236. *Preparation of* m-*Dialkylaminobenzaldehydes.*

By Wesley Cocker and J. O. Harris.

m-*Diethyl-*, *-di-*n*-propyl-*, *-diallyl-*, and *-dibenzyl-aminobenzaldehydes* have been prepared according to the method of Cocker, Harris, and Loach (J., 1938, 751). Their basic properties are discussed.

Investigations of the condensation products of *m*-dimethylaminobenzaldehyde with a number of compounds containing reactive methylene groups suggested the extension to other *m*-dialkylaminobenzaldehydes. The latter compounds are now described.

When *m*-aminobenzaldehydedimethylacetal was treated with ethyl sulphate or ethyl iodide in presence of sodium carbonate solution, the reaction stopped at the tertiary base stage even in presence of a large excess of the alkylating agent. This was confirmed by treating m-*diethylaminobenzaldehyde* with ethyl iodide: the reactants were recovered unchanged. However, *m*-diethylaminobenzaldehyde will form a methiodide and *m*-dimethylaminobenzaldehyde an ethiodide.

m-*Di-*n*-propyl-*, *-diallyl-*, and *-dibenzyl-aminobenzaldehydes* were similarly prepared and here again no quaternary salt was produced and even methyl iodide failed to react with the pure base in the last two cases. These properties, together with the facts that *m*-diallyl- and *m*-dibenzyl-aminobenzaldehydes are sparingly soluble in 3N-mineral acid and that the chloroplatinates of *m*-di-*n*-propyl-, -diallyl- and -dibenzyl-aminobenzaldehyde are decomposed even on warming with water, point to the weakly basic nature of the compounds.

Comment has already been made upon the unusual basic strengths of dimethyl-, diethyl-, and di-*n*-propyl-anilines (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469; Evans, Gordon, and Watson, J., 1938, 1443), in which series diethylaniline is predominantly the most basic and dimethylaniline the least. From the evidence obtained in the study of the *m*-dialkylaminobenzaldehydes it seems that the order of the basic strengths is not in accordance with the order of the unsubstituted alkylanilines, nor does it follow the theoretical order (compare also Watson, *Ann. Reports*, 1938, 248, etc.).

Fleissner (*Monatsh.*, 1882, **3**, 711) records that the chloroplatinate of di-*n*-propylaniline is decomposed by warm water and Matzuduira (*Ber.*, 1887, **20**, 1611) states that the hydrochloride of dibenzylaniline is similarly decomposed, observations which coincide with the present evidence.

It appears that steric effects cannot be ignored, since *m*-diethyl- and *m*-dipropyl-aminobenzaldehydes will form methiodides but not ethiodides, although ethyl iodide would be expected to be more reactive than methyl iodide.

EXPERIMENTAL.

m-*Diethylaminobenzaldehyde.*—Crude *m*-aminobenzaldehydedimethylacetal (prepared from *m*-nitrobenzaldehyde, 76 g.; Cocker, Harris, and Loach, *loc. cit.*) in ether (50 c.c.) was shaken for 7 days with 3/2N-sodium carbonate (3600 c.c.) and ethyl sulphate (300 g.; 2 mols.), each added in twelve equal portions. Any remaining ethyl sulphate was then destroyed by heating the mixture on the water-bath for 24 hours. The ethereal solution was extracted with two lots of 20% hydrochloric acid (200 c.c. each time) and the acid layer was basified and extracted several times with ether. Any unchanged *m*-aminobenzaldehyde was thrown down as an amorphous solid. The ethereal layer was then steam-distilled, the distillate extracted with ether, the extract dried over anhydrous sodium sulphate, and after removal of solvent the remaining oil was distilled under reduced pressure, m-*diethylaminobenzaldehyde* being obtained as a pale yellow oil (41—42 g.) at 137—138°/6—7 mm. (Found: C, 74·2; H, 8·7. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5%).

The *methiodide* separated from alcohol in clusters of colourless, transparent, pointed prisms, m. p. 167·5—168° (decomp.) (Found: I, 40·6. $C_{12}H_{18}ONI$ requires I, 39·8%). The *semicarbazone* crystallised from dilute alcohol in long, colourless, rectangular prisms, m. p. 165° (Found: C, 62·3; H, 7·7. $C_{12}H_{18}ON_4$ requires C, 61·5; H, 7·7%). 3 : 3′-*Bisdiethylaminobenzylideneazine* formed flat, greenish-yellow, pointed plates, m. p. 114—115°, when recrystallised from alcohol (Found: N, 15·8. $C_{22}H_{30}N_4$ requires N, 16·0%). The 2 : 4-*dinitrophenylhydrazone* formed chocolate-coloured micro-prisms, m. p. 197—198°, from alcohol (Found: C, 57·1; H, 5·2. $C_{17}H_{19}O_4N_5$ requires C, 57·1; H, 5·3%). The *picrate*, recrystallised from alcohol, formed large, transparent, greenish-yellow prisms, m. p. 145·5—146° (decomp.) (Found: N, 13·5. $C_{11}H_{15}ON,C_6H_3O_7N_3$ requires N, 13·8%). The *leuco-base* of the crystal-violet analogue crystallised from alcohol in yellowish-green, four-sided prisms, m. p. 108·5—109·5° (Found: N, 10·1. $C_{27}H_{35}N_3$ requires N, 10·4%). All attempts to form an ethiodide were abortive.

m-*Di*-n-*propylaminobenzaldehyde.*—*m*-Nitrobenzaldehyde (45 g.) was converted into *m*-aminobenzaldehydedimethylacetal, and this was propylated with *n*-propyl iodide (170 g.) in presence of 3N-sodium carbonate (1200 c.c.) by shaking at room temperature for 21 days and then refluxing for 4 days. The product was isolated as described for the lower homologue, except that the steam-distillation stage was omitted. As a result the yield of m-*di*-n-*propylaminobenzaldehyde* was lower than anticipated owing to charring during the distillation in a vacuum. On redistillation the required compound was obtained as a pale yellow oil (20 g.), b. p. 145—148°/5—6 mm. (Found: C, 75·5; H, 9·0. $C_{13}H_{19}ON$ requires C, 76·1; H, 9·3%). The *semicarbazone* separated from alcohol in clusters of colourless, transparent prisms, m. p. 172—172·5° (Found: C, 64·5; H, 8·3. $C_{14}H_{22}ON_4$ requires C, 64·1; H, 8·4%), and the 2 : 4-*dinitrophenylhydrazone* from benzene in long, chocolate-coloured needles, m. p. 207—208° (Found: C, 60·0; H, 6·1. $C_{19}H_{23}O_4N_5$ requires C, 59·2; H, 6·0%). The *picrate*, prepared in benzene, was precipitated as an oil, which solidified; recrystallisation from benzene yielded bright yellow prisms, m. p. 136—137° (Found: C, 53·0; H, 5·5. $C_{13}H_{19}ON,C_6H_3O_7N_3$ requires C, 52·6; H, 5·1%). The *methiodide*, obtained from the base and methyl iodide, crystallised from alcohol–ether in flat, transparent, silvery plates, m. p. 152° (Found: I, 40·1. $C_{14}H_{22}ONI$ requires I, 36·6%). The *chloroplatinate* separated from alcohol–ether in flat, irregular plates, m. p. 178° (decomp.) (Found: Pt, 23·9. $2C_{13}H_{19}ON,H_2PtCl_6$ requires Pt, 23·8%).

m-*Diallylaminobenzaldehyde.*—*m*-Aminobenzaldehydedimethylacetal (from *m*-nitrobenzaldehyde, 45 g.) was shaken during 14 days with 3/2N-sodium carbonate (2000 c.c.) and allyl bromide (123 g.; 1·7 mols.), each added in three equal portions. The reaction was completed by heating on the water-bath for 48 hours and m-*diallylaminobenzaldehyde* (20 g.) was isolated, as described under *m*-diethylaminobenzaldehyde, as a pale yellow oil, b. p. 131—132°/4 mm., which readily decolorised bromine water (Found: C, 77·5; H, 7·4. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

The *semicarbazone* formed colourless, flat, rectangular plates, m. p. 133·5—134°, from alcohol (Found : N, 21·8. $C_{14}H_{18}ON_4$ requires N, 21·7%), and the 2 : 4-*dinitrophenylhydrazone* long, deep red prisms or needles, m. p. 165—165·5° (Found : C, 60·4; H, 5·1. $C_{19}H_{19}O_4N_5$ requires C, 59·8; H, 5·0%). The *chloroplatinate*, prepared in the usual manner, appeared stable only in the presence of cold dilute hydrochloric acid and was decomposed on warming with water, yielding *m*-diallylaminobenzaldehyde. After much difficulty it was purified from alcohol containing ether and was then deposited in clusters of long, pale yellow needles, m. p. 161° (decomp.) with rapid heating. The m. p. varied with rate of heating (Found : Pt, 25·3. $2C_{13}H_{15}ON,H_2PtCl_6$ requires Pt, 24·0%). 3 : 3′-*Bisdiallylaminobenzylideneazine*, recrystallised from alcohol, consisted of long lemon-yellow prisms with violet fluorescence when viewed through the microscope; m. p. 70—71° (Found : C, 78·5; H, 7·5. $C_{26}H_{30}N_4$ requires C, 78·4; H, 7·5%). Attempts to form the *picrate* gave a solid which after long standing separated from alcohol in very dark red, wedge-shaped prisms, m. p. 108·5—109° (Found : N, 15·65. $C_{13}H_{15}ON,C_6H_3O_7N_3$ requires N, 13·0%). The analytical figures indicate its labile nature.

m-*Dibenzylaminobenzaldehyde*.—*m*-Aminobenzaldehydedimethylacetal (from *m*-nitrobenzaldehyde, 38 g.) was benzylated in ethereal solution with benzyl bromide (146 g.; 1·7 mols.) and 3N-sodium carbonate (1500 c.c.), added in five equal portions during 14 days. The reaction was completed on a steam-bath and the m-*dibenzylaminobenzaldehyde*, isolated as in the case of the other aldehydes, was purified by two distillations under reduced pressure. It had b. p. 230—231°/7 mm. and solidified on standing (25 g.). It was recrystallised with great difficulty from methyl alcohol, in which it was extremely soluble, forming almost colourless, short, rectangular prisms, m. p. 59—60° (Found : C, 83·3; H, 6·2; N, 5·1. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·3; N, 4·6%).

The *semicarbazone*, recrystallised from alcohol, consisted of colourless, transparent needles, m. p. 185—185·5 (Found : N, 16·1. $C_{22}H_{22}ON_4$ requires N, 15·6%). The *oxime* crystallised from dilute alcohol in flat, wedge-shaped plates, m. p. 125—126° (Found : C, 79·7; H, 6·2. $C_{21}H_{20}ON_2$ requires C, 79·7; H, 6·3%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in long orange prisms or needles, m. p. 230—231° (Found : C, 67·9; H, 5·1. $C_{27}H_{33}O_4N_5$ requires C, 67·4; H, 4·8%). 3 : 3′-*Bisdibenzylaminobenzylideneazine* was deposited from alcohol in pale yellow, pointed plates or prisms, m. p. 167—167·5° (Found : C, 83·9; H, 6·35. $C_{42}H_{38}N_4$ requires C, 84·3; H, 6·35%). Attempts to obtain a pure specimen of the chloroplatinate were abortive. The crude material had m. p. 124—125°. It was extremely soluble in alcohol and attempted recrystallisation from this solvent gave an oil. Attempted recrystallisation from hot water gave a strong odour of benzyl chloride. Attempts to form a methiodide were futile.

The authors' thanks are due to the Chemical Society for a grant.

THE WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

[*Received, May* 31*st*, 1939.]