749. *The Double Methopicrates of Certain Heterocyclic Tertiary Amines.*

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The methiodides of the heterocyclic tertiary amines listed in the Table, when added in solution to a similar solution of sodium picrate, may be converted into the normal methopicrates of type (I), or into double methopicrate–sodium picrates of type (II). The latter salts vary widely in stability: some can be recrystallised from certain solvents but undergo conversion into the simple methopicrates in other solvents. The double methopicrate–sodium picrate of 4-methylpyridine has exceptional stability and can be recrystallised from acetic acid.

The methiodides, when similarly added in solution to picric acid, usually afford the normal methopicrates (I). 4-Methylpyridine methiodide, however, gives both the methopicrate and a highly stable double methopicrate–hydrogen picrate of type (III).

The conditions of formation and the stability of these salts have been examined in detail.

TERTIARY amines are frequently characterised as their crystalline methiodides or metho-toluene-*p*-sulphonates. The methiodides of some amines, particularly the more complex heterocyclic amines, are sometimes obtained as viscous products which are difficult to crystallise: in such cases, the methiodides are often treated in aqueous or alcoholic solution with a similar solution of picric acid or sodium picrate, in order to precipitate the methopicrates, which can usually be readily recrystallised, have reasonably sharp m. p.s, and (unlike the methiodides) only rarely have solvent of crystallisation.

We find, however, that with heterocyclic amines the use of sodium picrate in this reaction may prove misleading, for whereas the use of picric acid usually gives the

$[\mathrm{B{\cdot}Me}]\mathrm{C_6H_2N_3O_7}$	$[\mathrm{B{\cdot}Me}]\mathrm{C_6H_2N_3O_7,NaC_6H_2N_3O_7}$	$[\mathrm{B{\cdot}Me}]\mathrm{C_6H_2N_3O_7,C_6H_3N_3O_7}$
(I)	(II)	(III)

normal methopicrate (I; where B is the base), the use of an excess of sodium picrate may give a crystalline double methopicrate–sodium picrate (II). The formation of pyridine methopicrate–sodium picrate has been briefly noted by Krollpfeiffer and Braun,[1] but all the heterocyclic amines which we have investigated (see annexed Table) afford these double methopicrate–sodium picrates, and their formation may therefore be reasonably (and unexpectedly) general.

B	$[\mathrm{B{\cdot}Me}]\mathrm{I}$	$[\mathrm{B{\cdot}Me}]\mathrm{C_6H_2N_3O_7}$	$[\mathrm{B{\cdot}Me}]\mathrm{C_6H_2N_3O_7,C_6H_2N_3NaO_7}$
Pyridine	118°	117°	216—219° [a,b,c]
2-Methylpyridine	229	113	211—212 [a,b,c]
3- ,,	99—100	120	169—172 [b,c,d]
4- ,,	150	151	216 [a,b,c]
Quinoline	134	169	204—206 [c,d,e]
Quinaldine	194	141	219—220 [b,c,d]
Lepidine	174	161	205—206 [d,e,f]
Isoquinoline	159	169	218—236 [d,e,f]

[a,b,c] Recrystallises unchanged from water, MeOH, and EtOH respectively.
[d,e,f] Gives normal methopicrate on recrystallisation from water, MeOH, and EtOH respectively.

The stability of the double methopicrate–sodium picrates (II) varies widely: the double picrate of pyridine can be recrystallised unchanged from water, methanol, or ethanol; that of quinaldine crystallises unchanged from methanol or ethanol, but from water deposits the normal methopicrate (I); that of quinoline is unchanged from ethanol, but deposits the methopicrate from water or methanol; that of lepidine deposits the methopicrate (I) from each of these solvents. The double sodium picrate of 4-methylpyridine has a remarkable stability, as it can be recrystallised unchanged, not only from the above solvents, but even from acetic acid.

The sparing addition of a sodium picrate solution to a methiodide solution in the same solvent may initially give a deposit of the normal methopicrate (I), but the increasing addition of the sodium picrate solution may contaminate the methopicrate (I) with the double sodium picrate (II), or even convert the deposited methopicrate completely into the double salt.

A methiodide is, therefore, best converted into the corresponding methopicrate by adding an aqueous or ethanolic solution of the methiodide to a similar solution of picric acid at suitable concentrations. (Some methopicrates have a high solubility in methanol, which in general should not be used as a solvent.) We have encountered, among amines listed in the Table, only two to which this conversion by picric acid into the methopicrate does not always apply. If pyridine methiodide is treated in aqueous solution with picric acid under special conditions, a crystalline double methopicrate–hydrogen picrate (III), m. p. 60—62°, can be isolated: this salt can be recrystallised from a saturated ethanolic solution of picric acid, but is readily converted into the normal methopicrate (I), m. p. 117°, on attempted crystallisation from water or ethanol. Since it is unlikely to be encountered under normal conditions, and is so readily broken down, it can usually be ignored.

We find, however, that although the addition of 4-methylpyridine methiodide in concentrated aqueous solution to a moderate quantity of aqueous picric acid rapidly deposits the methopicrate (I), m. p. 151°, the addition of the methiodide in more dilute solution causes the slower separation of the double methopicrate–hydrogen picrate (III), m. p. 113°. This process may occur if the total amount of picric acid available is insufficient

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[1] Krollpfeiffer and Braun, *Ber.*, 1936, **69**, 2523.

for complete conversion even into the normal methopicrate (I), and a portion of the methiodide therefore remains unchanged in solution (p. 3849). This hydrogen double picrate (III), unlike that in the pyridine series, has considerable stability and may be recrystallised unchanged from water or from ethanol.

4-Methylpyridine is, therefore, outstanding in its capacity to form stable double picrates with sodium picrate and with picric acid.

The amines listed in the Table were carefully but not exhaustively purified before use. Only pyridine and the three picolines require long and very thorough treatment for high purification. We are consequently greatly indebted to Dr. A. I. Vogel for samples of pure 2- and 4-methylpyridine,[2] and to the National Chemical Laboratory for samples (each of at least 99·8% purity) of pyridine and the three picolines. We have repeated with these samples the preparation of the methiodides, methopicrates (I), and double methopicrates–sodium picrates (II), but the m. p.s of these pure derivatives were (with one minor exception) identical with those of our previous compounds. Therefore, if our earlier samples of these four amines had been contaminated with traces of similar (or, in the picolines, isomeric) bases, the corresponding derivatives of these impurities must have been readily eliminated during recrystallisation.

EXPERIMENTAL

In the case of each amine, the reaction of its methiodide with sodium picrate in aqueous, methanolic, and ethanolic solution is recorded first, with the stability of the products on attempted recrystallisation from these solvents, and then the reaction of the methiodide with picric acid in the above solutions. The solutions of sodium picrate and of picric acid in the above solvents were saturated solutions at room temperature throughout, unless otherwise stated.

All compounds were yellow unless otherwise described. Certain compounds gave consistent m. p.s only if immersed in a preheated bath: in such cases, the temperature of immersion is given as (T.I. °) immediately after the m. p.

Pyridine.—The base, of "AnalaR" quality, was converted into the colourless methiodide, m. p. 118° (lit.,[3] 118°), from ethanol.

(a) *Sodium picrate*. (1) An aqueous solution of the methiodide, added to an excess of saturated aqueous sodium picrate, deposited crystals of the double picrate (II), which when collected, washed with a small quantity of water, and dried, had m. p. 211—219°, increased to 216—220° (lit.,[1] 210—211°) by recrystallisation from water (Found: C, 37·8; H, 2·1; N, 17·2. Calc. for $C_{12}H_{10}N_4O_7,C_6H_2N_3NaO_7$: C, 37·7; H, 2·1; N, 17·1%). This salt, when recrystallised from ethanol, had m. p. 212—220°.

(2) Repetition in methanolic solutions gave no deposit because of the high solubility of the product, but in ethanolic solutions, the double picrate, m. p. and mixed m. p. 215—218°, was deposited. This double picrate had m. p. 219° when prepared from highly purified pyridine (cf. above).

(b) *Picric acid*. (1) The products of this reaction in aqueous solution varied with the conditions. When, however, a solution of the methiodide (0·5 g.) in cold water (10 c.c.) was added to solution of picric acid (1·2 g., 2·3 mol.) in warm water (40 c.c.) and set aside overnight, large needles, m. p. 64—82°, presumably a mixture, were deposited. The filtrate, on chilling, gave crystals, m. p. 60—62° after thorough drying in a vacuum-desiccator, of the ***hydrogen double picrate*** (III) (Found: C, 39·2; H, 2·4; N, 17·9. $C_{12}H_{10}N_4O_7,C_6H_3N_3O_7$ requires C, 39·2; H, 2·4; N, 17·8%). This picrate was unaffected by crystallisation from saturated ethanolic picric acid, but when once crystallised from ethanol, or twice from water, afforded the methopicrate (I), m. p. 115—116°.

(2) Addition of the methiodide (0·5 g.) in methanol (5 c.c.) to picric acid (1 g., 1·95 mol.) in hot methanol (20 c.c.) gave no deposit on cooling. The solution was evaporated at room temperature; the crude orange crystals when dried in vacuum had m. p. 48—50° and afforded

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[2] Kyte, Jeffery, and Vogel, *J.*, 1960, 4454.

[3] Schmidt, *Arch. Pharm.*, 1905, **243**, 583.

the hydrogen double picrate (III), m. p. 59—60°, on crystallisation from ethanolic picric acid (Found: C, 39·2; H, 2·3; N, 18·1%).

(3) Addition of the methiodide to the acid, in ethanolic solutions, deposited the methopicrate (I), m. p. 113—114° (crude), from ethanol, 117° (lit.,[4] 113—114°,[5] 114—115°) (Found: C, 44·9; H, 3·1; N, 17·6. Calc. for $C_{12}H_{10}N_4O_7$: C, 44·7; H, 3·1; N, 17·4%).

When equimolecular quantities of the methopicrate (I) and picric acid were dissolved in ethanol and evaporated at room temperature, the heterogeneous residue, when thoroughly dried, had m. p. 58—92°.

2-*Methylpyridine*.—The purified base gave the colourless methiodide, m. p. 229° (lit.,[6] 224—224·5°), from ethanol.

(a) *Sodium picrate.* (1) Addition of the methiodide to a small excess of sodium picrate, both in aqueous solutions, gave the methopicrate (I), m. p. and mixed m. p. 111—112°. The use of a large excess of the acid gave the *double picrate* (II), m. p. 212—213°, unchanged by crystallisation from water, methanol, or ethanol (Found: C, 38·4; H, 2·4; N, 16·4; Na, 3·9. $C_{13}H_{12}N_4O_7,C_6H_2N_3NaO_7$ requires C, 38·8; H, 2·4; N, 16·7; Na, 3·9%). To illustrate the effect of changing the proportion of reagents, sodium picrate (0·107 g., 0·5 mol.) in cold saturated aqueous solution was added to the methiodide (0·2 g.) also in concentrated aqueous solution: crystals of the methopicrate (I), m. p. 112°, were rapidly deposited. When the filtrate was treated with a similar solution of sodium picrate (0·428 g.), the double picrate (II), m. p. 204—210°, slowly separated.

(2) Addition of the methiodide to an excess of sodium picrate, both in (*a*) methanol and (*b*) ethanol gave the double picrate (II), (*a*) m. p. 211—212°, (*b*) m. p. 212°.

An aqueous solution of the methopicrate (I), when added to aqueous sodium picrate, deposited the double picrate (II), m. p. 212—213°.

(b) *Picric acid.* The methiodide in aqueous-ethanolic solution, when added to an excess of saturated ethanolic picric acid, deposited the methopicrate (I), m. p. 110—112° (crude), from ethanol, 113° (Found: C, 46·3; H, 3·8. Calc. for $C_{13}H_{12}N_4O_7$: C, 46·4; H, 3·6%). The m. p. 138—139° given by Giua and Giua [5] is an error.

3-*Methylpyridine*.—The base was purified by conversion into the zinc chloride derivative, which after four crystallisations from ethanol had the constant m. p. 146° (Found: C, 40·4; H, 4·4; N, 7·5. Calc. for $2C_6H_7N,HCl_3Zn$: C, 40·15; H, 4·2; N, 7·8%): the regenerated base boiled at 144—145°. Addition of the base (4 g.) to a mixture of methyl iodide (4 c.c.) and methanol (5 c.c.) under reflux caused gentle boiling: the whole was then boiled for 2 hr. and the solvents were removed. The solid residue, when crystallised from acetone, gave the colourless *methiodide*, m. p. 99—100°, unchanged by further crystallisation (Found: C, 35·9; H, 4·05; N, 6·0. $C_7H_{10}IN$ requires C, 35·8; H, 4·3; N, 6·0%). After several hours' exposure to the atmosphere, the salt slowly liquefied.

(a) *Sodium picrate.* (1) Addition of the methiodide to a large excess of sodium picrate, both in aqueous solution, afforded the pale orange methopicrate (I), m. p. 118—120° (crude), unaffected by admixture with that in (3) below.

(2) Repetition of this experiment, but with methanolic solutions, gave the double picrate (II), m. p. 165—168° (crude), from methanol 167—169°.

(3) Repetition, but with ethanolic solutions, also gave the *double picrate* (II), m. p. 167—171° (crude), after crystallisation from ethanol, 169—172° (Found: C, 38·7; H, 2·4; N, 16·7. $C_{13}H_{12}N_4O_7,C_6H_2N_3NaO_7$ requires C, 38·8; H, 2·4; N, 16·7%). The pale yellow thread-like crystals, on crystallisation from water, deposited hard orange sand-like crystals, m. p. 120°, of the *methopicrate* (I) (Found: C, 46·7; H, 3·35. $C_{13}H_{12}N_4O_7$ requires C, 46·4; H, 3·6%).

(b) *Picric acid.* (1) When the methiodide was added to an excess of picric acid, in aqueous or in methanolic solutions, no crystals were deposited.

(2) From ethanolic solutions, orange crystals of the methopicrate (I), m. p. 117—119°, unchanged by crystallisation from water, were slowly deposited in low yield (Found: C, 46·65; H, 3·65%).

4-*Methylpyridine*.—The pure base gave colourless crystals of the methiodide, m. p. 149—150° (lit.,[7] 149—150°), from ethanol.

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[4] Decker and Kaufmann, *J. prakt. Chem.*, 1911, **84**, 436.

[5] Giua and Giua, *Gazzetta*, 1921, **51**, 314.

[6] Jones, *J.*, 1903, **83**, 415.

[7] Clemo and Gourlay, *J.*, 1938, 478.

(a) *Sodium picrate.* (1) The addition of the methiodide to an excess of sodium picrate, both in aqueous solutions, gave the *double sodium picrate* (II), m. p. 214—216° (crude), recrystallised from water, 216° (Found: C, 38·8; H, 2·35; N, 16·6; Na, 3·7. $C_{13}H_{12}N_4O_7,C_6H_2N_3NaO_7$ requires C, 38·8; H, 2·4; N, 16·7; Na, 3·9%).

(2) Repetition of experiment (1), but with (*a*) methanolic, (*b*) ethanolic solutions, gave the same product, m. p. and mixed m. p. 216°. The double picrate was also unaffected by recrystallisation from methanol, ethanol (Found: C, 38·7; H, 2·3; N, 16·6%), or acetic acid (Found: C, 39·0; H, 2·3%).

(b) *Picric acid.* (1) A concentrated aqueous solution of the methiodide, when added to a moderate quantity of saturated aqueous picric acid, gave a rapid deposition of the *methopicrate* (I), m. p. 151—152° unchanged by recrystallisation from water (Found: C, 46·2; H, 3·4. $C_{13}H_{12}N_4O_7$ requires C, 46·4; H, 3·6%). When a more dilute solution of the methiodide was rapidly added to a marked excess of the picric acid, the solution after a few minutes deposited the *double hydrogen picrate* (III), m. p. 110—113° (crude); crystallised from water or ethanol, this had m. p. 112° (Found: C, 40·44; H, 3·0; N, 17·55. $C_{13}H_{12}N_4O_7,C_6H_3N_3O_7$ requires C, 40·4; H, 2·7; N, 17·4%). A mixture of the salts (I) and (III) had m. p. 110—145°.

That the nature of the product depends in this case on the proportion of the reagents is shown by four experiments in which the following weights of the methiodide were dissolved in water (1 c.c.) and added to cold, stirred saturated aqueous picric acid (5 c.c.); (i) 0·1 g., (ii) 0·2 g., (iii) 0·3 g., (iv) 0·35 g.: the product deposited had m. p. (i) 110—112°, (ii) 112—115°, (iii) 142—147°, (iv) 147—149°. The products from experiments (i) and (iv) are the almost pure hydrogen double picrate (III) and the methopicrate (I) respectively. To investigate experiment (i) in greater detail, the methiodide (0·1 g.), dissolved in water (1 c.c.), was again added dropwise (*a*) to the stirred saturated picric acid (5 c.c., 0·06 g. picric acid, 0·62 mol.), and the deposit collected; (*b*) the filtrate was again added to aqueous picric acid (5 c.c.) and after collection of the deposit; (*c*) the filtrate was added to more picric acid (10 c.c.), giving a third crop of deposit. Further addition of the filtrate to picric acid solution gave no deposit. The weights and m. p.s of the crops were: (*a*) 0·0506 g., 111—112°; (*b*) 0·0626 g., 112° (Found: C, 40·45; H, 2·7%); (*c*) 0·0965 g., 111—112°. Total weight of double picrate, 0·2097 g., theoretical yield, 0·240 g. It follows that some unchanged methiodide must have been present in the filtrate from experiment (*a*) and probably in that from (*b*).

A sample of the powdered methopicrate (I), m. p. 149—151°, was added to saturated ethanolic picric acid, which was vigorously shaken for 5 min., the mixture containing undissolved material throughout: the final material when collected, washed with a trace of ethanol, and dried was the double picrate (III), m. p. 110—111° (recrystallised from water, 112°).

Quinoline.—The pure base was converted into the orange methiodide, m. p. 134° (lit.,[8] 133°) after crystallisation from ethanol and thorough drying.

(a) *Sodium picrate.* (1) Addition of the methiodide to a considerable excess of sodium picrate, both in aqueous solution, gave the methopicrate (I), m. p. 169° (lit.,[9] 169·5°), unchanged by crystallisation from water (Found: C, 51·45; H, 3·35; N, 15·35. Calc. for $C_{16}H_{12}N_4O_7$: C, 51·6; H, 3·25; N, 15·05%).

(2) Repetition of experiment (1), but with methanolic solutions, deposited the *double sodium picrate* (II), m. p. 204—206° (T.I. 180°) (Found: C, 42·35; H, 2·5; N, 15·8; Na, 3·6. $C_{16}H_{12}N_4O_7,C_6H_2N_3NaO_7$ requires C, 42·4; H, 2·3; N, 15·7; Na, 3·7%).

(3) Repetition of experiment (1), with ethanolic solutions, also gave the double picrate (II), m. p. 200—204° (crude), 204—206° (T.I. 180°) after crystallisation from ethanol.

The double picrate (II), when recrystallised from (i) water, (ii) methanol, afforded the methopicrate (I), (i) m. p. 168—169° (Found: C, 51·75; H, 3·4%), (ii) m. p. 168—169°.

(b) *Picric acid.* Addition of the methiodide to an excess of picric acid, both in cold aqueous solution, deposited the methopicrate (I), m. p. 164—166° (crude) (168—169° from water) (Found: C, 51·35; H, 3·3%). The same product was obtained when this experiment was conducted in methanolic and in ethanolic solutions.

Addition of the methopicrate (I) to an excess of picric acid, both in cold aqueous or methanolic solutions, caused slow separation of the unchanged methopicrate, m. p. 168°.

Quinaldine.—The pure base afforded the pale yellow methiodide, m. p. 195° (lit.,[10] 195°) after

[8] Marckwald and Meyer, *Ber.*, 1900, **33**, 1884; Hantzsch, *Ber.*, 1909, **42**, 80.

[9] Decker, *Ber.*, 1903, **36**, 1213.

[10] Doebner and Miller, *Ber.*, 1883, **16**, 2468.

three recrystallisations from ethanol (Found: C, 46·45; H, 4·4; N, 4·8. Calc. for $C_{11}H_{12}IN$: C, 46·3; H, 4·2; N, 4·9%).

(a) *Sodium picrate.* (1) The addition of the methiodide to an excess of sodium picrate, both in aqueous solutions, gave the crude *double sodium picrate* (II), m. p. 210—214° (Found: C, 42·3; H, 2·7; N, 15·7. $C_{17}H_{14}N_4O_7,C_6H_2N_3NaO_7$ requires C, 43·3; H, 2·5; N, 15·4; Na, 3·6%).

(2) Repetition of this experiment, with methanolic solutions, also gave the picrate (II), m. p. 218—220°, unchanged by crystallisation from methanol (Found: C, 43·2; H, 2·8%).

(3) The experiment, carried out with ethanolic solutions, also gave the picrate (II), m. p. 218—220° (crude), 219—220° from ethanol (Found: C, 43·3; H, 2·4; N, 15·2; Na, 3·45%).

The double salt (II), when recrystallised from water, gave the methopicrate (I), m. p. 140° (lit.,[11] 139° with shrinking at 134°) (Found: C, 52·7; H, 3·7; N, 14·4. Calc. for $C_{17}H_{14}N_4O_7$: C, 52·85; H, 3·65; N, 14·5%): when the double salt was even triturated with a small quantity of cold water for several minutes, a residue solely of the methopicrate (I), m. p. 140—142° (slight shrinking at 132°), was obtained.

A methanolic solution of the methopicrate (I), when added to an excess of sodium picrate in methanol, deposited the double picrate (II), m. p. 216—218° (Found: C, 42·7; H, 2·8%).

(b) *Picric acid.* (1) Addition of the methiodide to an excess of picric acid, both in cold aqueous solutions, deposited the methopicrate (I), m. p. 131—140° (crude), 140—142° after crystallisation from water (Found: C, 53·0; H, 3·7%).

(2) Repetition of this experiment, with methanolic solutions, gave no deposit: from ethanolic solutions, the methopicrate (I), m. p. 140—142°, was deposited.

When a warm aqueous solution of the methopicrate was added to cold saturated aqueous picric acid, the solution, on cooling, deposited only the unchanged methopicrate: use of ethanolic solutions gave the same result.

Lepidine.—The pure base gave the bright yellow methiodide, m. p. 174° (lit.,[12] 173—174°) from ethanol: this salt is very soluble in water and methanol.

(a) *Sodium picrate.* (1) The methiodide, added to an excess of sodium picrate, both in aqueous solutions, deposited the methopicrate (I), m. p. 160—162° (lit.,[11] 159°), both crude and after crystallisation from water (Found: C, 52·9; H, 3·8; N, 14·4. Calc. for $C_{17}H_{14}N_4O_7$: C, 52·85; H, 3·65; N, 14·5%).

(2) Repetition with methanolic solutions gave no deposit. From ethanolic solutions, the *double sodium picrate* (II), m. p. 205—206°, was deposited (Found: C, 43·6; H, 2·7; N, 15·6. $C_{17}H_{14}N_4O_7,C_6H_2N_3NaO_7$ requires C, 43·3; H, 2·5; N, 15·4%).

The double picrate (II) when recrystallised once from water, or thrice from ethanol, gave the methopicrate (I), m. p. 159—160°.

(b) *Picric acid.* Addition of the methiodide to an excess of picric acid, both in aqueous solution, gave the methopicrate (I), m. p. 161—162° (Found: C, 52·66; H, 3·5%). The methopicrate was also obtained by using methanolic (in low yield) and ethanolic solutions. The methopicrate, when added to picric acid, both reagents in aqueous or in ethanolic solutions, crystallised unchanged.

Isoquinoline.—The pure base, m. p. 24°, was isolated by Harris and Pope's method,[13] and gave the very pale yellow methiodide, m. p. 159° (lit.,[14] 159°), from ethanol.

(a) *Sodium picrate.* (1) The methiodide, added to an excess of sodium picrate, both in aqueous solutions, afforded the methopicrate (I), m. p. 166—168° (crude), 169° (lit.,[5] 161—162°) from water (Found: C, 51·35; H, 3·5. Calc. for $C_{16}H_{12}N_4O_7$: C, 51·6; H, 3·25%). The m. p. 187° given by Decker and Kaufmann [4] is incorrect.

(2) Repetition of this experiment, with methanolic solutions, gave a crude product, m. p. 198—205°, which after two recrystallisations afforded the methopicrate.

(3) Repetition with ethanolic solutions also gave a crude product, m. p. 188—255°, which on one recrystallisation from ethanol afforded the methopicrate, m. p. 167—168°. In view of the wide range in m. p. of this crude product, the following quantitative experiments were performed. (i) A solution of the methiodide (0·1 g.) in ethanol (2 c.c.) was added dropwise to a vigorously stirred solution of sodium picrate (0·232 g., 2·5 mol.) in ethanol (15 c.c.). The

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[11] Adams, Cymerman-Craig, Ralph, and Willis, *Austral. J. Chem.*, 1955, **8**, 392.

[12] Hoogewerff and van Dorp, *Rec. Trav. chim.*, 1883, **2**, 318.

[13] Harris and Pope, *J.*, 1922, **121**, 1030.

[14] Claus and Edinger, *J. prakt. Chem.*, 1888, **38**, 492.

crystalline deposit of the *double sodium picrate* (II), when collected, washed with a very small quantity of ethanol, and dried, had m. p. 200—225° with softening at 160°. It was recrystallised from ethanol containing some sodium picrate, and dried at 90°/0·1 mm. and then on heating, shrank at 212°, and melted at 218—236° to a red liquid, which on cooling crystallised to a dark yellow mass: this behaviour was unaffected by a second recrystallisation (Found: C, 42·7; H, 2·6; N, 15·4. $C_{16}H_{12}N_4O_7,C_6H_2N_3NaO_7$ requires C, 42·4; H, 2·3; N, 15·7%). (ii) Repetition of this experiment, but with sodium picrate (0·370 g., 4 mol.) in ethanol (20 c.c.), gave the same product, which even without recrystallisation shrank at 200° and melted at 212—236°. Attempted recrystallisation of this salt from water gave the methopicrate (I).

(b) *Picric acid.* The methopicrate (I) in hot aqueous solution was added to cold saturated aqueous sodium picrate, and crystallised unchanged (m. p. 164—165°) as the solution cooled.

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