

# Picrates of Some Tertiary Amines. Reply to Professor B. K. Singh.

By

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(Received September 5, 1922)

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Some years ago one of us proposed the picrate-method<sup>1</sup> for the identification of tertiary amines by determining the melting point of the picrates. K. B. Singh,<sup>2</sup> however, applying the method for identification of the amines formed by the decomposition of hydrazonium compounds, claimed that the tertiary amines used for the experiment by one of us were impure, since the picrates of the amines showed low melting points compared with his substances.

Now, in order to determine whether Prof. Singh's announcement is really true, the authors have undertaken the present study.

The aniline used for starting material was pure Kahlbaum's sample was purified by fractional distillation three times under ordinary pressure. 70 gm. of pure methyl aniline and 68 gm. of pure ethyl aniline were prepared from 250 gm. pure acetanilide (M. p. 112°) 65 gm. metallic sodium and 420 gm. pure methyl iodide (B. p. 43°) and from 250 gm. pure acetanilide and 430 gm. pure ethyl iodide (B. p. 72-3°) respectively, by following Hepp's direction,<sup>3</sup> and were separated from the aniline by means of carbon bisulphide.<sup>4</sup>

The secondary amines thus obtained were purified by fractional distillation three times under ordinary pressure and then once under

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<sup>1</sup> Mem. Coll. Sci. Engin. Kyoto, **3**,371 (1912).

<sup>2</sup> J. Chem. Soc., **109**,789 (1916).

<sup>3</sup> Ber. D. Chem. Ges., **10**,327 (1877).

<sup>4</sup> Ibid., **8**,105 (1875).

reduced pressure. They were colourless oils and showed the following physical constants:

Table I.

	$d_{40}^{25}$	$n_D^{25}$	B. p.	M. R.
Methyl aniline	0.97945	1.5630	190.5-191° (760.6 mm.) 85-85.5° (12 mm.)	35.53
Ethyl aniline	0.95645	1.5487	200.5-201° (755 mm.) 97° (18 mm.)	40.27

20 gm. pure diethyl aniline and 8 gm. pure methyl ethyl aniline were prepared from an equimolecular mixture of 32 gm. pure ethyl aniline and ethyl and methyl iodides respectively, particular care being taken to avoid the replacement of ethyl group in the amine molecule by methyl group during methylation of the secondary amine.<sup>1</sup> The tertiary amine was separated from the secondary amine by the aid of benzen-sulphonyl chloride,<sup>2</sup> and then fractionated on metallic sodium three times under ordinary pressure and once under reduced pressure. In the same way, 12 gm. pure dimethyl aniline and methyl ethyl aniline were obtained from 34 gm. methyl aniline and methyl iodide and ethyl iodide respectively, and were purified.

The tertiary amines thus obtained were colourless liquids, and the density and index of refraction of the base were determined, with the results shown in the following table:

Table II.

	$d_{40}^{25}$	$n_D^{25}$	B. p.	M. R.
Dimethyl aniline	0.9545	1.5551	{188.5-9.5° (752.5 mm.) 86.5-87° (19 mm.)	40.34
Diethyl aniline	0.93061	1.5376	{209.5-9.8° (748 mm.) 108.5° (18 mm.)	50.11
Methyl ethyl aniline from methylaniline	0.94028	1.5446	{97.5-98° (19 mm.) 200.5-1.5° (753 mm.)	45.42
„ ethyl aniline	0.94026	1.5444	{200.5-1.5° (753 mm.) 99-99.5° (25 mm.)	45.42
„ Merck	0.94426	1.5451	{200.5-1.5° (758 mm.) 119.5-20° (38 mm.)	45.16

<sup>1</sup> H. O. Jones: J. Chem. Soc., 87,1721 (1905); H.O. Jones and J. R. Hill; *Ibid.*, 91,2083 (1907).

<sup>2</sup> O. Hinsberg: Ber. D. Chem. Ges., 23,2963 (1890); O. Hinsberg and J. Kepler: *Ibid.*, 38,906 (1905).

The melting point of the picrates formed from equimolecular mixture of the tertiary amine and picric acid in an alcoholic solution, was determined, and the results are shown in the following table with that observed in the case of the picrate of methyl ethyl aniline from Merck, which was formerly used by one of us in the experiments with quaternary ammonium compounds, and was purified by fractional distillation under ordinary pressure and then under 19 mm. pressure.

Seeing that the methyl ethyl aniline prepared from methyl aniline and ethyl iodide was somewhat impure as indicated by the melting point of the picrate (*a*), the amine was again treated with benzenesulphonyl chloride to remove some secondary amine admixed, and then the tertiary amine was purified as usual. The physical constant of the base (Table II) and the melting point (*b*) of the picrate quite agree with those of methyl ethyl aniline from ethyl aniline and methyl iodide.

Table III.  
Melting Point of Picrates.

	Dimethyl aniline	Diethyl aniline	Methyl ethyl aniline from			
			methyl aniline ( <i>a</i> )	ethyl aniline ( <i>b</i> )	Merck.	
A	158-159.5°	137.5-139°	125.5-126°	126-127°	127.5-128°	125-127°
A <sub>1</sub>	157-158°	137.5-139°	125-126°	124.5-126°	127-128.3°	122-127°
A <sub>2</sub>	116-116.5°	122-135°	127-128°	123.5-124°	126.5-127°	94-118°
B	158-159.5°	137.5-139°	126-127°	126.5-127°	127.5-128.1°	128-129.5°
B <sub>1</sub>	157-159.5°	137.5-139°	123-124.5°	126-127.5°	127.8-128.2°	124.5-126.5°
C	—	137-138.5°	129-131°	126-127°	127.8-128.3°	128.5-130°
C <sub>1</sub>	—	137-139°	126-127°	126-127°	127.5-128.3°	128.5-130°
E	—	—	132-137.5°	125.5-127.3°	127.5-128°	127.5-128.5°
E <sub>1</sub>	—	—	—	125-126.5°	127-128.3°	128-129°

A<sub>1</sub> Crystals obtained on concentrating the filtrate from A in vacuo.

A<sub>2</sub> Crystals obtained on concentrating the filtrate from A<sub>1</sub> on water bath.

B Crystals obtained from A from alcohol solution.

B<sub>1</sub> Crystals deposited on concentrating the filtrate from B on water bath.

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C Crystal,—B recrystallized from alcoholic solution.

C<sub>1</sub> Crystal deposited on concentrating the filtrate from C on water bath.

E Crystal,—C recrystallized from alcoholic solution.

E<sub>1</sub> Crystal deposited on concentrating the filtrate from E on water bath.

Table IV.

M. p. of Picrates			
Amines	Komatsu <sup>1</sup>	Singh <sup>2</sup>	Authors
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	154–155°	163–164°	158–159.5°
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	135–136°	142°	137–138°
C <sub>6</sub> H <sub>5</sub> N.CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	124–125°	134–135°	127–128.3°

June, 1922, Laboratory of Organic and Bio-Chemistry.

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<sup>1</sup> Loc. cit.

<sup>2</sup> Loc. cit.