Calculated Spectra.—The calculated methyl and methylene nmr spectra of the perhydrodurene isomers were obtained through the use of a greatly modified version of the program by Stanley, Marquardt, and Ferguson, as modified by Scherr.[16]

TABLE VI

	% isomers				
Run no.	1	2	3	4	5[a]
1	59.13	6.12	32.97	1.78	
2	59.23	6.19	32.32	1.26	
3	59.52	6.06	32.62	1.80	
4	59.13	6.17	33.21	1.49	(0.20)
5	59.74	6.09	32.77	1.40	
6	59.25	6.10	32.84	1.81	
Av	59.33	6.12	32.96	1.59	

[a] The percentage of fraction 5 is an average value and is not totaled in with the percent of the other fractions.

Registry No.—A, 19899-39-9; B, 31328-42-4; C, 31328-43-5; D, 19899-42-4; E, 19903-06-1.

Acknowledgments.—The authors are greatly indebted to Dr. Paul Scherr, for the use of his program and for his advice and help in the calculation of nmr spectra to compare with the experimental spectra obtained in the present work; and to Dr. G. Karabatsos, for his kindness in helping us to obtain the 100-Hz nmr spectra.

(16) R. N. Stanley, O. W. Marquardt, and R. C. Ferguson, IBM Scherr Systems-SDA 3165 OPE NMR.

An Aminocyanoketenimine, Aminomalononitrile, and Aminocyanoimidazole from Diisobutene, Hydrogen Cyanide, and Hydrogen Fluoride. Preparation of Novel Diaminoethylenes and Diiminoethanes

L. DE VRIES

Chevron Research Company, Richmond, California 94802

Received January 18, 1971

Reaction of 2,4,4-trimethylpentene-2 (TMP), with HCN and HF gave three novel products $(TMP)_n(HCN)_m$: (1) *tert*-octylaminocyanoketen-*N*-*tert*-octylimine (**1**) ($n = 2$, $m = 3$); (2) *tert*-octylaminomalononitrile (**12**) ($n = 1$, $m = 3$); and (3) 4-cyano-5-*tert*-octylaminoimidazole (**14**) ($n = 1$, $m = 4$). Reaction of **1** with $(CN)^-$ or HCN gave di-*tert*-octylaminomaleonitrile (**4**). Compound **4** was dehydrogenated by benzoyl peroxide to give di-*tert*-octyliminosuccinonitrile (**7**). With diethylamine **1** gave 2,3-di-*tert*-octylamino-3-diethylaminoacrylonitrile (**3**), which autoxidized to give 2,3-di-*tert*-octylimino-3-diethylaminopropionitrile (**6**). It is proposed that protonated **1**, **12**, and **14** are the end products of a thermodynamically controlled process in which *tert*-octylisonitrile is an intermediate. Biological and prebiological implications are discussed.

The following investigation is concerned with the mechanism and the novel products of the reaction of 2,4,4-trimethylpentene-2 (TMP), a diisobutene isomer, with hydrogen cyanide and hydrogen fluoride in the absence of additional nucleophiles.

These products are quite different from those obtained in the related Ritter reaction.[1] In that reaction, olefins are allowed to react with nitriles and nucleophiles, such as water in sulfuric acid medium.

A patent[2a] and two recent articles[2b] describe the use of HF in the Ritter reaction. In this modification HCN may be used as the nitrile. Depending on the nature of the olefin and the reaction conditions, formamides, imidoylfluorides, or trialkyl-substituted aminomalonamides were obtained.

Results and Discussion

The reaction consisted of an initial stage in which TMP was allowed to react with hydrogen cyanide and hydrogen fluoride. This stage was followed by a work-up stage in which unreacted hydrogen cyanide and hydrogen fluoride were removed, and the residue was added to a dipotassium hydrogen phosphate solution. The product was separated into three fractions: (1) the main fraction obtained from the pentane extracts of the crude reaction mixture; (2) a base-soluble by-product; (3) a crystalline high melting by-product.

The product composition was highly dependent upon reaction variables. No attempt was made to establish conditions for optimum yields of specific products.

Treatment of the main fraction with methanesulfonic acid resulted in the precipitation of a colorless salt. Treatment of this salt with concentrated aqueous KOH gave pure **1**. Elemental analysis and spectral data were consistent with *tert*-octylaminocyanoketen-*N*-*tert*-octylimine (Scheme I), $C_{19}H_{35}N_3$. The infrared spectrum showed a very strong band at 2025 cm^{-1} which is diagnostic of only the ketenimine group (>C=C=N–).[3]

The nitrile band is located at an anomalously low frequency (2180 cm^{-1}). A similarly displaced nitrile band is found in enaminonitriles[4] ($N{\equiv}CC{=}C\ddot{N}R_2$) and is ascribed to a considerable contribution of a charge-separated structure ($^-{:}\ddot{N}{=}C{=}CC{=}\overset{+}{N}R_2$) to the ground-state resonance hybrid. In the case of **1** the low frequency is probably due to analogous delocalization, involving a charge-separated structure $^-{:}\ddot{N}{=}C{=}C\overset{+}{C}{\equiv}NR$.

In the absence of protic reagents, **1** was stable at room temperature as judged by the constancy of the infrared spectrum.

Treatment of **1** with concentrated aqueous sodium cyanide gave a crystalline compound **4**.

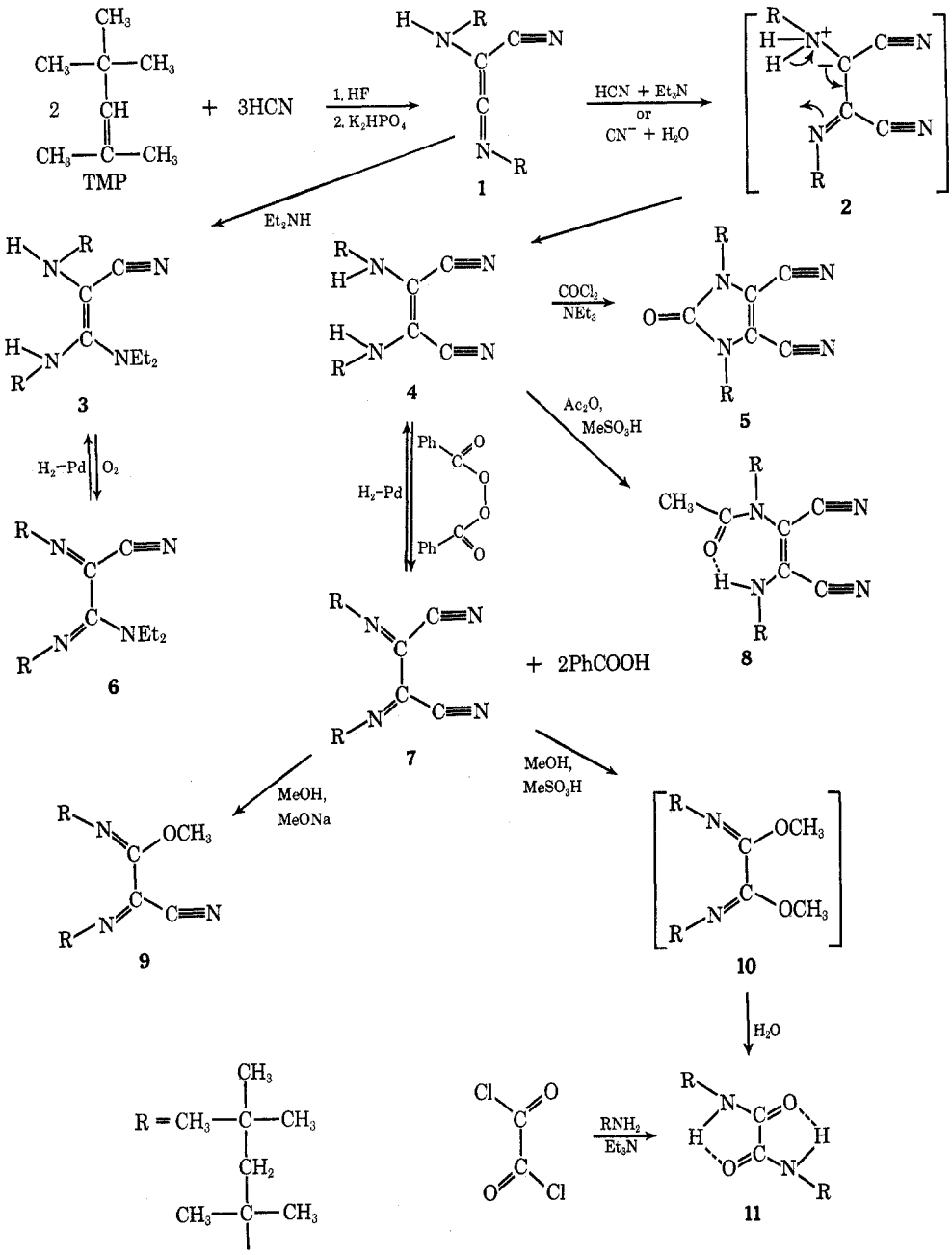
(1) L. J. Krimen and D. J. Cota, "The Ritter Reaction," Wiley, New York, N. Y., 1969, Chapter 3.

(2) (a) R. H. Potts, E. J. Miller, and A. Mais, British Patent 1,121,094 (1968); (b) J. R. Norell, *J. Org. Chem.*, **35**, 1611, 1619 (1970).

(3) C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, **77**, 3491 (1955).

(4) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).

SCHEME I



Elemental analysis and spectral data were consistent with di-*tert*-octylaminomaleonitrile, $C_{20}H_{36}N_4$ (Scheme I).

The frequencies of the C≡N (2190 cm^{-1}) and C=C (1575 cm^{-1}) bands are unusually low but are consistent with an enaminonitrile structure.[4]

When **1** was allowed to react with hydrogen cyanide in triethylamine at room temperature, **4** was also obtained.

Similarly, direct work-up of the reaction product of TMP with HCN and HF using triethylamine gave **4** in approximately 30% yield.

Upon exposure to atmospheric oxygen and light, **4** turned slowly orange. This orange material gave a strong epr signal whereas **4** did not. When **4** was treated in benzene solution with benzoyl peroxide, a bright orange color appeared, which faded after approximately 0.5 min. In a flow system in the epr spectrometer, an excellently defined, extremely strong epr spectrum was obtained (Figure 1), which persisted as long as the color remained. The spectrum is apparently due to a single radical species with a formation time and a decay time both of the order of several seconds.

When the reaction was run on a preparative scale, the color remained until 1 equiv of benzoyl peroxide had been added and then faded. From the resulting benzene solution, almost 2 equiv of benzoic acid and a colorless crystalline material **7** were obtained.

Elemental analysis and spectral data were consistent with di-*tert*-octyliminosuccinonitrile, $C_{20}H_{34}N_4$ (Scheme I).

The structure of **7** was proved by classical methods. Hydrolysis in methanol in the presence of methanesulfonic acid gave a compound **11** (Scheme I).

Mixture melting point determination, elemental analysis, and identity of infrared and nmr spectra proved **11** to be di-*tert*-octyloxamide.

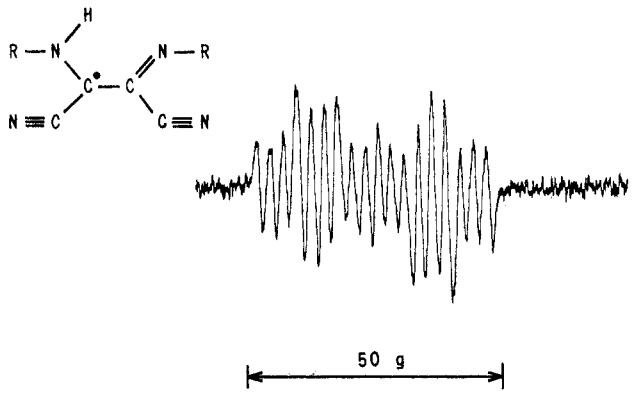
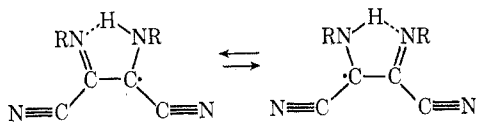


Figure 1.—Electron paramagnetic resonance spectrum of 4 + $(C_6H_5CO)_2O_2$.

The nitrile group in **7**, which is a bisiminonitrile, should be displaceable by nucleophiles.[5] Under the reaction conditions, methanolysis probably first gives the bismethylimidate **10** (Scheme I) which then hydrolyzes to **11**.

Catalytic hydrogenation of **7** gave a 90% yield of **4** so that the reaction by which **7** is made from **4** can be reversed in this manner (Scheme I).

The mechanism of the oxidation of **4** by benzoyl peroxide and the nature of the intermediate(s) has not been investigated.[6] In an apparently related reaction



of a tertiary enamine with benzoyl peroxide at room temperature a product containing a benzoyloxy group has been obtained.[7] In the oxidation of the flavins, which are structurally related to **4** (Scheme IV), two hydrogen atoms are similarly lost. The radical intermediates are the so-called flavin semiquinones.[8]

Further confirmation of the structure assigned to **4** comes from its ultraviolet spectrum. Compound **4** has uv max (isooctane) 308.0 mμ (log ε 4.23), in good agreement with the values observed for diaminomaleonitrile [uv max (EtOH) 300 mμ (log ε 4.15)],[9] the structure of which was unambiguously proven by X-ray analysis.[10]

Reaction of **4** with phosgene gave a crystalline product **5**. Elemental analysis and spectral data were consistent with 1,3-di-*tert*-octyl-4,5-dicyano-2(3*H*)-imidazolone, $C_{21}H_{34}NO$ (Scheme I).

The formation of **5** suggests the cis configuration for **4** but does not prove it in view of the possibility of easy trans–cis isomerization. This possibility is inferred by the observed conversion of diaminofumaronitrile into diaminomaleonitrile.[11]

In CCl_4 solution **4** shows a strong C=C stretching band at 1675 cm^{-1}, which is also Raman active. This rules out C_{2h} symmetry and thus confirms the cis configuration.[12] The observed magnetic equivalence of the *tert*-octyl groups in **4** argues against an asymmetrical trans configuration with marked deviation from C_{2h} symmetry. Such a configuration was invoked to account for an anomalous C=C stretching band in the ir spectrum of diaminofumaronitrile taken in the crystalline state.[11] In solution such a rigid asymmetrical configuration could probably not exist due to removal of rotational restrictions.

It has not been established why the cis structure is so strongly preferred. Possibly the formation of **4** involves a cyclic rearrangement of an "ylide" intermediate **2** (Scheme I).

Alternatively, hydrogen bonding between the amino groups may be the reason. These amino groups are vinylogously related to the amino groups in cyanamide in which intermolecular hydrogen bonding is known to be strong.

The evidence presented thus far allows an unequivocal structure assignment to **1** as follows. (1) The structure of **7** has been proven by hydrolytic conversion to di-*tert*-octyl oxamide (**11**). (2) The structure of **4** is established because **4** is obtained by hydrogenation of **7**. (3) The structure of **1** is established because addition of hydrogen cyanide to **1** gives **4**. This structure assignment is furthermore supported convincingly by the spectral data.

Two further reactions of **7** and **4** deserve mention. When **7** was treated with sodium methoxide in methanol, a new compound **9** was obtained. Elemental analysis and spectral data were consistent with 2,3-di-*tert*-octylimino-3-methoxypropionitrile, $C_{20}H_{37}N_3O$.

Acetylation of **4** in acetic anhydride with methanesulfonic acid catalysis gave a crystalline monoacetylation product **8** according to elemental analysis and spectral data.[13]

All compounds discussed thus far have been derived from **4**, which is the reaction product of **1** and HCN.

Compound **1** also reacts readily with diethylamine to give a crystalline compound **3**. Elemental analysis and spectral data were consistent with 2,3-di-*tert*-octylamino-3-diethylaminoacrylonitrile, $C_{23}H_{46}N_4$ (Scheme I). Compound **3** was also obtained directly in 49% yield when diethylamine was used in the work-up of the reaction product of TMP with HCN and HF.

Compound **3** autoxidizes with remarkable facility. The product is a new compound **6**. Elemental analysis and spectral data are consistent with 2,3-di-*tert*-octylimino-3-diethylaminopropionitrile, $C_{23}H_{44}N_4$. Compound **6** can be quantitatively reconverted to **3** by catalytic hydrogenation.

The ultraviolet spectra of **3** and **6** further support the assigned structures. In the spectrum of **3** a band at 275 mμ corresponds to an enaminonitrile chromophore (uv max 250–280 mμ)[4] and a band at 213 mμ to a conjugated enamine chromophore (uv max 220–240 mμ).[14]

(5) F. Kröhnke and H. M. Steuernagel, *Chem. Ber.*, **96**, 486 (1963).

(6) The cis configuration of **4** (*vide infra*) suggests the intriguing possibility that a pair of rapidly equilibrating hydrogen-bonded radical species is involved. This could account for the doublet nature of the epr spectrum.

(7) R. L. Augustine, *J. Org. Chem.*, **28**, 581 (1963).

(8) P. Hemmerich, C. Veeger, and H. C. S. Wood, *Angew. Chem.*, **77**, 699 (1965).

(9) R. L. Webb, S. Frank, and W. C. Schneider, *J. Amer. Chem. Soc.*, **77**, 3491 (1955).

(10) B. B. Penfold and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 4589 (1961).

(11) Y. Yamada, N. Nagashima, Y. Iwashita, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, 4529 (1968).

(12) R. M. Bly, unpublished work.

(13) The unusual magnetic nonequivalences in the nmr spectrum of **8** are ascribed to asymmetry arising from slow rotation of the bulky *tert*-octyl groups which are attached to a seven-membered, hydrogen-bonded ring with high barriers to conformational interconversion. This aspect will be reported separately.

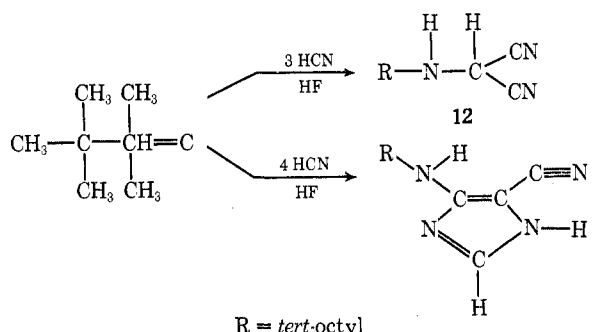
(14) G. Opitz, H. Hellmann, and H. W. Schubert, *Justus Liebigs Ann. Chem.*, **623**, 112 (1959).

The spectrum of **6** (uv max 237, 340 mμ) strikingly resembles that of the analogous **7** (uv max 234, 328 mμ).

The base-soluble by-product **12** from the reaction of TMP with HCN and HF was obtained as low-melting colorless crystals. It was purified through its methanesulfonic acid salt.

Elemental analysis and spectral data support the *N*-*tert*-octylaminomalononitrile structure, $C_{11}H_{19}N_3$ (Scheme II). In the mass spectrum the parent peak

SCHEME II



12

14

at mass 193 was absent; the first peak occurred at 178 (parent minus CH_3), and the dominant peak at mass 122 [parent minus $CH_2C(CH_3)_3$]. Amines often fail to show parent peaks,[15] and the above fragmentation pattern is in accordance with expectations. The ir spectrum showed a very weak nitrile band at 2200 cm^{-1}. The extreme weakness of this band agrees with Arnold's observation,[16] who could not discern the nitrile band in the ir spectrum of dimethylaminomalononitrile. The nmr spectrum showed two mutually coupled doublets assigned to NH and α CH. Both doublets disappeared upon exhaustive deuteration.[17]

Compound **12** is stable in the absence of oxygen. It is soluble in aqueous acid due to its alkylamino group and soluble in aqueous base due to the acidity of the hydrogen atom on the central carbon. Strong KOH causes precipitation of the crystalline salt, probably because of the common ion effect.

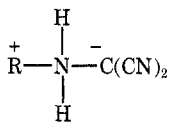
Work-up of the initial reaction product of TMP with hydrogen cyanide and hydrogen fluoride with a variety of reagents (KOH, $KHCO_3$, Et_3N, and Ph_3P[18]) yields, in all cases, a certain amount (yield ~4%) of a high-melting by-product **14**. According to elemental analysis, this product has the composition $C_{12}H_{21}N_4$ and, therefore, contains only a single TMP unit which has reacted with four molecules of hydrogen cyanide.

Spectral data, as well as the high melting point, suggest the 4-cyano-5-*tert*-octylaminoimidazole structure (Scheme II).

(15) F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

(16) Z. Arnold, *Collect. Czech. Chem. Commun.*, **26**, 1113 (1961).

(17) The exchange of CH as well as NH suggests a ylide intermediate **13**. This species is structurally analogous to trimethylammoniumdicyanomethylide, which was obtained as a stable compound by Arnold.[16]



13

R = *tert*-octyl

(18) The work-up with Ph_3P will be reported separately.

Compound **14** showed uv absorption at 248 mμ (log ε 4.03) in excellent agreement with the values reported by Ferris and Orgel[19] for unsubstituted 4-cyano-5-aminoimidazole [uv max (EtOH) 246 mμ (log ε 4.04)].

Mechanism.—The medium is highly acidic before the neutralization during the work-up. These conditions are singularly conducive to the accumulation of products of maximal thermodynamic stability (thermodynamic control).

It is postulated that the major product **1** is the result of a four-step process, each successive step resulting in the conversion of the intermediate or product formed in the preceding step into a new intermediate or product of increased thermodynamic stability. The steps involved in the ultimate formation of **1** are carbonium ion (step 1) → nitrilium ion (step 2)[20] → immonium ion (step 3) → ammonium ion (step 4). (See Scheme III.)

Ammonium ions are the most stable species obtainable under the reaction conditions. The principle of thermodynamic control also accounts for the apparent lack of products resulting from N-alkylation of a second molecule of HCN by the initial nitrilium ion, since this would give rise to another nitrilium ion which might not be more thermodynamically stable than the first one.

A molecule of TMP is first protonated to give a carbonium ion **15** (step 1) which adds a molecule of HCN to give the nitrilium ion or protonated isonitrile **16** (step 2).

HCN, which attacks through its nitrogen atom, is initially the only available nucleophile. However, once the nitrilium ion is formed, a protonation–deprotonation equilibrium with *tert*-octylisonitrile (**17**) can arise (step 2). The *tert*-octylisonitrile constitutes a second nucleophile which attacks protonated HCN **18** in the third step of the reaction to give, after an additional proton shift, the postulated intermediate **19**[21] (step 3) which is an immonium salt (protonated *tert*-octylformiminonitrile).

In the fourth step, **19** reacts with an additional molecule of *tert*-octyl isonitrile to give a new intermediate **20** which can stabilize itself to give an ammonium salt by three paths (a, b, and c), each of which leads to a protonated form of an isolated product. (a) Rearrangement of **20**, *via* path a, leads to the protonated aminocyanoketenimine **21**, which is the main product. (b) Loss of R^+ and subsequent protonation leads by path b to protonated *t*-octylaminomalononitrile **22** which is a by-product. (c) Reaction of **20** with an additional molecule of HCN leads to a cyclic intermediate **23** which is an ammonium salt that can be further stabilized by loss of R^+, rearrangement, and reprotonation (path c) to give protonated 4-cyano-5-*tert*-octylaminoimidazole (**24**), which is the second by-product.

The formation of **24** is assumed to take place before the addition of the work-up reagent because **24** is iso-

(19) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, **88**, 3829 (1966).

(20) F. Johnson and R. Madroñero, *Advan. Heterocycl. Chem.*, **6**, 95 (1966).

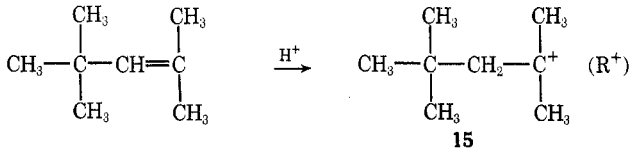
(21) It appears reasonable that in the strongly acidic solution HCN is also in equilibrium with "iso-HCN" through protonation–deprotonation (from carbon). "Iso-HCN" is expected to be far less stable than **17** because the hydride ion has a much greater migratory aptitude than the *tert*-octyl group. Therefore, the "iso-HCN" can easily revert to normal HCN by an intramolecular 1,2-hydride shift, thus keeping the concentration of "iso-HCN" quite low. Accordingly, unlike isonitriles, "iso-HCN" is not a stable compound and reactions involving it have not been reported thus far. The alternate possibility that **19** originates from the attack of "iso-HCN" on **16** appears therefore unlikely.

SCHEME III

REACTIONS BEFORE WORK-UP

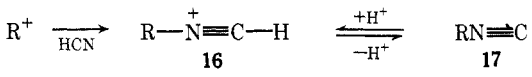
Steps 1-4 in Order of Increasing Thermodynamic Stability

Step 1: carbonium ion formation



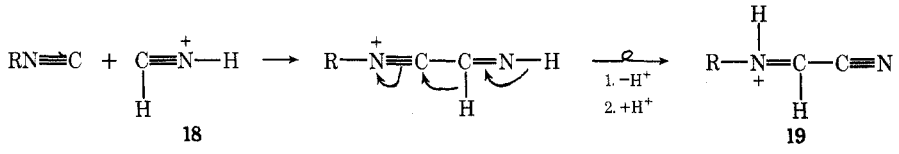
15

Step 2: nitrilium ion formation



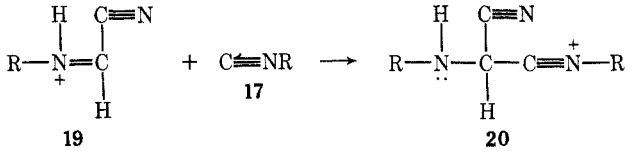
16 17

Step 3: immonium ion formation



18 19

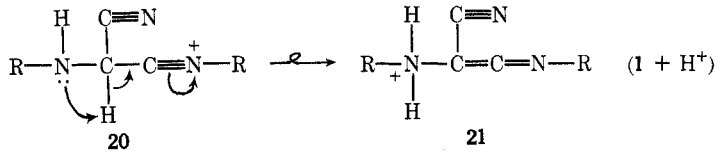
Step 4: ammonium ion formation



19 17 20

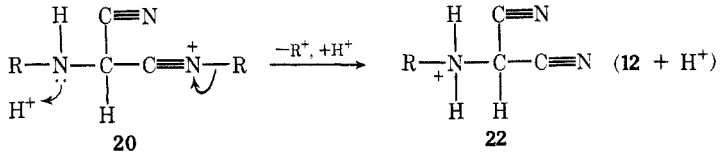
Paths a-c

Path a



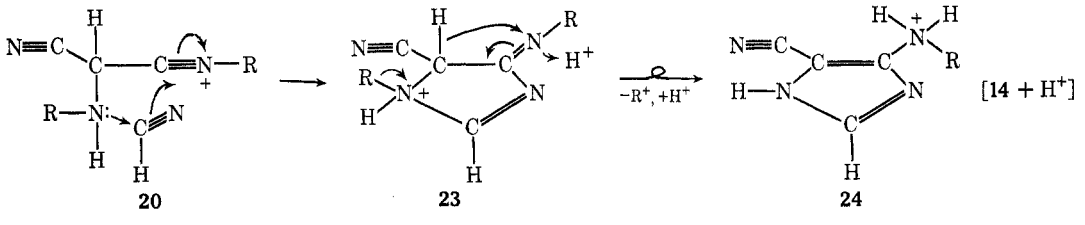
20 21

Path b



20 22

Path c



20 23 24

lated in approximately the same yield independent of the work-up reagent (KOH, Et_3N, Et_2NH). It is also obtained in the work-up with the highly nucleophilic but weakly basic reagent, triphenylphosphine.[18]

The first part of step 4, the reaction of an isonitrile **17** with an immonium salt **19**, is an example of a well-known reaction.[22]

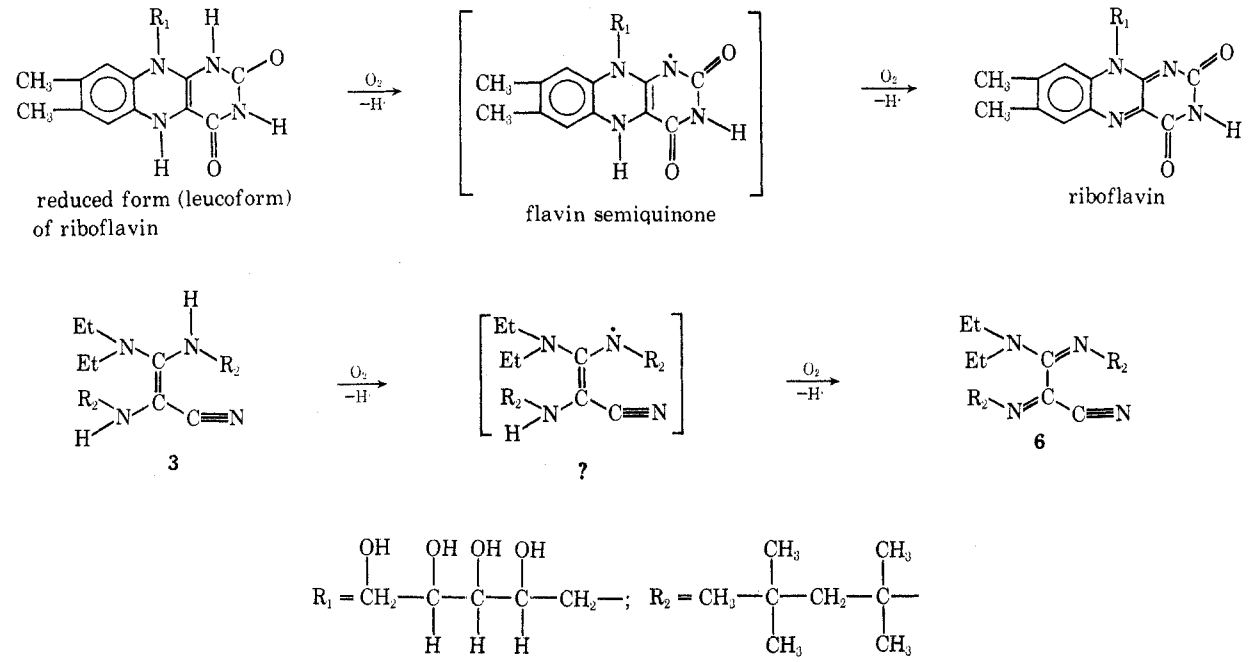
The second part of step 4, the rearrangement of intermediate **20** to give the protonated aminocyanoketenimine **21** (path a), is analogous to a standard method of synthesis for ketenimines which involves the elimination of HCl from imidoyl chlorides through the use of triethylamine.[23] In the present case, the reaction involves intramolecular proton abstraction by the *tert*-octylamino group.

Intermediate **19** in step 3 is obtained from the reac-

(22) I. Ugi, *Angew. Chem.*, **74**, 9 (1962).

(23) K. C. Brannock and R. D. Burpitt, *J. Org. Chem.*, **30**, 2564 (1965); P. Dimroth, German Patent 1,166,771 (1964); W. Ried and D. Junker, *Justus Liebigs Ann. Chem.*, **700**, 32 (1966); C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, **76**, 4398 (1954).

SCHEME IV



tion of an isonitrile with a nitrilium ion (protonated HCN **18** in this case). This type of reaction, which is closely related to the preceding reaction of an isonitrile with an immonium ion, has also been described recently.[24]

Work-up with aqueous potassium hydroxide liberates **1** and **14** from their salts. Both compounds are evidently stable to hydrolysis under the strongly basic conditions. Compound **12** dissolved in the aqueous phase as its potassium salt and is freed by neutralization.

In the work-up with triethylamine **1** was a product when the excess of hydrogen cyanide was carefully removed *in vacuo* before the addition of the work-up reagent. This was apparent from the ir spectrum of the crude product, which prominently showed the characteristic ketenimine band at 2025 cm^{-1}.

When all unreacted hydrogen cyanide was not removed before addition of triethylamine, the ir spectrum of the product showed the absence of **1** (no absorption at 2025 cm^{-1}). Instead **4** was the main recovered product. These results indicate that initially produced **1** reacts with hydrogen cyanide to give **4**.

Implications in Biological and Prebiological Chemistry.—Most of the novel compounds are actually oligomers of HCN with one or two *tert*-octyl "handles." Therefore the reported work may provide a model for the otherwise intractable oligomerization of HCN itself.

Unsubstituted aminomalononitrile and aminocyanoimidazole, which are analogous to **12** and **14**, have been claimed as key intermediates in the prebiological oligomerization of HCN which presumably led to the purines.[14] These two compounds have not been obtained from synthetic oligomerization of HCN but have been prepared by alternate routes by Ferris and Orgel, who found aminomalononitrile too unstable for analysis.

By contrast **12** is stable in the absence of oxygen. In the presence of bases it decomposes rapidly with elimination of HCN. Evidence has been obtained that the other fragment is the novel intermediate *tert*-octylaminocyanocarbene.[25] Unsubstituted aminocyanocarbene has been proposed as an intermediate in prebiological peptide synthesis.[26] Its photochemical generation in a matrix at very low temperature has been claimed.[27]

The aminocyanoketenime **1** is remarkably stable at room temperature, but at high temperatures it undergoes a remarkable rearrangement to give *N*-*tert*-octyl-*tert*-octylmalononitrile as well as decomposition giving **12** as a primary product. Secondary thermolysis of **12** generates HCN which reacts with **1** to give **4**.[25]

Finally, I want to point out the striking relationship between **3** and vitamin B_2, riboflavin. The reduced form of riboflavin readily loses two hydrogen atoms upon exposure to atmospheric oxygen to give riboflavin in a process that closely resembles the autoxidation of **3** to give **6** (Scheme IV).

Experimental Section

Materials.—The 2,4,4-trimethylpentene-2 used was technical grade (95 mol % minimum) supplied by Phillips Petroleum Co. It was purified by treatment with $LiAlH_4$ in ether solution to reduce carbonyl-containing impurities, followed by distillation through a spinning-band column.

Hydrogen cyanide and hydrogen fluoride were obtained from Fumico, Inc., and The Matheson Co., respectively.

Reaction of 2,4,4-Trimethylpentene-2 (TMP) with HF and HCN.—A polyethylene reactor with a polyethylene condenser and magnetic stirrer was charged with 150 g (1.34 mol) of TMP (freshly distilled and dried over CaH_2) and 250 cc of dichloromethane (dried over CaH_2). The reactor was cooled to 0°, and the condenser was filled with ice. Then 155.3 cc (108.8 g, 4.02 mol) of HCN was distilled in, followed by 81.5 cc (80.7 g, 4.06 mol) of HF. The reaction mixture was stirred at room temperature for 2 hr. The solvent and unreacted HCN and HF were removed by sparging with nitrogen. The viscous yellow residue was transferred to a polyethylene addition funnel and

(24) T. Saegusa, N. Taka-Ishi, and Y. Ito, *J. Org. Chem.*, **34**, 4040 (1969).

(25) These reactions will be discussed in forthcoming publications.

(26) C. N. Matthews and R. E. Moser, *Nature*, **215**, 1230 (1967); *Proc. Nat. Acad. Sci.*, **56**, 1087 (1966).

(27) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Amer. Chem. Soc.*, **89**, 5673 (1967).

was added during 25 min to a stirred mixture of 400 cc of pentane and a solution of 908 g of K_2HPO_4 in 1000 cc of water (external ice cooling).

The mixture was separated into three fractions: (1) an aqueous phase which was discarded; (2) a crystalline, high-melting precipitate, recovered by filtration; and (3) a pentane layer.

The pentane layer was extracted with two consecutive 200-cc portions of 20% aqueous KOH.

Methanesulfonic Acid Salt of *tert*-Octylaminocyanoketen-*N*-*tert*-octylimine (1 CH_3SO_3H).—After the KOH extraction the solvent was removed *in vacuo* from the above pentane solution, leaving 180.8 g of a light orange-colored oil. This residue was dissolved in 400 cc of anhydrous ether and cooled in an ice bath. Maintaining the cooling and under vigorous stirring, an ice cold solution of 55 g of anhydrous methanesulfonic acid in 150 cc of ether was slowly added. Immediately a precipitate started to form. After standing overnight in the refrigerator the supernatant was decanted. The remaining precipitate was washed by trituration with 300 cc of anhydrous ether followed by decantation, and this procedure was repeated four times. The washed, almost colorless precipitate was dried in a stream of dry nitrogen, yield ~166.8 g of essentially pure 1 CH_3SO_3H. For analysis a 10-g quantity of the salt was dissolved at room temperature in the minimum amount of anhydrous chloroform. A 100-cc quantity of anhydrous ether was added and crystallization started almost at once. After standing in the refrigerator overnight the colorless crystals were collected by filtration, washed with a small amount of anhydrous ether, and dried in a stream of dry nitrogen, yield ~8.04 g of the pure methanesulfonic acid salt of 1.

Anal. Calcd for $C_{20}H_{39}N_3SO_3$: C, 59.80; H, 9.81; N, 10.46; S, 7.98. Found: C, 59.65; H, 9.88; N, 10.36; S, 7.62.

The combined ether triturates were freed of solvent *in vacuo*, leaving 93 g of a residue which has not yet been investigated.

***tert*-Octylaminocyanoketen-*N*-*tert*-octylimine (1).**—A 25-g quantity of the methanesulfonic acid salt of 1 was dispersed in 150 cc of ether in a separatory funnel. Upon shaking with a cold concentrated KOH solution, the solid disappeared and the ether layer assumed a light yellow color. The aqueous layer was discarded, and the ether layer was dried over magnesium sulfate, filtered, and evaporated to dryness *in vacuo*. An 18.2-g quantity (96%) of 1 remained as a pale yellow oil, $n^{20}D$ 1.4851. This oil crystallized upon standing at −30° for 2 days: mp 14–16°; uv max (isooctane) 244, 315 mμ (log ε 4.13, 2.79); ir (neat) 3310 (m, NH), 2185 (m, C≡N), 2025 cm^{-1} (vs, C=C=N–); nmr (CCl_4) δ 1.00, 1.01 [18 H, 2 $C(CH_3)_3$], 1.18 [6 H, $C(CH_3)_2$], 1.43 [8 H, $C(CH_3)_2$ + CH_2], 1.61 (2 H, CH_2), 1.70 ppm (1 H, NH, disappears on deuteration); mass spectrum (70 eV) *m/e* parent 305; mol wt 307 (Thermonam).

Anal. Calcd for $C_{19}H_{35}N_3$: C, 74.68; H, 11.57; N, 13.75. Found: C, 74.21; H, 11.32; N, 13.73.

Reaction of 1 with $(C{\equiv}N)^-$. Di-*tert*-octylaminomaleonitrile (4). A. From Reaction of 1 with $(CN)^-$.—A 5.2-g quantity of crude 1 in ether solution was stirred for 2 hr with a concentrated aqueous solution of 5 g of sodium cyanide. The organic layer was then evaporated to dryness. The residue was crystallized from pentane at 0° and gave 3.85 g of crude 4, which was recrystallized once from hexane: mp 107.5–108°; uv max (isooctane) 308 mμ (log ε 4.23); ir (CCl_4) 3250 (m, NH), 2240 (m, C≡N), 2190 (s, C≡N), 1575 cm^{-1} (vs, C=N); nmr ($CDCl_3$) δ 1.02 [18 H, 2 $C(CH_3)_3$], 1.33 [12 H, 2 $C(CH_3)_2$], 1.60 (4 H, 2 CH_2), 3.54 ppm (2 H, 2 NH); mass spectrum (70 eV) *m/e* parent 332.

Anal. Calcd for $C_{20}H_{36}N_4$: C, 72.20; H, 10.92; N, 16.86; mol wt, 332.6. Found: C, 72.27; H, 11.00; N, 16.98; mol wt, 335 (Thermonam, acetone).

B. From Reaction of 1 and HCN in Triethylamine.–A 10-g quantity of crude 1 was dissolved in 20 cc of triethylamine, and 3 g of HCN was distilled in. After 2 hr, all volatiles were removed by sparging with nitrogen. The residue was recrystallized from methanol at −10° to give 4.6 g of a crystalline compound, which was identified as 4 by its ir spectrum and mixture melting point.

C. Directly from the Product of Reaction of TMP with HCN and HF.—Excess triethylamine was added to the cold reaction mixture obtained from 142 g (1.27 mol) of TMP, 51.0 g (1.89 mol) of HCN, and 38.0 g (1.92 mol) of HF. The volatiles were substantially removed by sparging with nitrogen and the residue was extracted with hot hexane, leaving the hydrogen fluoride salt of triethylamine undissolved. Cooling of the hexane extract to −10° gave a crystalline precipitate which was once recrystallized from hexane at −10° and once from methanol at −10°; 50 g (yield 31%, based on HCN) of 4 were obtained, mp 108°, ir spectrum identical with that of 4 obtained from 1. Also recovered were 5.3 g of a hexane-insoluble crystalline compound, which was identified as 14 (*vide infra*) by ir spectrum and mixture melting point determination.

Di-*tert*-octyliminosuccinonitrile (7).—A 9.45-g (0.039 mol) quantity of benzoyl peroxide dissolved in 50 cc of benzene was added dropwise with vigorous stirring to a solution of 13 g (0.039 mol) of 4 in 150 cc of benzene at room temperature. An orange color which developed upon the addition of the first drops of benzoyl peroxide solution remained until the addition was finished and then faded to light yellow within 1 min. The benzene solvent was removed *in vacuo*, and the residue was dissolved in hot hexane. Upon cooling 7.5 g (0.061 mol) of essentially pure benzoic acid (yield 78.4%) crystallized, identified by ir spectrum and mixture melting point with an authentic sample. The remaining benzoic acid was removed by washing with $NaHCO_3$ solution. Removal of the hexane *in vacuo* left a crystalline residue. Two recrystallizations from methanol (−10°) and one from hexane (−10°) gave 11.5 g (yield 88%) of 7: mp 65.5–67.0°; uv max (isooctane) 234.0, 328 mμ (log ε 4.15, 2.43); ir (CCl_4) 2220 (w, C≡N), 1625 cm^{-1} (s, C=N); nmr ($CDCl_3$) δ 0.97 [18 H, 2 $C(CH_3)_3$], 1.53 [12 H, 2 $C(CH_3)_2$], 1.85 ppm (4 H, 2 CH_2); mass spectrum (70 eV) *m/e* parent 330.

Anal. Calcd for $C_{20}H_{34}N_4$: C, 72.77; H, 10.38; N, 16.95; mol wt, 330.58. Found: C, 72.58; H, 10.15; N, 16.82; mol wt, 331 (Thermonam, acetone).

Hydrogenation of 7 to Give 4.—A 1-g quantity of 7 in ethyl acetate solution was hydrogenated using 75 mg of a 5% palladium-on-carbon catalyst. When 1 g-atom of hydrogen had been absorbed, the hydrogen uptake virtually stopped. After removal of the catalyst by filtration and of the solvent by evaporation *in vacuo*, 0.87 g of a crystalline residue remained which was identified as 4 by ir spectrum and mixture melting point determination.

Di-*tert*-octyl Oxamide (11) from 7.—A 2-g quantity of 7 was dissolved in 100 cc of methanol. To this solution was added 1 cc of water and 0.29 g of methanesulfonic acid, dissolved in 10 cc of methanol. The mixture was allowed to stand overnight at room temperature and was then poured into water. A crystalline precipitate formed which was recrystallized from a small amount of methanol at −30°. The product (1.58 g, yield 83.5%) was identified as di-*t*-octyl oxamide (11), mp 77–78.5°. The mixture melting point with an authentic sample of di-*tert*-octyl oxamide (prepared from oxalyl chloride and *tert*-octylamine) was undepressed and the ir and nmr spectra were identical with those of an authentic sample.

Anal. Calcd for $C_{18}H_{36}N_2O_2$: C, 69.16; H, 11.63; N, 8.96. Found: C, 69.48; H, 11.60; N, 8.97.

1,3-Di-*tert*-octyl-4,5-dicyano-2(3*H*)-imidazolone (5).—Into a Fisher–Porter bottle containing a magnetic stirring bar were introduced 5 g of 4, 20 cc of benzene, and 100 cc of triethylamine. The bottle was cooled to −30° and 5 cc of liquid phosgene was distilled into it. The bottle was then closed and the contents were stirred at room temperature for 72 hr. At that time the volatiles were removed by purging with nitrogen. The liquid residue was dissolved in pentane and chromatographed through a silica gel column. Unreacted 4 (2.1 g) was eluted with pentane–5% ether. From the 100% ether eluate 5 (1.8 g), mp 112.5–114°, was recovered: ir ($CHCl_3$) 2220 (m, C≡N), 1715 cm^{-1} (vs, C=O); nmr ($CDCl_3$) δ 0.90 [18 H, 2 $C(CH_3)_3$], 1.75 [12 H, 2 $C(CH_3)_2$], 2.05 ppm (4, H, $2CH_2$).

Anal. Calcd for $C_{21}H_{34}N_4O$: C, 70.33; H, 9.57; N, 15.62. Found: C, 69.97; H, 9.62; N, 15.45.

2,3-Di-*tert*-octylimino-3-methoxypropionitrile (9).—A 2-g quantity of 7 was dissolved in 100 cc of methanol. To this solution was added 20 cc of methanol containing 0.67 g of sodium methoxide. After 3 days at room temperature, the solvent was evaporated *in vacuo* and the residue was extracted with hot hexane.

Upon concentration and subsequent cooling (−50°) of this extract 0.8 g of crystalline 7 was obtained. A considerable amount of product remained dissolved in the hexane solution and did not crystallize even at −50°. This solution was chromatographed through a silica column. From the pentane eluate 0.67 g of 9 was recovered. It could be recrystallized from methanol at −50°, but the melting point was below room temperature: $n^{20}D$ 1.4686; ir (neat) 2210 (w, C≡N), 1690 and 1625 (m, two different C=N–), 1078 (s), and 985 cm^{-1} (s) ($COCH_3$); nmr (CCl_4) δ 0.94 and 0.96 [18 H, 2 $C(CH_3)_3$], 1.26 and 1.47 [each

6 H, 2 $C(CH_3)_2$], 1.57 and 1.77 (each 2 H, 2 CH_2), 3.63 ppm (3 H, OCH_3).

Anal. Calcd for $C_{20}H_{37}N_3O$: C, 71.57; H, 11.15; N, 12.52. Found: C, 71.71; H, 11.12; N, 12.33.

1-*tert*-Octylamino-2(*N*-*tert*-octyl)acetamidosuccinonitrile (8).—A 2-g quantity of **4** was dissolved in 40 cc of acetic anhydride containing 100 mg of methanesulfonic acid. The solution was allowed to stand at room temperature for 72 hr and was then added dropwise under stirring to 200 cc of concentrated potassium bicarbonate solution. This solution was extracted in a separatory funnel with three 30-cc quantities of benzene. Evaporation of the solvent *in vacuo* from the combined extracts left a crystalline residue.

After three recrystallizations from hot hexane, 0.93 g of **8**, mp 115.0–115.7° was obtained: ir (CCl_4) 3385 (m, NH), 2235 (m) 2195 (s) (C≡N), 1685 (vs, C=O), 1580 cm^{-1} (vs, C=C); nmr (100 MHz, $CHCl_3$) δ 0.98, 1.00 [18 H, 2 $C(CH_3)_3$], 1.42, 1.45, 1.49, 1.52 [12 H, four heterosteric CH_3, 2 $C(CH_3)_2$], 1.71, 1.72 [2 H, (heterosteric), CH_2], 1.68, 1.82, and 2.18, 2.32 [2 H (heterosteric), AB quartet, J = 14 Hz, CH_2], 4.80 ppm (1 H, NH, disappears upon deuteration).

Anal. Calcd for $C_{22}H_{38}N_4O$: C, 70.53; H, 10.24; N, 14.96. Found: C, 70.32; H, 9.98; N, 14.97.

The separations (in cycles) between the four heterosteric methyl resonances and the two heterosteric proton resonances (at 1.71 and 1.72 ppm) were dependent upon the applied field (100 MHz, 60 MHz), but the separations of the quartet resonances were unaffected.

2,3-Di-*tert*-octylamino-3-diethylaminoacrylonitrile (3). A. From Reaction of 1 with Diethylamine.—A 10-cc quantity of diethylamine was added to 10 g of crude **1** dissolved in 20 cc of triethylamine. There was an immediate exothermic reaction. After 1 hr at room temperature, all volatiles were removed *in vacuo*, and the residue was twice recrystallized from methanol at −30° to give 7.10 g of **3**: mp 51.0–52.5°; uv max (isooctane) 213, 275 mμ (log ε 3.91, 4.13); ir (CCl_4) 3310 (w, NH), 2170 (s, C≡N), 1580 (vs, C=C); nmr (CCl_4) δ 1.01, 1.03 [18 H, 2 $C(CH_3)_3$], 1.09 (t, J = 7 Hz, 6 H, 2 CH_2CH_3), 1.18, 1.26 [each 6 H, 2 $C(CH_3)_2$], 1.49, 1.52 (4 H, 2 CH_2), 1.89 (1 H, NH disappears upon deuteration), 3.22 (q, J = 7 Hz, 4 H, 2 CH_2CH_3), 4.95 ppm (1 H, NH, disappears upon deuteration); mass spectrum (70 eV) *m/e* parent 378.

Anal. Calcd. for $C_{23}H_{46}N_4$: C, 73.00; H, 12.27; N, 14.80. Found: C, 73.07; H, 11.87; N, 14.98.

B. From Product of Reaction of TMP with HCN and HF.—Excess diethylamine was added to the cold reaction mixture obtained from 71 g (0.635 mol) of TMP, 25 g (0.90 mol) of HCN, and 19 g (0.96 mol) of HF. All volatiles were removed by sparging with nitrogen, and the residue was extracted with hot hexane, leaving the hydrogen fluoride salt of triethylamine undissolved. Cooling of the hexane extract to −30° gave a crystalline precipitate which was recrystallized once from methanol (−30°) to give 57 g (yield 49% based on HCN) of **3**, melting point and ir identical with those of **3** prepared from **1**. Also recovered were 3.1 g of a crystalline, hexane-insoluble compound which was identified as **14** (*vide infra*) by ir spectrum and mixture melting point determination.

2,3-Di-*tert*-octylimino-3-diethylaminopropionitrile (6).—A 5-g quantity of **3** was allowed to stand for 48 hr at room temperature in contact with air. The originally colorless crystals deliquesced, and the product was a slightly yellow oil which was dissolved in pentane and chromatographed over an alumina column. Almost all of the product was eluted with pentane. After three recrystallizations from methanol (−30°), 3.55 g (yield 71%) of **6**, mp 28.0–29.5°, was obtained as light yellow crystals: uv max (isooctane) 237, 340 mμ (log ε 3.96, 2.92); ir (CCl_4) 2190 (w, C≡N), 1625 cm^{-1} (vs, C=N); nmr (CCl_4) δ 1.00, 1.02 [18 H, 2 $C(CH_3)_3$], 1.08 [t, 6 H, J = 7.4 Hz, $N(CH_2CH_3)_2$], 1.28 [6 H, $C(CH_3)_2$], 1.57 [8 H, CH_2 + $C(CH_3)_2$], 1.72 (2 H, CH_2), 3.24 ppm [q, 4 H, J = 7.4 Hz, $N(CH_2CH_3)_2$]; mass spectrum (70 eV) *m/e* parent 376.

Anal. Calcd for $C_{23}H_{44}N_4$: C, 73.32; H, 11.81; N, 14.87; mol wt, 376.71. Found: C, 73.71; H, 11.70; N, 14.43; mol wt, 375 (Thermonam, acetone).

Hydrogenation of 6 to Give 3.—A 1-g quantity of **6** in ethyl acetate solution was hydrogenated using 75 mg of a 5% palladium-on-carbon catalyst. When 1 equiv of hydrogen had been absorbed, the uptake virtually stopped. After removal of the catalyst by filtration and of the solvent by evaporation *in vacuo*, 0.93 g of a crystalline residue remained which was identified as **3** by ir spectrum and mixture melting point determination.

Methanesulfonic Acid Salt of N-*tert*-octylaminomalononitrile (12 CH_3SO_3H).—The two aqueous KOH extracts (I and II) obtained in the reaction of TMP with HF and HCN were separately neutralized by dropwise addition of concentrated (37%) hydrochloric acid (~50 cc) under stirring and external ice cooling. An orange-colored oil (crude *N*-*tert*-octylaminomalononitrile) separated, which was recovered from the aqueous layer by extraction with pentane followed by drying ($MgSO_4$) and removal of the solvent *in vacuo*, yield from extract I 4.54 g and from extract II 0.55 g. This residue (4.54 g) was dissolved in 30 cc of anhydrous ether and cooled in an ice bath. Maintaining the cooling and under vigorous stirring an ice-cold solution of 1.9 g of methane sulfonic acid in 30 cc of ether was slowly added. Immediately a precipitate formed. After standing in the refrigerator for 2 hr the supernatant was decanted. The precipitate was triturated with three 50-cc portions of anhydrous ether, collected by filtration, and dried in a stream of dry nitrogen, yield 5.38 g of essentially pure methanesulfonic acid salt of **12**. For analysis a small quantity of the salt was dissolved in an excess of cold acetonitrile; the solution was treated with charcoal, filtered, and concentrated *in vacuo* until crystallization started. After standing in the refrigerator for 2 hr the colorless salt was collected by filtration. It was stable at −10° but decomposed upon prolonged standing at room temperature.

Anal. Calcd for $C_{12}H_{23}N_3SO_3$: C, 49.79; H, 8.02; N, 14.52; S, 11.07. Found: C, 49.27; H, 7.69; N, 14.83; S, 11.47.

***t*-Octylaminomalononitrile (12).**—A 3-g quantity of the methanesulfonic acid salt of **12** was dispersed in 50 cc of ether contained in a separatory funnel. Upon shaking with a concentrated aqueous solution of $KHCO_3$ the salt dissolved completely. The ether layer was dried ($MgSO_4$) and evaporated to dryness *in vacuo*, leaving an almost colorless oil. This oil was diluted with 10 cc of pentane and crystallized almost entirely upon cooling to −10°. Filtration yielded 1.74 g (87%) of **12** as colorless needles, which were stable at −10° but darkened upon standing at room temperature in air: ir (neat) 3380 (m, NH), 2200 cm^{-1} (w, C≡N); nmr (CCl_4) δ 1.01 [9 H, $C(CH_3)_3$], 1.23 [6 H, $C(CH_3)_2$], 1.42 (2 H, CH_2), 1.91 and 2.02 (d, 1 H, J = 10.6 Hz, NH, disappears on deuteration), 4.58 and 4.69 ppm (d, 1 H, J = 10.6 Hz, CH disappears on deuteration); mass spectrum (70 eV) *m/e* 193 (parent) absent, 178 (parent − CH_3), 122 [parent − $CH_2C(CH_3)_3$].

Anal. Calcd for $C_{11}H_{19}N_3$: C, 68.37; H, 9.88; N, 21.75; mol wt, 193.33. Found: C, 68.12; H, 9.92; N, 21.23; mol wt, 207 (Thermonam, acetone).

4-Cyano-5-*tert*-octylaminoimidazole (14).—The crystalline high-melting by-product obtained in the reaction of TMP with HF and HCN was recrystallized twice from chloroform, using charcoal treatment the first time to give 8.7 g of **14**: mp 195–196°; uv max (methanol) 248 mμ (log ε 4.03); ir ($CHCl_3$) 3430, 3360 (m, NH), 2210 (vs, C≡N), 1620 (s), 1555 (s), 1495 cm^{-1} (m); nmr ($CDCl_3$ + DMSO-d_6) δ 0.81 [9 H, $C(CH_3)_3$], 1.63 [6 H, $C(CH_3)_2$], 1.89 (2 H, CH_2), 4.94 (2 H, NH, disappears upon deuteration), 7.12 ppm (1 H, =CH); mass spectrum (70 eV) *m/e* parent 220.

Anal. Calcd for $C_{12}H_{21}N_4$: C, 65.40; H, 9.16; N, 25.43. Found: C, 65.14; H, 9.21; N, 25.47.

Compound **14** is easily soluble in dilute (1 *N*) aqueous HCl and may also be purified by filtration of the solution thus obtained, followed by neutralization with a solution of $KHCO_3$. The reprecipitated **14** is collected by filtration, washed with water, and recrystallized from hot chloroform after drying ($MgSO_4$).

When the reaction mixture of TMP with HCN and HF is worked up directly with $KHCO_3$, Et_3N, Et_2NH, or Ph_3P,[18] small amounts of **14** are also among the recovered products.

Registry No.—**1**, 30768-56-0; **1** (CH_3SO_3H), 30768-57-1; **3**, 31819-44-0; **4**, 30768-59-3; **5**, 30768-60-6; **6**, 30768-61-7; **7**, 30768-62-8; **8**, 31819-49-5; **9**, 30768-64-0; **11**, 30826-52-9; **12**, 31819-52-0; **12**

(CH_3SO_3H), 30768-66-2; **14**, 30771-61-0; TMP, 107-40-4; HCN, 74-90-8; HF, 7664-39-3.

Acknowledgment.—I wish to thank Dr. T. V. Liston for his valuable suggestions in organizing this manuscript and for proofreading it; Dr. J. M. King for helpful discussions; and Drs. R. M. Teeter, R. M. Bly, D. Rabenstein, and J. Q. Adams for their assistance in interpreting the mass spectra, ir and Raman spectra, nmr spectra, and epr spectra, respectively.

Arylnaphthalene Lignans. Synthesis of Justicidin E, Taiwanin C, Dehydrodimethylconidendrin, and Dehydrodimethylretrodendrin

T. L. HOLMES AND ROBERT STEVENSON*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

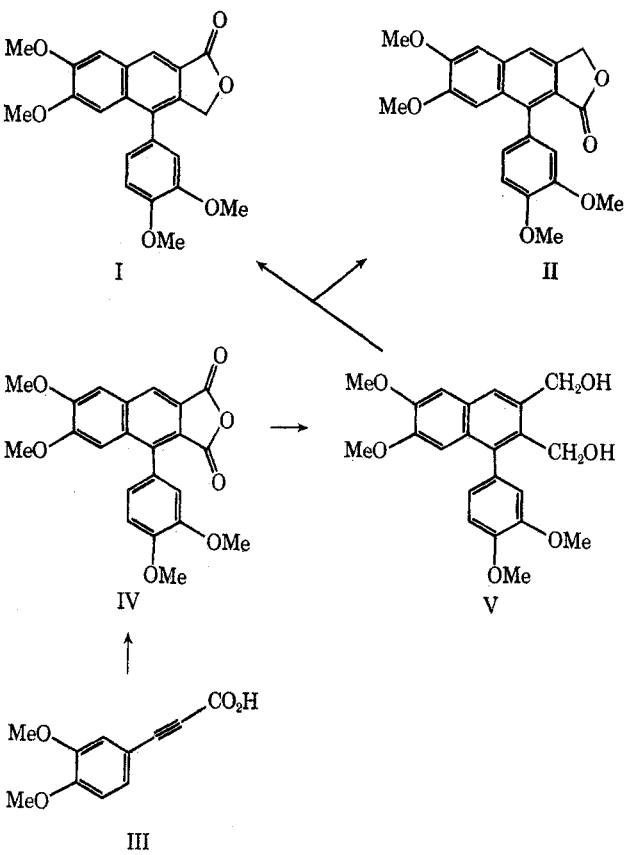
Received March 9, 1971

The naturally occurring lactones, justicidin E (VII) and taiwanin C (VI), have been synthesized by a short pathway starting from piperonylpropiolic acid. The tetramethoxy analogs, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), have been correspondingly obtained. Application of nmr spectroscopy to the structure elucidation of lignan arylnaphthalene lactones is discussed.

The arylnaphthalene lactones, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), although not yet reported to be naturally occurring, have been significant in the development of lignan chemistry, notably in the pioneering work of Haworth. Several interconversions with other classes of lignans have been achieved and syntheses of varying degree of complexity reported.[1-10]

We have sought to examine the generality of our recently reported synthesis[11] of helioxanthin by extension to a short convenient synthesis of dehydrodimethylconidendrin (I). Treatment of 3,4-dimethoxyphenylpropiolic acid (III) with acetic anhydride yielded 6,7-dimethoxy-1-(3′,4′-dimethoxyphenyl)naphthalene-2,3-dicarboxylic acid anhydride (IV),[2,12] which on reduction with lithium aluminum hydride in tetrahydrofuran solution gave the corresponding diol V. Treatment of V with silver carbonate–Celite (Fétizon's reagent)[13] resulted in smooth oxidation to a mixture of the lactones, dehydrodimethylconidendrin (I) and dehydrodimethylretrodendrin (II), in a ratio of approximately 9:1, as indicated by integration of the nmr spectrum of the lactone mixture. The lactone I was readily obtained by direct crystallization and the minor component, the lactone II, was isolated by thin layer chromatography of the crystallization mother liquors.

Although the methylenedioxy analogs VI and VII were first synthesized[14] in 1936 by the multistep procedures developed by Haworth for the tetramethoxy lactones I and II, they have only recently been reported to be of natural occurrence and no direct comparison, other than melting point proximity, has been made. Several crystalline extractives have been isolated[15] from the heartwood of *Taiwania cryptomerioides* Hayata and for one of these, taiwanin C, the structure 6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (VI) has been proposed.[16] The isomeric structure VII has been proposed for a lactone, justicidin E, isolated as a piscicidal constituent from *Justicia procumbens*, and the conversion of (−)-parabenzlactone (VIII) to justicidin E is indicated in the same communication.[17]



(1) R. D. Haworth and T. Richardson, *J. Chem. Soc.*, 633 (1935).
(2) R. D. Haworth and G. Sheldrick, *ibid.*, 636 (1935).
(3) R. D. Haworth, T. Richardson, and G. Sheldrick, *ibid.*, 1576 (1935).
(4) G. N. Walker, *J. Amer. Chem. Soc.*, **75**, 3387, 3393 (1953).
(5) R. D. Haworth and G. N. Walker, *ibid.*, **76**, 3596 (1954).
(6) R. D. Haworth, W. Kelly, and T. Richardson, *J. Chem. Soc.*, 725 (1936).
(7) R. D. Haworth and J. R. Atkinson, *ibid.*, 797 (1938).
(8) D. C. Ayres and J. W. Mundy, *ibid.*, 637 (1969).
(9) M. E. Cisney, W. L. Shilling, W. M. Hearon, and D. W. Goheen, *J. Amer. Chem. Soc.*, **76**, 5083 (1954).
(10) L. H. Klemm, K. W. Gopinath, D. Hsu Lee, F. W. Kelly, E. Trod, and T. M. McGuire, *Tetrahedron*, **22**, 1797 (1966).
(11) T. L. Holmes and R. Stevenson, *Tetrahedron Lett.*, 199 (1970).
(12) G. Traverso, *Gazz. Chim Ital.*, **88**, 653 (1958).
(13) M. Fétizon, M. Golfier, and J.-M. Louis, *Chem. Commun.*, 1102, 1118 (1969).
(14) R. D. Haworth and W. Kelly, *J. Chem. Soc.*, 745 (1936).
(15) Y.-T. Lin, T.-B. Lo, and E.-H. Shih, *J. Chin. Chem. Soc.* (*Taipei*), **2**, 87 (1955).
(16) Y.-T. Lin, T.-B. Lo, K.-T. Wang, and B. Weinstein, *Tetrahedron Lett.*, 849 (1967).
(17) K. Wada and K. Munakata, *ibid.*, 2017 (1970).