

Ortho-para-isomerism in the preparataion of diaminodiphenylmethane / by Harold King.

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CIX.—*Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane.*

By HAROLD KING.

IN the course of an investigation of the nitro-derivatives of diaminodiphenylmethane, prepared either from dianilinomethane or from anhydroformaldehydeaniline and aniline, it was found that the crude, distilled diaminodiphenylmethane was a mixture of the 4:4'- and 2:4'-derivatives in the proportion of about 9 to 1. By crystallising the nitration products, 2:2'-dinitro-4:4'-diaminodiphenylmethane was first isolated, and from the mother liquors a mononitro-derivative, which, on removal of the amino-groups, subsequent reduction, and acetylation, gave 4-acetylaminodiphenylmethane. The mononitro-derivative must have arisen from 2:4'-diaminodiphenylmethane present in the starting material, as was confirmed by the separation of the two isomeric bases and the mono-nitration of the unsymmetrical base.

EXPERIMENTAL.

Preparation of Diaminodiphenylmethane.

From Dianilinomethane.—Fifty grams of crystalline dianilinomethane were digested with 59 c.c. of aniline, 31 c.c. of concentrated hydrochloric acid, and 24 c.c. of water for twelve hours at 95°. The product was made alkaline and completely freed from aniline by steam distillation. The residual non-volatile base, after washing by agitating with fresh quantities of water, was distilled

under reduced pressure, yielding 33 grams of crude diaminodiphenylmethane, which boiled at $236\text{--}240^{\circ}/11$ mm.

From Anhydroformaldehydeaniline.—One hundred grams of solid anhydroformaldehydeaniline, 249 c.c. of aniline, 43 c.c. of water, and 130 c.c. of concentrated hydrochloric acid were mixed and heated on the water-bath for twelve hours. The crude, distilled aniline-free base boiled at $238\text{--}242^{\circ}/15$ mm., and amounted to 148.5 grams.

*Nitration of Diaminodiphenylmethane and Isolation of
4-Nitro-2:4'-diaminodiphenylmethane.*

Fifty grams of distilled diaminodiphenylmethane were nitrated by Benda's method (*Ber.*, 1912, **45**, 1787). The crude nitration product was collected and extracted once when dry with a limited volume of boiling alcohol. The insoluble solid consisted of 2:2'-dinitro-4:4'-diaminodiphenylmethane, and amounted to 60.5 grams, which is 83 per cent. of the theoretical yield. As the material soluble in alcohol could not be purified by further crystallisation, the solution was evaporated to dryness, and the residual solid, amounting to 14.4 grams, dissolved in hot 10 per cent. hydrochloric acid solution and fractionally precipitated by addition of 10 per cent. solution of ammonia. After removal of tarry matter, further addition of ammonia to the hot solution caused the separation of a crystalline precipitate, and eventually a point was reached at which a turbidity developed, due to the incipient formation of an oil. The crystalline material was collected, and consisted of 6.3 grams of almost pure 2:2'-dinitro-4:4'-diaminodiphenylmethane. The filtrate was now completely precipitated with ammonia, and, when cold, the crude 4-nitro-2:4'-diaminodiphenylmethane (4.3 grams) was collected. The total yield of dinitro-base was about 92 per cent., and of the crude mononitro-base 7 per cent.

Another experiment, in which Ehrlich and Bauer's method (*Ber.*, 1915, **48**, 502) of nitration was employed, furnished a 10 per cent. yield of crude mononitrodiaminodiphenylmethane.

4-Nitro-2:4'-diaminodiphenylmethane dissolves in about twenty-three parts of boiling alcohol, and crystallises in glistening, orange needles melting at $157\text{--}158^{\circ}$ (corr.) (Found: C=64.4; H=5.5. $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$ requires C=64.2; H=5.4 per cent.).

The *dihydrochloride* crystallises in microscopic, hexagonal-shaped leaflets melting and decomposing at 262° (corr.) (Found: Cl=22.3. $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3 \cdot 2\text{HCl}$ requires Cl=22.4 per cent.).

The *diacetyl* derivative crystallises from acetic anhydride or

boiling methyl alcohol, in which it dissolves to the extent of 1.2 per cent. in pale buff-coloured, woolly needles melting at 239—240° (corr.) (Found: C=62.2; H=5.3. $C_{17}H_{17}O_4N_3$ requires C=62.4; H=5.2 per cent.).

The *tetra-acetyl* derivative obtained when the diacetyl derivative is boiled with excess of acetic anhydride is soluble in about one hundred times its weight of boiling alcohol, and separates in clear, oblique prisms melting at 201.5—202.5° (corr.) (Found: C=61.6; H=5.4. $C_{21}H_{21}O_6N_3$ requires C=61.3; H=5.1 per cent.).

4:3'-Dinitro-2:4'-diacetylaminodiphenylmethane.

4-Nitro-2:4'-diacetylaminodiphenylmethane (1.3 grams), when nitrated with a mixture of sulphuric and nitric acids, gave 1.45 grams of the crude dinitrated anilide. It was recrystallised twice from glacial acetic acid, yielding, finally, 1.15 grams. It dissolves in fifty volumes of the boiling solvent, and crystallises as a voluminous mass of golden needles melting at 264—265° (corr.). A mixture with the isomeric 3:3'-dinitro-4:4'-diacetylaminodiphenylmethane, which melts at 259—260° (uncorr.), melted at 233° (Found: C=55.3; H=4.4. $C_{17}H_{16}O_6N_4$ requires C=54.8; H=4.3 per cent.).

3':4-Dinitro-2:4'-diaminodiphenylmethane.

The free aniline prepared from the above anilide, when recrystallised from boiling alcohol (twenty-four parts), separates in glistening, orange needles, very similar in appearance to 4-nitro-2:4'-diaminodiphenylmethane. It melts at 148.5—149.5° (corr.) (Found: C=54.5; H=4.2. $C_{13}H_{12}O_4N_4$ requires C=54.2; H=4.2 per cent.).

4-Acetylaminodiphenylmethane.

4-Nitro-2:4'-diaminodiphenylmethane was deprived of the amino-groups by the diazo-reaction, the product reduced, and acetylated. Purification by recrystallisation from alcohol gave the compound in the form of large, pearly leaflets melting at 128—129° (corr.), and a mixed melting point with 4-acetylaminodiphenylmethane, prepared from benzene and *p*-nitrobenzyl chloride by the Friedel and Crafts synthesis, followed by reduction and acetylation, showed no depression (Found: N=6.2. $C_{15}H_{15}ON$ requires N=6.2 per cent.).

Separation of 2:4'- and 4:4'-Diaminodiphenylmethanes.

(a) *Use of Benzylidene Derivative.*—Crude, distilled diaminodiphenylmethane (148.5 grams) was converted into its dibenzylidene derivative. The alcoholic mother liquors were evaporated to dryness, and the residual semi-solid material was digested on the water-bath for two hours with 200 c.c. of 10 per cent. hydrochloric acid. The product was extracted with ether, and the acid aqueous solution rendered alkaline with ammonia and similarly extracted with ether. In this way, on removal of the solvent, 22.5 grams of syrup were obtained, which, on distillation under diminished pressure, gave 12 grams of a pale yellow oil. On acetylation, a crude diacetylaminodiphenylmethane was obtained, which was fractionally crystallised from alcohol. 9.5 Grams of pure 2:4'-diacetylaminodiphenylmethane were obtained, representing a minimum content of 4.5 per cent. of the ortho-para-base in the original material. The separation is difficult, and is only possible when the acetylated product contains excess of the ortho-para-isomeride.

(b) *Use of differing Basicities.*—Seventy grams of crude, distilled diaminodiphenylmethane were dissolved in chloroform, and the solution was extracted thirty-two times by means of dilute sulphuric acid solution. Each extract contained 10 c.c. of 10 per cent. sulphuric acid solution diluted to such a volume as would keep the sparingly soluble sulphates in solution. In this way, solubility relationships were avoided, as attempts to separate the two bases by fractional crystallisation or precipitation of salts led to no result. The progress of the separation was followed by precipitating the acid fractions at intervals, by means of ammonia, and comparing the melting point of the acetyl derivatives with a mixed melting point with pure 4:4'-diacetylaminodiphenylmethane. By this means, it was found that the 2:4'-disubstituted base was concentrated in the last four extracts, which on acetylation gave 10.4 grams of solid material. This was fractionally crystallised from alcohol, when 5.0 grams of pure 2:4'-diacetylaminodiphenylmethane were obtained.

2:4'-Diacetylaminodiphenylmethane crystallises from boiling 95 per cent. alcohol (14 parts) in glistening, delicate, rectangular leaflets melting at 224—225° (corr.). It often melts at 209—210° (uncorr.), and if the molten contents are allowed to cool, it re-solidifies, and then re-melts at 224°. Occasionally the substance becomes semi-transparent at 210°, and then clears and forms a definite meniscus at 223—224°. Zincke and Prentzell (*Ber.*, 1905, **38**, 4121), by recrystallisation from alcohol, obtained two modifications, white tablets melting at 208° and small needles melting

at 218°. The author has only once succeeded in reproducing the needle form, by inoculating a hot saturated solution of the anilide with the powdered, re-solidified material melting at 224°. Both forms separated simultaneously, the needle form in much the smaller proportion.

The identity of the 2:4'-diacetylaminodiphenylmethane was proved by direct comparison with a sample prepared by Staedel's method (*Annalen*, 1894, **283**, 162) from 2:4'-dinitrodiphenylmethane. Both showed the characteristic double melting point, and a mixture of the two showed no depression (Found: N=10.1. Calc.: N=10.1 per cent.).

2:4'-Diaminodiphenylmethane is readily soluble in hot benzene, but crystallises well from the cold solution in pearly leaflets. It melts at 88—89° (corr.) and boils at 222°/9 mm.

The *dibenzylidene* derivative is readily soluble in ether, and is precipitated on addition of light petroleum as an oil.

4:4'-Diaminodiphenylmethane, free from the isomeride, is best prepared through the intermediary of the dibenzylidene derivative. It crystallises well from benzene in clusters of rectangular plates melting at 92—93° (corr.) and boiling at 232°/9 mm.

4:4'-Diamino-2:2'-azoxydiphenylmethane.

Pure 2:2'-dinitro-4:4'-diaminodiphenylmethane (1 gram) was suspended in 20 c.c. of alcohol, and 4 grams of crystalline, hydrated sodium sulphide, dissolved in 4 c.c. of water, were added. The solution was boiled for half an hour, and, when cold, the product, which separated in glistening, orange needles, was collected. The yield was 0.45 gram.

4:4'-Diamino-2:2'-azoxydiphenylmethane melts and decomposes at 265° (corr.) (Duval, *Compt. rend.*, 1905, **141**, 198, gives 272°). The only solvent at all suitable for its recrystallisation is pyridine (Found: C=64.9; H=5.3. Calc.: C=65.0; H=5.0 per cent.).

It forms a stable *dihydrochloride* crystallising in microscopic, six-sided leaflets, which are readily soluble in water without separation of the base. It has no definite melting point (Found: H₂O=8.6; Cl=20.8. C₁₃H₁₂ON₄·2HCl, 1½H₂O requires H₂O=7.3; Cl=20.8 per cent.).

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