rule tertiary amines containing a benzyl radical are decomposed when heated with acetic anhydride yielding benzyl acetate and the acetyl derivative of the secondary amine.[2] Attempts to decompose the nitrated tertiary amine either by boiling with acetic anhydride or by heating with the reagent in sealed tubes at 180–190° proved fruitless, but when the nitro-compound is reduced and the resulting primary amine is heated with an excess of concentrated hydrochloric acid at 170–175° it yields *p*-aminodiphenylamine and benzyl chloride. The former can be identified by conversion into its mono-acetyl derivative[3] melting at 158°, and the latter by conversion into dibenzylaniline.

p-Nitrobenzyldiphenylamine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(C_6H_5)_2$. *p*-Nitrobenzyl chloride was prepared by a slight modification of the method described by Alway,[4] *viz.*, by adopting mechanical stirring. By this method the time is reduced from 2·5 to 1·8 hours and the yield increased from 50 to 66 per cent. It crystallises from alcohol in yellowish white prismatic needles melting at 71°, and condenses, when heated for 12 hours at 95–100° with diphenylamine in the

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[1] *Ber.*, 1887, **20**, 1611.

[2] Tiffeneau, *Bull. Soc.*, 1911, [iv], **9**, 828 ; Douetteau, 1912, [iv], **11**, 654.

[3] Nietzki and Witt, *Ber.*, 1879, **12**, 1402.

[4] *J. Amer. Chem. Soc.*, 1902, **24**, 1060.

presence of anhydrous sodium acetate (1 mol.) and a trace of iodine, to *p*-nitrobenzyldiphenylamine, which crystallises from alcohol in lustrous, yellow plates melting at 93·5°. The yield is 70 per cent. of the theoretical and the compound dissolves readily in most organic solvents with the exception of light petroleum. 0·2174 gave 20·1 cc. of nitrogen at 26° and 668 mm. N = 9·35. $C_{19}H_{16}O_2N_2$ requires 9·21 per cent.

p-Aminobenzyldiphenylamine, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(C_6H_5)_2$, is readily obtained by reducing a solution of the nitro-compound in alcoholic hydrochloric acid (5:1) with zinc dust. It is deposited as the zinc double chloride when the alcohol is removed and the solution diluted. The free base is a viscid oil which darkens in contact with the air.

The *acetyl derivative*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(C_6H_5)_2$, crystallises from 50 per cent. alcohol in minute colourless needles melting at 165-166°. 0·1366 gave 12·1 cc. of nitrogen at 26° and 668 mm. N = 8·90; $C_{21}H_{20}ON_2$ requires 8·86 per cent.

The *benzoyl derivative*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(C_6H_5)_2$, obtained by the action of benzoyl chloride in the presence of pyridine, crystallises from alcohol (85 per cent.) in slender colourless needles melting at 136-137°. 0·1674 gave 12·5 cc. of nitrogen at 25° and 669 mm. N = 7·53; $C_{26}H_{22}ON_2$ requires 7-41 per cent.

Decomposition of benzylphenyl-p-*phenylenediamine*, $C_6H_5{\cdot}CH_2{\cdot}NPh{\cdot}C_6H_4{\cdot}NH_2$ with hydrochloric acid.

(*a*) *Reduction of the nitro-compound*[1] *melting at 163° to the corresponding primary amine.* To a solution of 2·5 grams of pure nitro-compound in 50 cc. of alcohol and 10 cc. of concentrated hydrochloric acid contained in a reflux apparatus and heated on a water-bath, zinc dust is gradually added until the solution, which at first is deep yellow, becomes colourless. After removing the excess of zinc dust and allowing the solution to cool the *zinc double chloride* is deposited as slender colourless needles; a further quantity is obtained by removing the alcohol from the filtrate and adding water. (Total yield, 3·2 grams.) The salt melts at 215-220° and tends to oxidise on exposure to air. The free base, obtained by decomposing the zinc salt with excess of sodium hydroxide and extraction with ether, crystallises in brownish microscopic plates melting at 100–101°. The hydrochloride gives a green colouration with ferric chloride and a dark purple colouration with dichromate and sulphuric acid.

The *acetyl derivative* $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NPh{\cdot}CH_2{\cdot}C_6H_5$, obtained by adding acetic anhydride to an ethereal solution of the base, crystal-

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[1] P. 242.

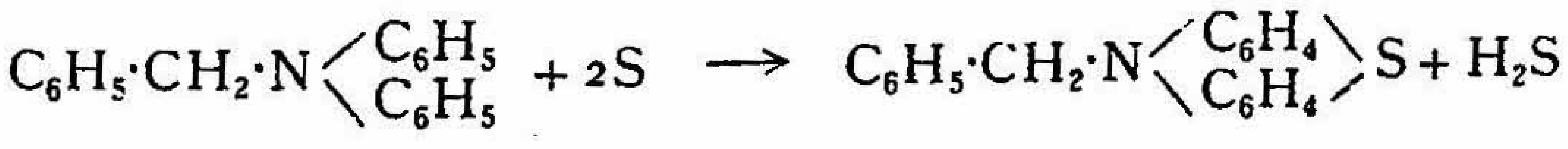
lises from ether or dilute alcohol (50 per cent.) in glistening, colourless needles melting at 201°. 0·1220 gave 0·3558 of carbon dioxide and 0·072 of water. C = 79·6 and H = 6·5 : $C_{21}H_{20}ON_2$ requires C = 79·7 and H = 6·3 per cent.

The *benzoyl derivative*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NPh{\cdot}CH_2{\cdot}C_6H_5$, obtained by benzoylating the base in pyridine solution, crystallises from alcohol (90 per cent.) in colourless microscopic needles melting at 245–246°. 0·1485 gram gave 11·0 cc. of nitrogen at 25° and 669 mm. N = 7·47 : $C_{26}H_{22}ON_2$ requires 7·41 per cent.

(*b*) *Decomposition of the base.*—0·4 gram of the base melting at 100–101° was heated in a sealed tube for 6 hours at 170–175° with 15cc. of concentrated hydrochloric acid. The acid solution, on extraction with ether, gave 0·2 gram of an oil smelling strongly of benzyl chloride, and it was proved to be benzyl chloride by condensing it with aniline in the presence of anhydrous sodium acetate and a trace of iodine when dibenzylaniline melting at 67·5° was isolated.

After extraction with ether the acid liquor was made alkaline with sodium hydroxide and again shaken with ether. The residue after removal of the ether weighed 0·22 gram and was dark coloured, but when warmed with acetic anhydride gave an acetyl derivative which crystallised from alcohol in needles melting at 158° and identical with the mono-acetyl derivative of *p*-aminodiphenylamine.

Production of benzylthiodiphenylamine from benzyldiphenylamine and sulphur.

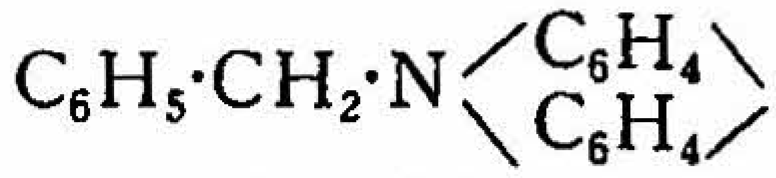


$$C_6H_5{\cdot}CH_2{\cdot}N\begin{matrix}\diagup C_6H_5\\ \diagdown C_6H_5\end{matrix} + 2S \longrightarrow C_6H_5{\cdot}CH_2{\cdot}N\begin{matrix}\diagup C_6H_4 \diagdown\\ \diagdown C_6H_4 \diagup\end{matrix}S + H_2S$$

The method adopted was that due to Knoevenagel [1] and the following procedure was found to give fair yields. 5 grams of benzyldiphenylamine (1 mol.) and 1·25 grams of sulphur (2·5 atoms) are heated in a short hard glass tube by means of an oil bath. At 210° the mass begins to turn green and hydrogen sulphide is evolved. The reaction is completed by heating at 220–225° for 8 hours. The product is extracted 4 times with 90 per cent. alcohol using 25 cc. at each operation and the total extract is decolourised with animal charcoal. The product separates from its alcoholic solution in microscopic yellow plates melting at 90·5–91·0°, and dissolves readily in all organic solvents including light petroleum. The yield is 25 per cent. of the weight of the base taken.

Analyses:—0·2126 gave 0·1730 of barium sulphate and 0·2032 gram gave 9·8 cc. of nitrogen at 26° and 669 mm. S = 11·16 and N = 4·85. $C_{19}H_{15}NS$ requires S = 11·07 and N = 4·85 per cent.

The thio-compound dissolves in concentrated sulphuric acid giving a reddish brown solution and its solution in alcoholic hydrogen chloride gives a pink colouration with ferric chloride.



The corresponding *sulphone*, $C_6H_5\cdot CH_2\cdot N\left\langle\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right\rangle SO_2$, is obtained by oxidising an acetone solution of the thio-compound with an acetone glacial acetic acid solution of permanganate. It crystallises from alcohol in slender needles melting at 211–212° and is practically insoluble in light petroleum.

0·2262 gave 0·1642 barium sulphate, S = 9·95; $C_{19}H_{15}O_2NS$ requires 9·97 per cent.

The same compound can be obtained by benzylating thiodiphenylamine in dry toluene at 110° and oxidising the product.

IV. Action of Carbon Tetrachloride on Diphenylamine.

When equimolecular quantities of carbon tetrachloride and diphenylamine are heated at 97° or even at 100–105° for several hours no colour is developed, but in presence of 0·1 per cent. of iodine a deep blue colour is observed and after the removal of unaltered reacting substances a colouring matter can be isolated which is identified as triphenylpararosaniline hydrochloride by the tests given by Rosenthäler.[1] The yields are small: with 0·2 per cent. of iodine and heating at 97° for 20 hours the yield is only 9·0 per cent. of the theoretical based upon the weight of diphenylamine, and by increasing the temperature to 105°, or by increasing the catalyst to 1·0 per cent., or by the addition of pyridine it has not been found possible to increase the yield. The unchanged carbon tetrachloride is removed by distillation and the unaltered diphenylamine by extraction with benzene. The residue after filtering, washing and drying is taken as dye.

V. Action of Benzyl Chloride on Diethylaniline.

Benzyl chloride and diethylaniline in molecular proportions do not react at 100° in the presence of anhydrous sodium acetate and a little iodine. At 150–160° the benzyl chloride reacts with the sodium acetate and benzyl acetate is formed; hence all later experiments were made in the absence of sodium acetate.

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[1] Nachweis Organischer Verbindungen, p. 875.

A mixture of 100 grams of diethylaniline, (2 mols.), 42 grams of benzyl chloride (1 mol.) and 1·0 gram of iodine was heated in an oil-bath at 148–150° during 20 hours, and after the reaction was over, 85 cc. of concentrated hydrochloric acid were added and the mass extracted with ether to remove unaltered benzyl chloride, 8·5 grams of which were recovered. The acid liquid was made alkaline with sodium hydroxide and the oily bases extracted with ether and after drying with anhydrous sodium sulphate the ether was removed leaving 116 grams of an oil, the preliminary fractionation of which, under a pressure of 50 mm., gave the following results.

TABLE IV.

Bases from Diethylaniline and Benzyl Chloride.

Fraction	Boiling point	Weight in grams
1	132°	55·10
2	166–190°	3·81
3	190–200°	2·56
4	208–210°	21·44
5	213–260°	24·83
Residue	not below 300°	7·02

Fraction 1 consists of practically pure diethylaniline and fractions 4 and 5 of bases of higher molecular weight. These two fractions were carefully distilled from a small Claisen flask under a pressure of 9 mm. and the products subjected to a second fractionation when the following were obtained.

TABLE V.

Higher bases from Diethylaniline and Benzyl Chloride.

Fraction	Pressure in mm.	Temperature	Weight in grams
C1	6	155–160	8·41
C2	6	163–164	15·90
C3	8	175–176	6·67
C4	8	190–200	4·11
Residue	...	...	2·10

Carbon and hydrogen determinations of fractions C2 and C3 showed that they were identical, and this was confirmed by the fact that their picrates melt at the same temperature.

It is thus clear that considerable chemical reaction had taken place between the benzyl chloride and the diethylaniline as only 20 per cent. of the benzyl chloride and rather more than 50 per cent. of the diethylaniline were recovered unaltered. The chief product is a base boiling at 163–164° under a pressure of 6 mm. and containing 85·1 per cent. of carbon and 8·8 per cent. of hydrogen. It yields a platinichloride in the form of microscopic orange plates containing 22·0 per cent. of platinum and a picrate crystallising in yellow prisms or plates melting at 113–114° and containing 49·8 per cent. of picric acid as determined by titration with standard sodium hydroxide solution using phenolphthalein as indicator. Attempts to prepare a nitroso-derivative proved unsuccessful.

With the exception of the last reaction all the above properties point to the base being ethylbenzylaniline $C_6H_5{\cdot}N(C_2H_5){\cdot}CH_2{\cdot}C_6H_5$. This contains 85·3 per cent. of carbon and 8·1 per cent. of hydrogen and yields a picrate melting at 113–114° and closely resembling the above picrate in appearance, and when mixed with this also melts at 113–114°.

The identity of the base with ethylbenzylaniline appears to be conclusively proved by a crystallographic examination of the two picrates kindly made by Professor P. Sampat Iyengar of the Central College, Bangalore. He states that ' Both picrates are triclinic having usually the forms two macropinacoids (*a*) ; four prisms m, m_1, m_2, m_3; one macrodome t and two basal planes c (cf Fig. 1). Very rarely two macrodomes t and t′ are developed as in figures 2 and 3. The broad tabular faces are the macropinacoids which show step-like

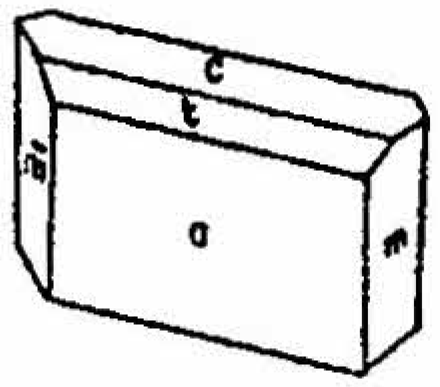


Fig. 1.

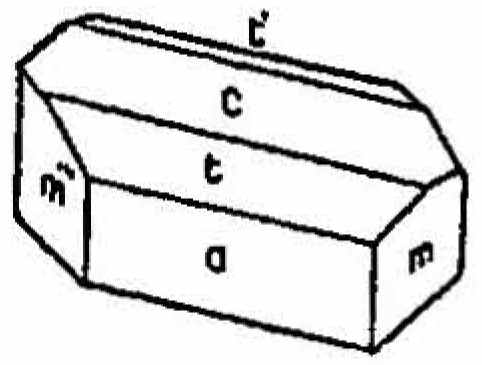


Fig. 2.

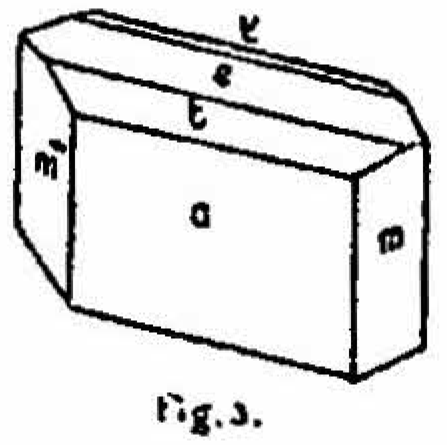


Fig. 3.

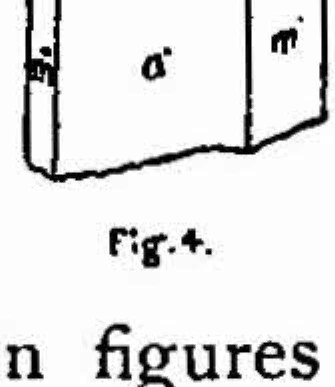


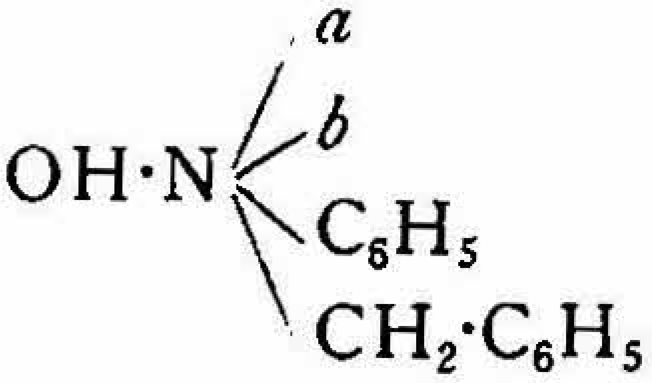
Fig. 4.

square etchings similar to those found on salt crystals. The basal planes show, in some cases, hexagonal etchings. Both picrates are similar in crystallographic form and in the possession of similar faces. Both picrates show good cleavage parallel to the base c, and in the direction parallel to the brachy-pinacoid also there is cleavage.'

It thus appears that the effect of heating diethylaniline at 150° with benzyl chloride and a trace of iodine is to cause one of the ethyl groups to be displaced by benzyl.

This reaction is interesting as, although Jones[1] has shown that a methyl group readily replaces ethyl or allyl groups when a quaternary ammonium salt is heated with methyl iodide, no instances of the replacement of methyl or ethyl in an amine by the more complex benzyl group appear to have been recorded, although Wedekind[2] has obtained dibenzylaniline by the action of benzyl chloride on allyl benzylaniline at 100°.

Komatsu[3] has shown that when quaternary ammonium hydroxides of the type,



$$OH\cdot N(a)(b)(C_6H_5)(CH_2\cdot C_6H_5)$$

undergo thermal decomposition the benzyl group is eliminated as benzyl alcohol and the smaller groups remain attached to the nitrogen atom.

It is intended to study the action of benzyl chloride on dialkylated anilines containing more complex alkyl groups.

Action of benzyl chloride on dimethylaniline.—The reaction between benzyl chloride and dimethylaniline has been studied under conditions exactly similar to those described under diethylaniline. From 80 grams of dimethylaniline and 40 grams of benzyl chloride 4·5 grams of unaltered benzyl chloride and 94·3 grams of mixed bases were isolated. The latter when distilled under a pressure of 55 mm. gave 38·1 grams boiling at 140–145° and consisting of nearly pure dimethylaniline and a second fraction boiling at 210–240° and weighing 50·2 grams. This latter fraction when further fractionated under a pressure of 8 mm. gave 41·3 grams of an oil boiling at 161–162° which proved to be identical with methylbenzylaniline obtained by

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[1] *J. Chem. Soc.*, 1905, 87, 1726; 1907, 91, 2083.
[2] *Ber.*, 1899, 32, 521; cf. also *Ber.*, 1902, 35, 766, 1075.
[3] *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 1912, 3, 371.

benzylating monomethylaniline with benzyl chloride in the presence of anhydrous sodium acetate and a little iodine, as shown by the data given in Table VI.

TABLE VI.

Properties of Methylbenzylaniline.

—	B. P. at 8 mm.	$d^{26\cdot5}_{26\cdot5}$	$n^{29\cdot5}_{D}$	Melting point of picrate
From monomethylaniline ...	161–162	1·0422	1·6008	128·0–128·5
From dimethylaniline	162–163	1·0421	1·6006	128·0–128·5

The melting point of the picrate does not agree with the values given by earlier authorities. Komatsu,[1] who prepared the base by decomposing methyldibenzylphenylammonium hydroxide, gives the melting point of the picrate as 103·0–103·5° and Singh,[2] who prepared it by the action of magnesium powder on phenylbenzylmethylazonium iodide, states that the picrate melts at 109°.

VI. Action of Chloro-, Bromo-, and Iodo-benzene on Aniline and Acetanilide.

A number of experiments were made in order to ascertain whether diphenylamine could be synthesised from aniline and a halogenated benzene in the presence of a little iodine. The results indicate that at temperatures between 135 and 255° condensation does not occur, and similar negative results were obtained by using acetanilide in place of the free base. The original reagents were recovered and in no case was there indication of the presence of diphenylamine or of its acetyl derivative.

SUMMARY.

1. Small quantities of iodine act as a positive catalyst in the benzylation of aniline but the best results in the case of dibenzylaniline are obtained by using both fused sodium acetate (2 mols.) and iodine 0·5 per cent.

2. The same reagents can be used with advantage in the preparation of benzyldiphenylamine from benzyl chloride and diphenylamine.

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[1] *Loc. cit.*
[2] *J. Chem. Soc.*, 1916, 109, 790.

3. By the nitration of benzyldiphenylamine, followed by reduction, the compound obtained is benzylphenyl-*p*-phenylenediamine $C_6H_5{\cdot}CH_2{\cdot}N(C_6H_5){\cdot}C_6H_4{\cdot}NH_2$, and it yields an acetyl derivative melting at 201^0 and a benzoyl derivative melting at $245-246^0$.

The isomeric *p*-aminobenzyldiphenylamine,

$$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(C_6H_5)_2,$$

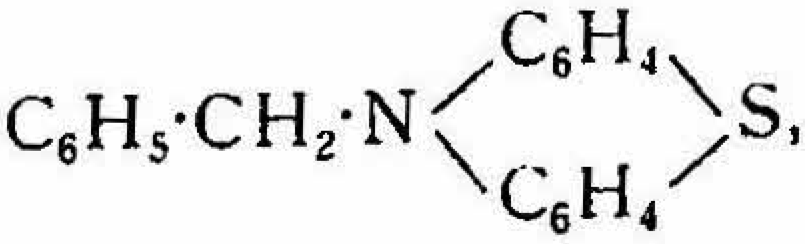
obtained by reducing the condensation product of diphenylamine and *p*-nitrobenzyl chloride yields an acetyl derivative melting at 165^0 and a benzoyl derivative melting at $136-137^0$.

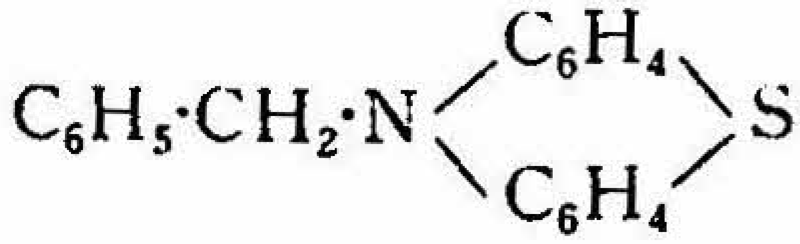
4. Small amounts of triphenylpararosaniline are formed by the condensation of diphenylamine with carbon tetrachloride at 100^0 in the presence of iodine.

5. Benzyl chloride reacts with diethylaniline at 150^0 in presence of iodine (1 per cent.) yielding ethylbenzylaniline, which forms a picrate melting at $113-114^0$ and crystallising in well developed yellow triclinic prisms.

Benzyl chloride and dimethylaniline behave in a similar manner yielding methylbenzylaniline, the picrate of which melts at $128{\cdot}0-128{\cdot}5^0$ and not at $103{\cdot}0-103{\cdot}5^0$ as stated by Komatsu or at 109^0 as given by Singh.

6. Iodine does not facilitate the condensation of phenyl halides with aniline or acetaniline.

7. Benzyldiphenylamine reacts with sulphur at 220^0 yielding a benzylthiodiphenylamine,  $C_6H_5{\cdot}CH_2{\cdot}N\begin{matrix}C_6H_4\\C_6H_4\end{matrix}S$, melting at $90{\cdot}5-91{\cdot}0^0$ and this on oxidation with permanganate gives the sulphone,



$C_6H_5{\cdot}CH_2{\cdot}N\begin{matrix}C_6H_4\\C_6H_4\end{matrix}SO_2$, melting at $211-212^0$.

In conclusion I have great pleasure in expressing my sincere thanks to Dr. J. J. Sudborough for the interest he has taken in this work and for his valuable suggestions and timely encouragement, and I also tender my best thanks to Dr. H. E. Watson for his unfailing interest in the progress of the work.

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