582. *The Preparation of Bis-2-cyanoethyl Derivatives of Aromatic Primary Amines, and their Conversion into* 1 : 6-*Diketojulolidines.*

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The conditions are described for the conversion of certain aromatic primary amines into their bis-2-cyanoethyl derivatives, and for the cyclisation of the latter to the corresponding 1 : 6-diketojulolidines. The properties of the diketo-compounds have been investigated; the dioxime of the unsubstituted 1 : 6-diketojulolidine shows unexpected stability.

It has been shown by R. C. Cookson and Mann (*J.*, 1949, 67) that heating aniline with an excess of vinyl cyanide in acetic acid at 150° gives a mixture of *N*-2-cyanoethylaniline, $Ph\cdot NH\cdot CH_2\cdot CH_2\cdot CN$, and *NN*-bis-2-cyanoethylaniline, $Ph\cdot N(CH_2\cdot CH_2\cdot CN)_2$. This is apparently the first recorded example of an aromatic primary amine undergoing dicyanoethylation, although Elderfield, Gensler, Bembry, Kremer, Brody, Hageman, and Head (*J. Amer. Chem. Soc.*, 1946, **68**, 1262) had shown that *p*-anisidine under similar conditions gave the monocyanoethyl derivative.

We have therefore investigated further the reaction of aromatic primary amines with vinyl cyanide, and find that the production of the biscyanoethyl derivative is apparently a general process. Our results are summarised in the following Table, in which are recorded the products obtained by heating various amines with vinyl cyanide (2·5 mols.) and acetic acid (2·4—2·5 mols.) at 140—145° for 3—6 hours.

Amine	Time of heating (hours)	Mono-deriv. $R\cdot NH\cdot C_2H_4\cdot CN$ M. p.	Yield, %	Di-deriv. $R\cdot N(C_2H_4\cdot CN)_2$ M. p.	Yield, %
Aniline	3·5	51·5°	32	80—82°	13
m-Toluidine	4·5	47·5—48·5	50	85—86	32
p-Toluidine	6	103—104	54	61—62	42
p-Anisidine	5·5	64 [1]	—	100—101	52
p-Chloroaniline	3·25	76 [2]	—	91	4

[1] Elderfield *et al.* (*loc. cit.*). [2] Bauer, Cymerman, and Sheldon, *J.*, 1951, 3312; these mono-derivatives were not isolated in our experiments.

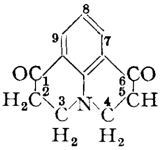
Although the experiments have been repeated many times, it is not claimed that the yields given in the Table (which represent those of the crude material once recrystallised) could not be further improved. It is noteworthy that the addition of a mixture of copper powder and copper acetate to the reaction mixture (cf. B.P. 457,621) did not appreciably affect the yield of the products from *m*-toluidine and *p*-chloroaniline : furthermore, *p*-toluidine when heated with vinyl cyanide, formic acid, copper powder, and copper formate gave only the monocyanoethyl derivative, and when heated with vinyl cyanide, *cyclo*hexane, and a trace of sodium methoxide remained unaffected. These observations indicate that the probable function of the acetic acid is to form the ion, $R{\cdot}NH_3^+$, which is apparently more susceptible to cyanoethylation than the free base. The other possibility, namely, that acetanilide (or its analogues) is the reactive intermediate, is disproved, because we have found that acetanilide, after being heated with vinyl cyanide and acetic acid under conditions similar to those cited in the preceding paragraph, was recovered in almost theoretical quantity.

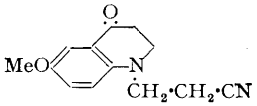
Certain properties of the biscyanoethyl derivatives have been investigated. It will be noted that, with one exception, all have melting points above those of the corresponding monocyanoethyl derivatives : no explanation of the exception (*p*-toluidine) is apparent.

It has been pointed out (R. C. Cookson and Mann, *J.*, 1947, 618 ; Mann and Watson, *J. Org. Chem.*, 1948, **13**, 502) that the inductive effect of the cyano-groups in bis-2-cyanoethylphenylarsine, $Ph{\cdot}As(CH_2{\cdot}CH_2{\cdot}CN)_2$, partly suppresses the normal reactivity of the tertiary arsine, which, for example, is stable to air for long periods, but gives a quaternary salt in the presence of boiling methyl iodide. A similar partial inactivation of the nitrogen atom occurs in bis-2-cyanoethylaniline. This forms a crystalline hydrochloride and a chloroplatinate, but these when mixed with water immediately deposit the free base. On the other hand it does not apparently form a picrate, and does not combine with boiling methyl iodide or molten methyl toluene-*p*-sulphonate : it is also unaffected by 30% hydrogen peroxide. These properties are in marked contrast to those of *N*-2-cyanoethyl-*N*-methylaniline, $Ph{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, in which the inductive effect of the cyano-group upon the tertiary nitrogen atom is necessarily much weaker ; the amine consequently forms a picrate (Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Amer. Chem. Soc.*, 1944, **66**, 725) and we find that it also readily forms a methiodide.

Bis-2-cyanoethylaniline and its *m*-toluidine homologue behave as typical dialkylarylamines in that they form green crystalline *p*-nitroso-derivatives.

Mann and Smith (*J.*, 1951, 1898) have shown that bis-2-cyanoethylaniline when heated with aluminium chloride in chlorobenzene undergoes cyclisation to 1 : 6-diketojulolidine (I). We have both extended the scope of this reaction and investigated certain properties of the diketone (I). Bis-2-cyanoethyl-*m*-toluidine undergoes ready cyclisation to 1 : 6-diketo-7-methyljulolidine, but the *p*-toluidine analogue gives the 8-methyldiketone in only 7% yield, and the *p*-anisidine analogue undergoes cyclisation and demethylation to give 8-hydroxy-1 : 6-diketojulolidine, also in 7% yield. All these diketojulolidines are crystalline and readily give crystalline but almost insoluble bisphenylhydrazones.


(I)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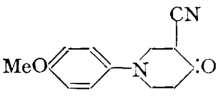
(III)

Solutions of the diketones in polar solvents show marked fluorescence, ranging from yellow-green to orange, which, however, is much feebler in solvents such as benzene and *cyclo*hexane. It has been claimed (F.P. 806,715) that cyclisations of the above type can be carried out by heating appropriate nitriles with a mixture of aluminium chloride, potassium chloride, and sodium chloride, but this method proved useless for our purpose. The production of 1 : 6-diketo-7-methyl- and 8-hydroxy-1 : 6-diketo-julolidine was accompanied by that of corresponding monoketones, the structures of which are discussed below.

The diketone (I) also readily gives a crystalline dioxime, which possesses unexpected stability : we have failed to reduce it by sodium and methanol, sodium amalgam, lithium aluminium hydride, or hydrogen and a palladium–carbon catalyst. During these experiments we have isolated the dibenzoate, ditoluene-*p*-sulphonate, and diacetate of the dioxime. The first of these derivatives shows a remarkable variation in melting-point : one sample when thrice recrystallised from ethanol–acetone had m. p.s 172°, 186°, and 175·5°; another sample, recrystallised from ethanol–acetone, had m. p. 204°, depressed to 201° by admixture with the sample of m. p. 175·5°. The dioxime and its esters can theoretically exist as *syn-*, *anti-*, and *amphi*-forms, and it is possible that the above variation may be due to a very ready interconversion of two or three of these isomeric forms. Furthermore, the dioxime ditoluene-*p*-sulphonate, when analytically pure, began to melt at 145° but was not completely molten at 200°, possibly owing to its being a mixture of isomeric forms or to the slow conversion of one form into another; on the other hand, it may have been due to the onset of the Beckmann rearrangement, for Kuhara ("On the Beckmann Rearrangement," Imp. Univ. Kyoto, Tokyo, 1926; cf. also Chapman, *J.*, 1933, 806; 1934, 1550; 1936, 448) has shown that the benzenesulphonate esters of oximes may undergo the Beckmann rearrangement spontaneously at room temperature, and rapidly when heated. We hope later to examine these esters more fully.

When, however, the cyclisation of bis-2-cyanoethyl-*m*-toluidine was performed with a smaller proportion of aluminium chloride, a pale yellow crystalline monoketone, $C_{13}H_{14}ON_2$, was isolated in small yield: bis-2-cyanoethyl-*p*-anisidine similarly gave a monoketone, $C_{13}H_{14}O_2N_2$, which, unlike the diketone, still retained the methoxyl group intact. It will be clear that the *p*-methoxyphenyl monoketone, for example, might be either 1-2′-cyanoethyl-1 : 2 : 3 : 4-tetrahydro-6-methoxyquinol-4-one (II) or the isomeric 3-cyano-1-*p*-methoxyphenylpiperid-4-one (III). The small amount of these monoketones available precluded a ready chemical identification of their structure. It is a reasonable assumption, however, that the ultra-violet absorption of (III) should be not markedly different from that of the parent compound, $MeO{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CH_2{\cdot}CN)_2$, whereas that of the quinolone (II) would undoubtedly show considerable differences, particularly as the carbonyl group is now directly conjugated to the aromatic ring. The spectrum of the parent dinitrile in ethanol shows maxima at 312 ($\varepsilon_{max.}$ 1830) and 251 mμ ($\varepsilon_{max.}$ 11,600) with minima at 277 ($\varepsilon_{min.}$ 795) and 220 mμ ($\varepsilon_{min.}$ 4860). That of the monoketone, also in ethanol, shows maxima at 410 ($\varepsilon_{max.}$ 5070), 264 ($\varepsilon_{max.}$ 7760) and 239 mμ ($\varepsilon_{max.}$ 22,400), with minima at 297 ($\varepsilon_{min.}$ 100) and 259 mμ ($\varepsilon_{min.}$ 7460). These wide differences make it highly probable that the monoketone is the quinolone (II). This receives some chemical suppport in the *p*-methoxyphenyl series from the fact that the action of the aluminium chloride is clearly milder in the formation of the monoketone than in that of the diketone: consequently the methoxyl group is not demethylated and apparently only one of the 2-cyanoethyl groups undergoes cyclisation. Quinol-4-ones of type (II) would be of great value, because hydrolysis of the nitrile group followed by decarboxylation would yield the 1-alkyltetrahydroquinol-4-ones, which are otherwise difficult to prepare.

EXPERIMENTAL

Certain compounds gave sharp m. p.s only in an evacuated tube; these are denoted by (E.T.).

Cyanoethylation.—This process was carried out in all cases by heating the mixture of the amine, vinyl cyanide, and acetic acid (see p. 3046) in a glass tube which formed the lining of a stainless-steel autoclave. Only the treatment of the product is therefore described below.

Aniline. Cyanoethylation was performed under conditions similar to those of R. C. Cookson and Mann (*loc. cit.*), and distillation of the higher-boiling material gave two fractions: (*a*), b. p. 120—130°/0·35 mm., gave 2-cyanoethylaniline (32%), m. p. 49—50° after one recrystallisation from aqueous ethanol; (*b*), b. p. 180—190°/0·35 mm., similarly recrystallised, gave bis-2-cyanoethylaniline (13%), m. p. 79—80°.

Dry hydrogen chloride was passed into a cold acetone solution of bis-2-cyanoethylaniline, which, when subsequently diluted with ether, deposited the white crystalline *hydrochloride*, m. p. 115·5—116·5° after being washed with dry ether and dried over calcium chloride (Found: N, 17·9. $C_{12}H_{13}N_3,HCl$ requires N, 17·9%). A solution of amine in warm concentrated hydrochloric acid was added to concentrated aqueous chloroplatinic acid: the mixture when cooled deposited orange-brown crystals of the *chloroplatinate*, which when washed with ice-cold concentrated hydrochloric acid and dried in a vacuum-desiccator, had m. p. 148—149° (decomp.) [Found: C, 35·2; H, 3·6; N, 10·3; Pt, 24·1. $(C_{12}H_{13}N_3)_2,H_2PtCl_6$ requires C, 35·6; H, 3·5; N, 10·4; Pt, 24·1%].

Bis-2-cyanoethylaniline was recovered unchanged after (*a*) its solution in an excess of methyl iodide had been heated at 100° in a sealed tube for 14 hours, (*b*) its solution in methyl iodide containing nitromethane had been boiled under reflux for 1·25 hours, (*c*) a mixture with an excess of methyl toluene-*p*-sulphonate had been heated at 165° for 30 minutes, and (*d*) a solution in acetone containing an excess of 30% hydrogen peroxide had been set aside at room temperature for 15 hours.

NN-*Bis*-2-*cyanoethyl*-p-*nitrosoaniline*, prepared in the usual way, formed shining green plates (from ethanol), m. p. 138—139° (Found : C, 63·4; H, 5·35; N, 24·3. $C_{12}H_{12}ON_4$ requires C, 63·2; H, 5·3; N, 24·5%).

m-*Toluidine*. The crude cyanoethylation product, a dark brown viscous liquid, was first heated at 18 mm. to remove low-boiling constituents; the residue when distilled at 0·2 mm. gave the fractions : (*a*), b. p. 125—150°, which slowly solidified, (*b*), b. p. 160—190°, which rapidly solidified. Fraction (*a*), after recrystallisation from ethanol, gave 2-*cyanoethyl*-m-*toluidine*, colourless plates, m. p. 47·5—48·5° (50%) (Found : C, 75·2; H, 7·5; N, 17·35. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·5; N, 17·5%). Fraction (*b*), after repeated recrystallisation from ethanol, gave *bis*-2-*cyanoethyl*-m-*toluidine*, colourless needles, m. p. 85—86° (32%) (Found : C, 73·3; H, 7·3; N, 19·9. $C_{13}H_{15}N_3$ requires C, 73·2; H, 7·0; N, 19·7%).

Treatment with nitrous acid in the usual way gave NN-*bis*-2′-*cyanoethyl*-4-*nitroso*-m-*toluidine* (NH_2 = 1), dark green plates (from ethanol), m. p. 157—158° (Found : C, 64·4; H, 5·8; N, 22·9. $C_{13}H_{14}ON_4$ requires C, 64·4; H, 5·8; N, 23·1).

p-*Toluidine*. The crude product, when treated as above, also gave two fractions on distillation at 0·2 mm., both rapidly solidifying. Fraction (*a*), b. p. 140—180°, recrystallised from ethanol, gave N-2-*cyanoethyl*-p-*toluidine*, colourless plates, m. p. 103—104° (54%) (Found: C, 75·2; H, 7·5; N, 17·3%). Fraction (*b*), b. p. 180—205°, similarly recrystallised, gave NN-*bis*-2-*cyanoethyl*-p-*toluidine*, colourless needles, m. p. 61—62° (42%) (Found : C, 73·05; H, 7·1; N, 20·1%).

When a mixture of *p*-toluidine (11 g.), vinyl cyanide (17·5 c.c., 2·6 mols.), *cyclo*hexane (15 c.c.), and sodium methoxide (0·5 g.) was heated at 140—150° for 3 hours, the product showed evidence of polymerisation, and distillation at 0·5 mm. yielded unchanged *p*-toluidine (8·5 g., 77%) and no cyanoethyl derivatives.

When a mixture of *p*-toluidine (11 g.), vinyl cyanide (20 c.c., 3 mols.), formic acid (10 c.c.), copper powder (1 g.), and copper formate (0·5 g.) was heated at 180—190° for 3 hours, distillation gave unchanged *p*-toluidine, a small yield of the above fraction (*a*), and a very small higher-boiling fraction.

p-*Anisidine*. The cold reaction product solidified in all experiments except the first, and when recrystallised from ethanol gave NN-*bis*-2-*cyanoethyl*-p-*anisidine*, colourless crystals, m. p. 100—101°, b. p. 214—218°/0·2 mm. (52%) (Found : C, 68·3; H, 6·4; N, 18·5. $C_{13}H_{15}ON_3$ requires C, 68·1; H, 6·55; N, 18·3%).

p-*Chloroaniline*. The crude reaction product was distilled at 0·1 mm. after low-boiling constituents had been removed, and furnished (*a*) unchanged *p*-chloroaniline, (*b*) *p*-chloroacetanilide, m. p. 175—176° (Found : N, 8·15. Calc. for C_8H_8ONCl : N, 8·3%), (*c*) a yellow oil, b. p. 180—210°, which slowly solidified and when recrystallised from ethanol gave p-*chloro*-NN-*bis*-2-*cyanoethylaniline*, colourless needles, m. p. 91° (4%) (Found : C, 62·0; H, 5·1; N, 17·9. $C_{12}H_{12}N_3Cl$ requires C, 61·7; H, 5·1; N, 18·0%). No indication of the monocyanoethylamine was obtained.

Acetanilide. (*a*) When a mixture of acetanilide (3 g.), vinyl cyanide (1·9 c.c., 1·25 mols.), and acetic acid (1·65 c.c., 1·25 mols.) was similarly heated at 140° for 14 hours, the straw-coloured viscous liquid on cooling deposited unchanged acetanilide in almost theoretical yield. (*b*) An identical result was obtained when a mixture of acetanilide (22·5 g.), vinyl cyanide (18·8 c.c.), acetic acid (12·5 c.c.), and water (3 c.c.) was heated at 142° for 4·5 hours. The water added to this mixture was equivalent to that which would have been formed in the cyanoethylation of the primary amines had they undergone acetylation as an intermediate stage in cyanoethylation process.

N-2-*Cyanoethyl*-NN-*dimethylanilinium Iodide*.—This salt readily crystallised when a solution of 2-cyanoethyl-*N*-methylaniline in an excess of methyl iodide was boiled under reflux for 1 hour and cooled; recrystallisation from ethanol gave the colourless *iodide*, m. p. 126° (Found : C, 43·8; H, 5·1; N, 9·4. $C_{11}H_{15}N_2I$ requires C, 43·7; H, 5·0; N, 9·3%).

1 : 6-*Diketojulolidine* (I). This was prepared by the following modification of Mann and Smith's method (*loc. cit.*). Bis-2-cyanoethylaniline (9 g.) was added to a mixture of powdered aluminium chloride (40 g., 6·7 mols.), chlorobenzene (26 c.c.), and concentrated hydrochloric acid (1·5 c.c.),

which was then heated at 150° for 7·5 hours with vigorous stirring. The red oily mixture was then cooled, hydrolysed with ice-water, and distilled in steam to remove chlorobenzene. The aqueous residue (*ca.* 150 c.c.), when allowed to cool slowly, deposited the crude diketone, which when once recrystallised from ethanol had m. p. 134—136° (yield 8 g., 89%); this material was not quite pure, however, because Mann and Smith (*loc. cit.*) gave m. p. 145—146°. Consistent yields in this and analogous preparations described below were obtained only if aluminium chloride of high purity were used, and if the hydrolysis was carefully performed to prevent any appreciable rise in temperature.

The Dioxime of (I).—A mixture of the diketone (0·25 g.) and a solution of hydroxylamine hydrochloride (2 g.) in 10% aqueous sodium carbonate (24 c.c.) and ethanol (5 c.c.) was boiled under reflux for 3 hours, and on cooling deposited the *dioxime* as pale yellow needles (0·2 g., 70%) which when recrystallised from aqueous ethanol had m. p. 237·5—238·5° (decomp.) (Found: C, 62·5; H, 5·3; N, 18·3. $C_{12}H_{13}O_2N_3$ requires C, 62·3; H, 5·7; N, 18·2%).

When the dioxime was shaken with an excess of benzoyl chloride in 10% aqueous sodium hydroxide suspension, the *dibenzoate* was readily obtained and after successive recrystallisations from ethanol–acetone had m. p. 172°, 186°, 175·5° (decomp. throughout); the final product was analysed (Found: N, 9·7. $C_{26}H_{21}O_4N_3$ requires N, 9·6%).

Attempted reduction. (*a*) Sodium (4·5 g., 16·5 atomic proportions) was added during 1·5 hours to a boiling solution of dioxime (1·4 g.) in methanol (50 c.c.). The solution was then distilled in steam, superheated steam being finally used, but the collected distillate (400 c.c.) when acidified with hydrochloric acid and evaporated gave no residue. The strongly alkaline residual solution was then divided into two portions. (i) One portion was vigorously shaken for 1 hour with an excess of benzoyl chloride, and the dibenzoate of the dioxime obtained as a fine yellow crystalline powder, which when thrice recrystallised from ethanol–acetone had m. p. 143°, 193°, 204° (decomp. throughout); the last sample was analysed (Found: C, 70·8; H, 4·7; N, 9·6. Calc. for $C_{26}H_{21}O_4N_3$: C, 71·1; H, 4·8; N, 9·6%). A mixture of the sample of m. p. 204° with that of m. p. 175·5° obtained directly had m. p. 201°. (ii) The second portion was similarly treated with an excess of toluene-*p*-sulphonyl chloride and gave the *ditoluene*-p-*sulphonate* of the dioxime, which after two recrystallisations from ethanol–acetone formed pale yellow needles, which softened at 154° but were not completely molten at 200°: after a third recrystallisation they melted similarly from 145° to *ca.* 200° (Found: for material twice recrystallised, N, 7·8; thrice recrystallised, C, 58·0; H, 4·8; N, 7·7. $C_{26}H_{25}O_6N_3S_2$ requires C, 57·9; H, 4·7; N, 7·8%). The crystals darkened slowly on exposure to light and air.

(*b*) A solution of the dioxime (1 g.) in methanol (15 c.c.) was treated with 2·5% sodium amalgam (100 g.) and acetic acid in alternate portions during 2 hours so that the solution remained slightly acid, but no amine could subsequently be isolated.

(*c*) A solution of lithium aluminium hydride (1 g.) in ether (50 c.c.) was boiled under reflux in a Soxhlet apparatus having the dioxime (0·5 g.) in the thimble. After 5 hours' boiling, the unchanged dioxime was recovered from the solution. The experiment was repeated, and the final extraction mixture, when boiled again with an acetic acid–anhydride mixture, yielded the *diacetate* of the dioxime as yellow crystals, m. p. 192·5° (decomp.) (E.T.) after two recrystallisations from ethanol–acetone (Found: C, 61·0; H, 5·3; N, 12·9. $C_{16}H_{17}O_4N_3$ requires C, 61·0; H, 5·4; N, 13·3%).

(*d*) A solution of the dioxime (0·2 g.) in ether (35 c.c.) and 2-methoxyethanol (5 c.c.) containing palladium–carbon was unaffected when vigorously shaken with hydrogen for 2 hours at room temperature and pressure.

1 : 6-*Diketo*-7-*methyljulolidine*.—This was prepared similarly to (I), the reaction mixture being heated at 150° for 9 hours and, after removal of the chlorobenzene by steam-distillation, the residual mixture on slow cooling deposited the *diketone*, which when thrice recrystallised from ethanol formed bright yellow needles, m. p. 121—122° (35%) (Found: C, 72·7; H, 6·4; N, 6·6. $C_{13}H_{13}O_2N$ requires C, 72·5; H, 6·1; N, 6·5%).

When a methanolic solution of the diketone was boiled with phenylhydrazine and a few drops of acetic acid, the *bisphenylhydrazone* readily separated as fine bright yellow crystals, which when collected, washed with boiling methanol, and dried had m. p. 207—208° (97% yield) (Found: C, 75·8; H, 6·4; N, 17·7. $C_{25}H_{25}N_5$ requires C, 75·9; H, 6·4; N, 17·7%). The hydrazone was almost insoluble in all the usual solvents.

The *dioxime*, prepared similarly to that of (I), with 4·5 hours' boiling, formed pale yellow needles, m. p. 211—212° (decomp.) (E.T.) (88% yield), from aqueous ethanol (Found: C, 63·9; H, 5·9; N, 16·8. $C_{13}H_{15}O_2N_3$ requires C, 63·7; H, 6·2; N, 17·1%).

To determine the effect of a smaller proportion of aluminium chloride, a mixture of the dinitrile (1·4 g.), aluminium chloride (4·7 g., 5 mols.), chlorobenzene (4·7 c.c.), and concentrated hydrochloric acid (0·2 c.c.) was heated at 140° for 8 hours. The cold mixture was then hydrolysed and steam-distilled as before, and the aqueous residue extracted with chloroform. Removal of the solvent left a red gum which solidified when mixed with light petroleum and was then heated at 110°/0·2 mm. to remove impurities by sublimation. The residue, when recrystallised from benzene–*cyclo*hexane, gave (in extremely low yield) pale straw-coloured crystals of a *monoketone* (presumably 1-2′-cyanoethyl-1 : 2 : 3 : 4-tetrahydro-5-methylquinol-4-one, as II), m. p. 114—115° (Found : N, 13·2. $C_{13}H_{14}ON_2$ requires N, 13·1%).

1 : 6-*Diketo*-8-*methyljulolidine*.—This *diketone* was prepared as (I), with heating of the reaction mixture at 160° for 14 hours, and after repeated recrystallisation from *cyclo*hexane was obtained as bright yellow needles, m. p. 151—152° (7% yield) (Found : C, 72·8; H, 6·2; N, 6·6. $C_{13}H_{13}O_2N$ requires C, 72·5; H, 6·1; N, 6·5%).

It formed a yellow crystalline *bisphenylhydrazone*, m. p. 269° (decomp.) (E.T.) (Found : C, 75·3; H, 6·0; N, 17·7. $C_{25}H_{25}N_5$ requires C, 75·9; H, 6·4; N, 17·7%), and a *dioxime*, pale yellow needles (from aqueous ethanol), m. p. 218° (decomp.) (E.T.) (85% yield) (Found : C, 63·7; H, 5·9; N, 17·2. $C_{13}H_{15}O_2N_3$ requires C, 63·7; H, 6·2; N, 17·1%).

8-*Hydroxy*-1 : 6-*diketojulolidine*.—This *diketone* was obtained by the usual cyclisation of bis-2-cyanoethyl-*p*-anisidine, with 15 hours' heating at 165°; it formed brilliant orange needles (from ethanol), m. p. 258—259° (decomp.) (7%) (Found : C, 66·7; H, 5·3; N, 6·5. $C_{12}H_{11}O_3N$ requires C, 66·4; H, 5·1; N, 6·45%).

It formed a bisphenylhydrazone, bright yellow crystals (from methanol), m. p. 271—272° (decomp.) (E.T.), which rapidly darkened on exposure to light.

When a solution of the diketone in acetic anhydride containing fused sodium acetate was boiled for 1 hour, cooled and poured into water, bright yellow needles of 8-*acetoxy*-1 : 6-*diketojulolidine* slowly separated from the oily deposit, and when recrystallised from ethanol had m. p. 208·5—209·5° (decomp.) (E.T.) (67% yield) (Found : C, 65·1; H, 4·9; N, 5·6. $C_{14}H_{13}O_4N$ requires C, 64·9; H, 5·05; N, 5·4%). It gave a yellow *bisphenylhydrazone*, m. p. 263° (decomp.) (E.T.) after crystallisation from ethanol (Found : C, 71·2; H, 6·05; N, 16·0. $C_{26}H_{25}O_2N_5$ requires C, 71·1; H, 5·8; N, 15·9%).

A mixture of the dinitrile (5 g.), aluminium chloride (15 g., 4·9 mols.), chlorobenzene (15 c.c.), and concentrated hydrochloric acid (1 c.c.) was heated at 180—190° for 5·5 hours. The mixture was hydrolysed and steam-distilled as usual, and the aqueous residue extracted with chloroform. Evaporation of the latter gave an orange-yellow solid, which after four recrystallisations from ethanol, afforded a small yield of bright yellow crystals of a *monoketone* (presumably II), m. p. 174—174·5° (E.T.) (Found : C, 67·5; H, 6·25; N, 12·0. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1; N, 12·2%).

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