

**699.** *Reaction of Pyrylium Salts with Alkali Cyanides.*

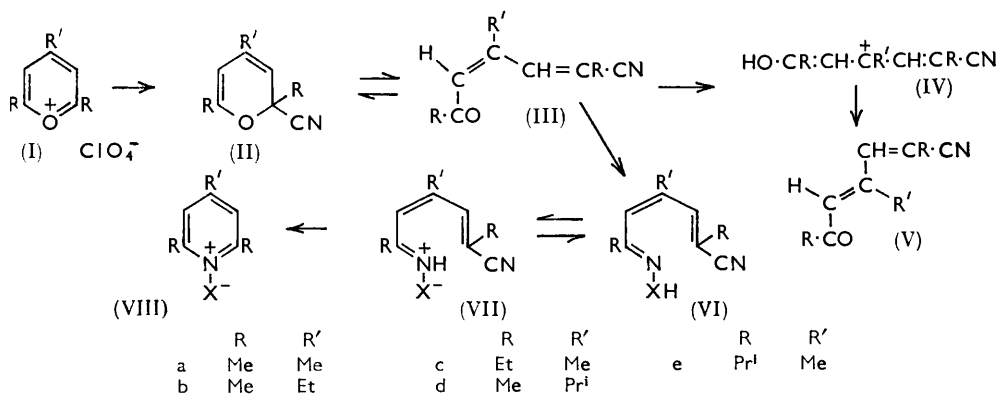
By A. T. BALABAN and C. D. NENITZESCU.

Alkyl-substituted pyrylium salts readily react with aqueous solutions of conjugated alkali cyanides, yielding unsaturated cyano-*cis*-alkadienones (III). These are rapidly converted by concentrated acids into their *trans*-isomers (V). Carbonyl derivatives of the *cis*-products undergo an unexpected 1,6-elimination of hydrogen cyanide with formation of pyridinium derivatives; *e.g.*, the oximes yield the pyridine *N*-oxides (VIII; X = O).

ALTHOUGH pyrylium salts react with nearly all nucleophilic reagents,<sup>1</sup> the reaction of monocyclic pyrylium salts with cyanide ion has not hitherto been investigated.

<sup>1</sup> Dimroth, *Angew. Chem.*, 1960, **72**, 331; Katritzky and Lagowski, "Heterocyclic Chemistry," Methuen, London, 1960, chapter 2, and especially p. 69; *Studii si Cercetări Chim. (Acad. R.P.R.)*, 1961, **9**, 251.

Trimethylpyrylium perchlorate<sup>2</sup> (Ia) reacts smoothly with cold aqueous sodium cyanide, with practically no thermal effect, yielding a yellow oil, C<sub>9</sub>H<sub>11</sub>NO, which gradually evolves hydrogen cyanide but can be distilled at reduced pressure. It readily yields carbonyl derivatives and is oxidised by hypobromite to a crystalline acid C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>. Whereas the ketone is resinified by hot alkali, the acid undergoes alkaline hydrolysis to a dibasic acid C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>. The infrared absorption spectrum of the ketone shows a carbonyl-stretching band at 1616 and a sharp nitrile band at 2216 cm.<sup>-1</sup> and is therefore assigned formula (IIIa). This accords with the usual addition of nucleophilic agents to the α-position of the pyrylium cation (*e.g.*, with hydroxide ion to yield pseudobases and phenols,<sup>3</sup> with



hydrogen peroxide to yield 2-acyl-furans,<sup>4</sup> etc.) The process is depicted by us as involving a cyclic intermediate (II), though no experimental support has been found in the present case for tautomerism (II)  $\rightleftharpoons$  (III).<sup>5</sup>

The ketone (IIIa) gives two unexpected reactions. First, it shows a surprisingly high basicity; it dissolves at once in concentrated acids, the solution gradually becoming pink. If the solution in concentrated hydrochloric acid is immediately diluted with water, a stable solid isomeric form of the ketone is obtained. The carbonyl derivatives of this and the acid obtained from it by hypobromite melt higher than the corresponding derivatives of the ketone (IIIa). We postulate a cation, for example (IVa), in concentrated acids, that assumes the most stable configuration and on dilution affords the new form (Va), obtained. We postulate a *cis*  $\rightarrow$  *trans*-isomerisation on the following grounds: If the double bond next to the cyano-group were also involved, four stereoisomers should be obtained, whereas we obtained only two. The other double bond certainly has a *cis*-configuration in the original product (II) since this originates from the cyclic compound (I), but one cannot determine *a priori* the spatial arrangement of the CR·CN group since the cyanide ion may approach from either side of the plane of the aromatic ring. On ring opening, however, only one—the more stable—arrangement of the CR·CN group will be formed, because on passing from the cyclic product (II) to the open-chain form (III) the carbon atom changes from *sp*<sup>2</sup>- back to *sp*<sup>2</sup>-hybridisation and the R and the CN group are equivalent in this process. Since, then, the CR·CN group has already the more stable configuration in the ketone (III), no isomerisation of it can occur on treatment with the acid catalyst, so that only two of the four *cis-trans*-isomers are isolated.

The infrared absorption spectra of the cyano-ketones (IIIa) and (Va) are consistent with these assumptions. There is only one other instance of a butadiene substituted in

<sup>2</sup> Balaban and Nenitzescu, *J.*, 1961, 3553; Praill and Whitear, *Proc. Chem. Soc.*, 1959, 312.

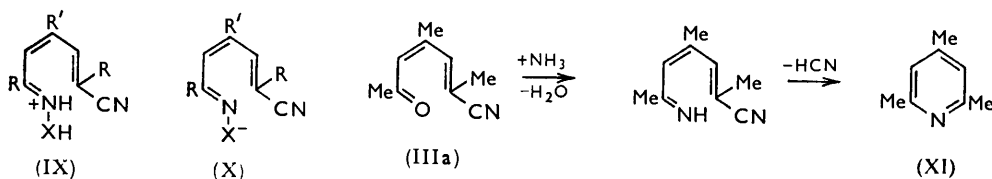
<sup>3</sup> (a) Baeyer and Piccard, *Annalen*, 1911, 394, 208; 1914, 407, 332; (b) Balaban and Nenitzescu, *Annalen*, 1959, 625, 77.

<sup>4</sup> Balaban and Nenitzescu, *Chem. Ber.*, 1960, 93, 599.

<sup>5</sup> (a) Köbrich, *Angew. Chem.*, 1960, 72, 348; (b) Berson, *J. Amer. Chem. Soc.*, 1952, 74, 358.

1 and 4 positions with electron-attracting substituents, namely, 1,4-dinitrobutadiene,<sup>6</sup> and this does not show the usual diene reactions.

The second unexpected reaction was observed with the carbonyl derivatives of compound (III). The 2,4-dinitrophenylhydrazone of (IIIa) melted with decomposition at 140°, then resolidified to give a higher-melting derivative. On a larger scale, it was established that hydrogen cyanide was evolved at 140°, and an orange-coloured compound melting at 225° remained. The ultraviolet spectrum of this was similar to that of the 2,4-dinitrophenylhydrazones of the ketones (IIIa) and (Va), so that it was difficult to



suppose that it was a diazepine derivative (formed through 1,7-elimination of CN and of N-bound hydrogen) or a hydrazobenzene derivative (through 1,6-elimination of CN and of methyl-hydrogen). The same decomposition occurred at 140–145° with the 2,6-di- and the 2,4,6-tri-nitrophenylhydrazones, but the phenylhydrazone and *p*-nitrophenylhydrazone of (III) did not behave in this way.

The course of this curious elimination of hydrogen cyanide was made clear by a study of the oximes. The oxime slowly evolved hydrogen cyanide, even at room temperature, and after a few days became a liquid, which on exposure to the atmosphere, crystallised to a colourless compound, m. p. 45°. Distillation of the liquid afforded a single product, 2,4,6-trimethylpyridinium 1-oxide. The solid of m. p. 45° is its hydrate. The reaction thus involves the formation of a pyridinium compound pictured as a 1,6-elimination (VII → VIII) (no mechanistic implication is to be attached to these formulæ). The reaction seems to be catalysed by acids (through IX) and bases (through X), so that the term "1,6-elimination" does not properly apply to the latter process, but here is meant to imply the formation of a 6-membered ring. In confirmation of this elimination the ketone (IIIa) with aqueous-ethanolic ammonia gave 1,3,5-collidine (XI) in 35% yield.

By analogy, we assume the formation of the compound (VIII; X = NAr) in the decomposition of arylhydrazones. Such anhydropyridinium betaines may be prepared from pyrylium salts and phenylhydrazine derivatives.<sup>7</sup> Spectral studies of these compounds are in progress.

It is noteworthy that the semicarbazone does not eliminate hydrogen cyanide, which is undoubtedly related to the lack of reactivity of pyrylium salts towards urea since the two reactions would afford the same pyridinium betaine (VIII; X = CO·NH<sub>2</sub>).

These reactions were applied to other symmetrically substituted 2,4,6-trialkylpyrylium salts (I). The new compounds thus prepared are recorded in Tables 1–4. With increasing bulk of the alkyl groups, the *cis* → *trans*-isomerisation became more difficult and it did not occur with ketone (IIIe). All 2,4-dinitrophenylhydrazones of the *cis*-ketones (IIIa–e) eliminated hydrogen cyanide with formation of higher-melting pyridinium betaines, and no such reaction was observed with any of the derivatives of the *trans*-ketones (V).

Reactions of pyrylium salts with nucleophiles proceed in one of three ways: (i) with ring opening to give unsaturated ketones (with one mole of Grignard reagent,<sup>5a</sup> or with CN<sup>-</sup>); (ii) with formation of a new ring embodying the nucleophile (with X·CH<sub>2</sub><sup>-</sup>,<sup>1</sup> primary

<sup>6</sup> Perekalin and Lerner, *Doklady Akad. Nauk S.S.S.R.*, 1959, **129**, 1303; Novikov, Korsakova, and Babievsky, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 944.

<sup>7</sup> Schneider and his co-workers, *Annalen*, 1924, **438**, 115, 147; *Ber.*, 1928, **61**, 2445; 1941, **74**, 1252; Dimroth, Arnoldy, von Eicken, and Schiffer, *Annalen*, 1957, **604**, 221.

TABLE 1. Derivatives of the cyano-ketones (IIIa) and (Va).

Compound	Formula	Required (%)			cis (IIIa)			trans (Va)				
		C	H	N	M. p.	C	H	N	M. p.	C	H	N
Ketone	$C_8H_{11}NO$	72.45	7.4	9.4	Liq.	72.3	7.6	10.6 <sup>a</sup>	50°	72.7	7.5	9.4
Oxime	$C_9H_{12}N_2O$	65.8	7.4	17.1	95°	65.8	7.5	17.25	101	65.7	7.4	17.0
Semicarbazone	$C_{10}H_{14}N_4O$	58.2	6.8	27.2	256	58.6	6.9	27.2	227	58.4	6.9	27.1
<i>p</i> -Nitrophenylhydrazone	$C_{10}H_{12}N_4O_2$	63.4	5.7	19.7	121	63.2	5.7	19.9	181	63.6	5.9	19.7
2,6-Dinitrophenylhydrazone	$C_{18}H_{15}N_5O_4$	54.7	4.6	21.3	144	54.7	4.6	21.3	167-168 <sup>b</sup>	54.8	4.8	21.5
									140 <sup>c</sup>	55.0	4.75	21.6
2,4,6-Trinitrophenylhydrazone	$C_{18}H_{14}N_6O_6$	48.1	3.8	22.45	145	48.2	3.9	22.5	180	48.3	4.0	22.4

<sup>a</sup> High values were always obtained for nitrogen owing to slight decomposition. <sup>b</sup> Two forms were obtained: a more soluble yellow form (*syn*) on slow cooling, and a red form, m. p. 167-168°, on rapid cooling and scratching (*anti*). By seeding the ethanolic solution of one form with the other, the latter form was obtained, a ditropic conversion. The yellow form does not melt, but goes over into the red form at 140° with sudden modification of the crystal structure, and then melts at 167-168°.

TABLE 2. 2,4-Dinitrophenylhydrazones of cyano-ketones (III) and (V).<sup>c</sup>

Compound	Formula	Required (%)			cis (III)			trans (V)				
		C	H	N	M. p.	C	H	N	M. p.	C	H	N
a	$C_{16}H_{16}N_5O_4$	54.7	4.6	21.3	140°	54.5	4.8	21.6	205°	55.0	4.7	21.2
b	$C_{16}H_{17}N_5O_4$	56.0	5.0	20.4	110	56.1	5.15	20.3	171	56.2	4.9	20.4
c	$C_{17}H_{19}N_5O_4$	57.1	5.4	19.6	119 <sup>d</sup>	57.2	5.4	19.4	162	57.0	5.4	19.7
d	$C_{17}H_{19}N_5O_4$	57.1	5.4	19.6	111 <sup>d</sup>	57.1	5.5	19.5	199	57.1	5.4	19.55
e	$C_{19}H_{23}N_5O_4$	59.2	6.0	18.2	144 <sup>e</sup>	59.1	6.1	18.3	— <sup>f</sup>	—	—	—
					100 <sup>e</sup>	59.1	6.1	18.2				

<sup>c</sup> Recrystallized from ethanol-benzene or ethanol. All are red or deep orange, except where specified. <sup>d</sup> Elimination of hydrogen cyanide takes place very rapidly, even in warm ethanol. For purification, the dimitrophenylhydrazone of the *cis*-ketone was dissolved in cold benzene, filtered off, and crystallized by addition of cold ethanol. <sup>e</sup> Two non-interconvertible forms were obtained: a more soluble yellow form, m. p. 100°, which does not evolve HCN even at 200°, and an orange form which decomposes at 144° with evolution of HCN. The *cis*-ketone (IIIe) was recovered unchanged from concentrated hydrochloric acid.

TABLE 3. Cyano-acids<sup>g</sup> obtained through degradation of cyano-ketones (III) and (V) by sodium hypobromite.

Compound	Formula	Required (%)			cis			trans				
		C	H	N	M. p.	C	H	N	M. p.	C	H	N
a	$C_8H_9NO_2$	63.6	6.0	9.3	118°	63.8	6.1	9.3	160°	63.8	5.9	9.5
b	$C_9H_{11}NO_2$	65.4	6.7	8.5	54	65.7	6.6	8.6	146	65.3	6.75	8.7

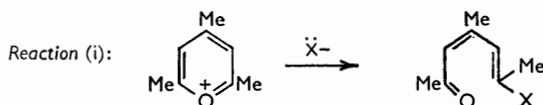
<sup>g</sup> Recrystallized from water or from 20% ethanol.

TABLE 4. *Anhydro-pyridinium betaines*<sup>b</sup> (VIII; X = NAr) obtained through elimination of HCN from arylhydrazones of *cis*-cyano-ketones (III).

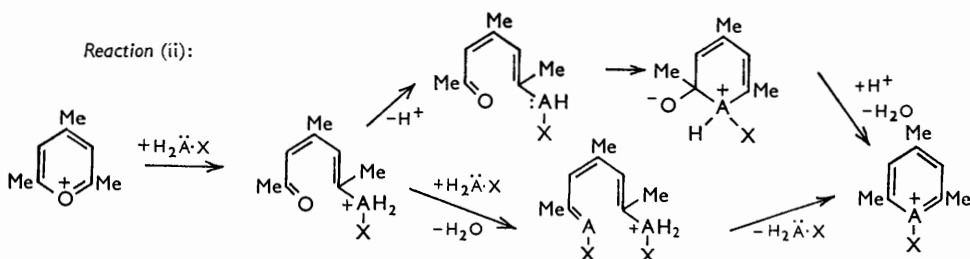
	Compound <sup>c</sup> which eliminates HCN	Formula	M. p.	Required (%)			Found (%)		
				C	H	N	C	H	N
a	2,4-DNP	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	225°	55.6	4.7	18.5	55.6	4.75	18.6
	2,6-DNP	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	210	55.6	4.7	18.5	55.9	4.8	18.7
	2,4,6-TNP	C <sub>14</sub> H <sub>13</sub> N <sub>5</sub> O <sub>5</sub>	259	48.4	3.8	20.2	48.3	3.9	20.2
b	2,4-DNP	C <sub>15</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub>	173	56.95	5.1	17.7	57.2	5.0	17.7
c	"	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	153	58.2	5.5	17.0	58.2	5.5	17.0
d	"	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	200	58.2	5.5	17.0	57.9	5.6	17.1
e	"	C <sub>18</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>	220	60.3	6.2	15.6	60.5	6.2	15.7

<sup>a</sup> Recrystallized from ethanol or 50% ethanol. DNP = dinitrophenylhydrazone; TNP = trinitrophenylhydrazone.

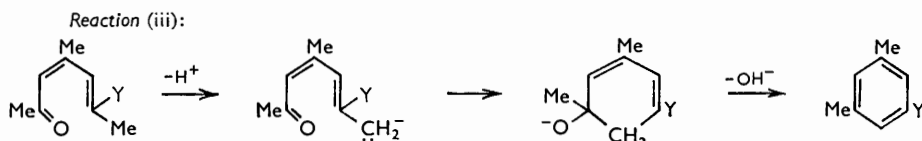
amines,<sup>1</sup> hydrogen sulphide,<sup>8</sup> and probably H<sub>2</sub><sup>18</sup>O); and (iii) with formation of a new ring embodying the side-chain (with HO<sup>-</sup>,<sup>3</sup> secondary amines,<sup>5a</sup> and *p*-Me<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·MgBr<sup>9</sup>).



These reactions may be unified by the following generalisation: if the nucleophile has two hydrogen atoms, path (ii) is followed; if it does not have two hydrogen atoms, the nucleophile cannot take part in an aromatic ring and yields either the unsaturated ketone (path i)



if it introduces an electron-attracting group, or the benzene derivative (path iii) if the substituent is electron-repelling and the pyrylium cation has an  $\alpha$ -methylene group.



This generalisation may be accounted for as follows: The conjugation energy favours formation of a new aromatic system, when possible; this happens in reaction (ii). In reaction (i) condensation between the carbonyl and the methyl group is prevented by a substituent X that does not allow the localization of an unshared electron pair on the methyl-carbon atom. With electron-donating substituents Y (reaction iii), the unsaturated ketone formed as intermediate may undergo a crotonic condensation in a basic medium and at higher temperatures.

The *cis-trans*-relation are also of importance in all three types of reactions (see also ref. 10).

The readiness of the reaction between pyrylium salts and cyanide ion, and the absence of significant thermal effect, are a proof of the high chemical potential of the pyrylium

<sup>8</sup> Wizinger and Ulrich, *Helv. Chim. Acta*, 1956, **39**, 207, 217.

<sup>9</sup> Diels and Alder, *Ber.*, 1927, **60**, 716.

<sup>10</sup> Kröhnke and Dickoré, *Chem. Ber.*, 1959, **92**, 46.

nucleus which, despite its aromaticity, is easily opened in such mild conditions. By contrast, the opening of nitrogen-heterocycles requires more drastic conditions (cf., for instance, the ring opening of pyridinium derivatives with electron-attracting *N*-substituents). In the reaction of nitrogen heterocycles with cyanide ion, *e.g.*, in the formation of Reissert compounds from quinoline<sup>11</sup> or of cyanopyridines from *N*-alkoxy-pyridinium salts,<sup>12</sup> the cyclic structure of the starting materials is preserved.

## EXPERIMENTAL

*Reaction of Pyrylium Perchlorates with Alkali Cyanides.*—Sodium cyanide was preferred to potassium cyanide because no insoluble perchlorate crystallised in the former case; in other respects the two salts reacted similarly. Pyrylium perchlorates (I) were prepared as previously.<sup>2,3b</sup>

The pyrylium perchlorate (1 mol.) was shaken at room temperature for 0.5–1 hr. with 15–25% aqueous sodium cyanide (2 mol.), sometimes in the presence of ether to assist separation. When the pyrylium perchlorate was completely dissolved, the upper brownish-yellow layer was separated, washed with water, dried (CaCl<sub>2</sub>), and either distilled under reduced pressure (for IIIa) or used as such (for IIIb–e). The *cis*-cyano-ketone distilled almost all at one temperature, with no forerun and no residue, and the yield was 95–98%.

*Conversion into trans-Isomers.*—The *cis*-cyano-ketone (0.1 mol.) was added to hydrochloric acid (*d* 1.19; 40 ml.) and after 30–90 seconds was diluted with water (150 ml.). The product was either extracted with ether and converted into derivatives (for Vb–e) after removal of ether or was cooled and filtered (for Va) to yield the solid *trans*-isomer. The conversion usually was over 80%, and all *trans*-isomers were easily purified owing to their smaller solubility and higher m. p.s. The *ketones* and their carbonyl *derivatives* are recorded in Tables 1 and 2.

2,4-Dimethyl-6-oxohepta-1,cis-5-dienonitrile (IIIa), b. p. 96°/1 mm., distilled as a pale yellow liquid which rapidly became orange-red; it had *d*<sub>4</sub><sup>25</sup> 0.9829, *n*<sub>D</sub><sup>25</sup> 1.5222, [*M*<sub>R</sub>]<sub>D</sub> 60.24 [calc., from bond increments: 42.66 (IIIa), 42.34 (IIa)]. The large exaltation is due to conjugation. The ketone (1 mol.) (IIIa) and phenylhydrazine (1 mol.) in an equal volume of acetic acid were kept in an ice-salt bath; the mixture slowly deposited, on scratching, yellow crystals, m. p. 136°, identical with the compound that was formed very rapidly from the *trans*-isomer (Va) under similar conditions; this is therefore the *trans*-phenylhydrazone (Found: C, 75.5; H, 7.2; N, 17.8. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub> requires C, 75.3; H, 7.2; N, 17.6%). The *cis*-phenylhydrazone was obtained from the ketone and phenylhydrazine in aqueous-ethanolic hydrochloric acid, as a liquid that was slowly converted in ethanolic or acetic acid solution into the *trans*-isomer, m. p. 136°.

*Catalytic Reduction of the cis-Compound (IIIa).*—In methanol in the presence of palladium-calcium carbonate the ketone consumed two mol. of hydrogen, yielding a colourless stable substance, b. p. 100°/3 mm., 251°/760 mm., which did not form a 2,4-dinitrophenylhydrazone (Found: C, 69.9; H, 9.4; N, 9.3. C<sub>9</sub>H<sub>15</sub>NO requires C, 70.5; H, 9.9; N, 9.1%).

Catalytic reduction of the *trans*-compound (Va) in the same conditions (absorption 1 mol.) yielded a liquid which gave a *semicarbazone*, m. p. 154° (from dilute ethanol) (Found: C, 57.6; H, 7.9; N, 26.6. C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>O requires C, 57.7; H, 7.7; N, 26.9%), and a yellow 2,4-dinitrophenylhydrazone, m. p. 100° (Found: C, 54.2; H, 5.1; N, 21.3. C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>O<sub>4</sub> requires C, 54.4; H, 5.2; N, 21.1%).

*Hypobromite Oxidations.*—*cis*-5-Cyano-3-methylsorbic acid, m. p. 118° was obtained in 80% yield (crude; 50% recrystallized) on oxidation of the cyano-ketone (IIIa) with aqueous sodium hypobromite (the yield was lower when a water-dioxan solution was used). Similar oxidation of the *trans*-cyano-ketone (Va) yielded the *trans*-cyano-acid, m. p. 160°.

M. p.s and analyses of *cyano-acids* similarly prepared are shown in Table 3. The *cis*-acids are not converted by concentrated hydrochloric acid into the *trans*-isomers.

2,4-Dimethylmuconic acid was obtained on alkaline hydrolysis of the above-mentioned *cis*-cyano-acid (m. p. 118°) with refluxing 10% aqueous sodium or potassium hydroxide (2 equiv.; 10–12 hr.). Acidification with hydrochloric acid precipitated the muconic acid (12%), m. p. 202° (from water) (Found: C, 56.3; H, 5.7. C<sub>8</sub>H<sub>10</sub>O<sub>4</sub> requires C, 56.5; H, 5.9%). Continuous extraction of the filtrate with ether and evaporation left a more soluble dibasic acid, m. p.

<sup>11</sup> McEwen and Cobb, *Chem. Rev.*, 1955, **55**, 511.

<sup>12</sup> Feely and Beavers, *J. Amer. Chem. Soc.*, 1959, **81**, 4004.

ca. 150°, which could not be conveniently purified but was identical with the only acid obtained on similar hydrolysis of the *trans*-cyano-acid (m. p. 160°).

*Betaines* (VIII; X = NAr).—The *betaines* obtained on elimination of hydrogen cyanide from molten 2,4-dinitrophenylhydrazones of the *cis*-ketones are shown in Table 4.

2,4,6-Trimethylpyridine 1-Oxide.—The oxime of the cyano-ketone (IIIa) was prepared with hydroxylamine hydrochloride and an excess of sodium acetate in water, enough ethanol being added to give a homogeneous solution at 40°; the mixture was cooled at 0° and filtered after  $\frac{1}{2}$  hr. The crude oxime could be kept for 2 days; the oxime recrystallised from ethanol-water at <50° was stable for 4 days. It slowly evolved hydrogen cyanide and became a clear yellow hygroscopic liquid, more rapidly on mild heating. Distillation under reduced pressure then gave a small forerun (water), and a colourless liquid, b. p. 118°/2 mm. (88% yield), that in air yielded white crystals, m. p. 45–46°, of 2,4,6-collidine 1-oxide hydrate. Schmitz<sup>13</sup> reported the formation of pyridine oxides from pyrylium salts and hydroxylamine. We independently described this reaction later.<sup>3b</sup>

The oxide was converted into the following derivatives: picrate, m. p. 173° (from methanol), no depression with collidine oxide picrate, prepared from trimethylpyrylium perchlorate and hydroxylamine or from collidine and hydrogen peroxide;<sup>3b,13</sup> *picrolonate*, m. p. 195° (from methanol) (Found: N, 17.4. C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>O<sub>6</sub> requires N, 17.4%); *chloroplatinate*, m. p. 216° (decomp.) (from 1% hydrochloric acid) (Found: C, 28.4; H, 3.6; N, 4.0; Cl, 30.95; Pt, 28.4. C<sub>16</sub>H<sub>24</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt requires C, 28.1; H, 3.5; N, 4.1; Cl, 31.1; Pt, 28.5%); and *perchlorate*, m. p. 176° (Found: N, 5.7. C<sub>8</sub>H<sub>12</sub>ClNO<sub>5</sub> requires N, 5.9%).

*Reaction with Ammonia*.—2,4,6-Trimethylpyridine was obtained in 35% yield when the ketone (IIIa) (15 g.) was refluxed for 15 hr. with aqueous ammonia (*d* 0.88; 75 ml.) and ethanol (50 ml.); dilution with water, extraction with ether, drying (NaOH), and distillation at 90 mm. gave a small forerun and a residue which deposited crystals, m. p. ca. 125°; but the bulk of the distillate had b. p. 102°/90 mm. and yielded 2,4,6-trimethylpyridine picrate, m. p. and mixed m. p. 157°.

*Spectra*.—(a) Ultraviolet absorption spectra were determined for methanol solutions unless otherwise specified. Wavelengths are given in m $\mu$  and  $\epsilon$  in parentheses:

- (i) *cis*-Cyano-ketone (IIIa): min. 226 (3400); max. 279 (13,200).
- (ii) *cis*-Cyano-acid, m. p. 118°, from NaOBr oxidation of the foregoing ketone: min. 217 (3800); max. 268 (17,400).
- (iii) 2,4-Dimethylmuconic acid, m. p. 202°, from alkaline hydrolysis of the previous acid: min. 223 (4900); max. 267 (10,900).
- (iv) *trans*-Cyano-ketone (Va): min. 225 (2200); max. 279 (15,200).
- (v) 2,4-Dinitrophenylhydrazone of the *cis*-cyano-ketone (IIIa): max. 248 (19,700); min. 307 (4400); max. 334 (23,000). In chloroform: max. 258 (22,000); min. 310 (6500); max. 328 (22,600).
- (vi) Pyridinium betaine from the preceding compound: max. 245 (19,000); 302 (700); max. 390 (27,500).
- (vii) 2,4-Dinitrophenylhydrazone of the *trans*-cyano-ketone (Va): max. 245 (18,500), with fine structure; min. 288 (10,200); max. 301 (10,800); min. 326 (7100); max. 390 (31,500).

(b) Infrared absorption spectra were determined for CCl<sub>4</sub> and CS<sub>2</sub> solutions:

- (i) *cis*-Cyano-ketone (IIIa): 513w, 542w, 579m, 612s, 624s, 659m, 762m, 792m, 837s, 883w, 908m, 972vs, 1025m, 1034s, 1074w, 1180vs, 1205w, 1252s, 1293m, 1362vs, 1390vs, 1430w, 1452vs, 1582vs, 1616vs, 1687vs, 1692vs, 1804w, 2216s, 2859m, 2884m, 2925s, 2962s, 2895m, 3049m, 3067m, 3352w, 3345w, 3633w.
- (ii) *trans*-Cyano-ketone (Va): 512m, 542w, 581m, 606vs, 624s, 658m, 673m, 690m, 762m, 793s, 838s, 914s, 972vs, 1020m, 1038s, 1180vs, 1248s, 1295w, 1361vs, 1388vs, 1430w, 1450vs, 1581vs, 1614vs, 1685vs, 1693vs, 1800w, 2217s, 2858m, 2888m, 2926s, 2960s, 3000m, 3040vw, 3070vw, 3358w, 3560w, 3630w.

All analyses were performed by Miss Elvira Sliam and Miss Violeta Săndulescu. Infrared spectra were recorded with an automatic UR10 spectrophotometer by G. Mateescu.

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[Received, August 11th, 1960.]

<sup>13</sup> Schmitz, *Chem. Ber.*, 1958, **91**, 1488.