methane. Removal of solvent and chromatography over alumina, eluting with hexane–ether (19:1), gave **7,9(11)-diene 3a** (0.15 g): mp 106–108°; λ_{max} 237, 244 mμ (ε 12,000), and 253; glpc showed a major component (~90%), *t* 4.8 min.

Ozonolysis of Diene 3a.—Ozonized oxygen (from a Welsbach ozonizer) was passed into a solution of **3a** (0.8 g) in chloroform (50 cc) at 0° until no further ozone was absorbed. Hydrogen peroxide 20% (20 cc) was added to the concentrated solution (residue taken up in methanol) and left at 20° for 24 hr. Water (50 cc) was added, the mixture was concentrated to remove methanol, and the mixture was ether extracted. The extracts were washed with aqueous ferrous sulfate solution and water and then dried. Removal of solvent gave a colorless resinous solid (0.9 g), neut equiv 231 (theory for diacid 227).

The above diacid was esterified with excess ethereal diazomethane to give the triester **5** as a viscous liquid: ν_{max} 1735 (ester C=O), 1715 (1,2 diketone), 1710–1715 (CH_2CO), and 1430 cm^{-1} (CH_2 deformation); glpc showed a major peak, *t* 8.5 min, with two impurities having shorter retention times.

Anal. Calcd for $C_{25}H_{38}O_9$: C, 62.10; H, 7.92. Found: C, 61.80; H, 7.65.

Lithium Aluminum Hydride Reduction of Triester 5.—Triester (0.3 g) was refluxed 2 hr with lithium aluminum hydride (0.5 g) in dry ether (50 cc). Addition of water and dilute hydrochloric acid (1:1) to pH 2.0, ether extraction, and concentration *in vacuo* gave the crude pentaol **6** as a resinous solid (0.21 g), which was not purified.

Lead Tetraacetate Oxidation of 6.—The crude pentaol (0.20 g) was left at room temperature with lead tetraacetate (0.2 g) in acetic acid (10 cc) for 3 hr. Addition of a few drops of ethylene glycol, standing 10 min, dilution with water, ether extraction, and washing gave a viscous liquid (0.2 g). Glpc showed the presence of three major components, *t* 4.5, 7.5, and 12.5 min. Preparative glpc (similar conditions) gave the component having *t* 7.5 min as a viscous liquid (65 mg) identified as the pyran (**7**): ν_{max} (CCl_4) 3400 (OH), 2800 (CHO), 1720 (aldehyde C=O), 1360 and 1380 (Me_2CH), and 1090 cm^{-1} (COC); nmr signals appeared at 0.98 and 0.85 (broad, isopropyl group, J = 7.0 cps), 2.95 (OH), and a doublet centered at 9.56 ppm (J = 2 cps, CHO).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.12; H, 9.64.

Ozonolysis of Methyl 12,14-(2-Oxapropano)abiet-8,9-enoate (1b).—Ester **1b** (2.0 g) in dry chloroform (100 cc) was cooled in ice and ozonized oxygen was passed through for 30 min (progress of the reaction was followed directly by glpc). Concentration *in vacuo* gave a viscous liquid (2.6 g) which on glpc showed a major peak, *t* 6.5 (~60%), and another peak at *t* 4.0 min (ester **1b**) with minor components having longer retention times.

Chromatography over alumina (50 g) and elution with hexane–ether (4:1) gave a forerun of starting material (0.3 g) followed by a mixture (0.7 g) of two components, *t* 7.0 and 7.2 min. Preparative glpc gave the component with *t* 7.0 min as a viscous liquid (0.3 g): ν_{max} ($CHCl_3$) 1725 (ester C=O) and 875 cm^{-1} (epoxide); end absorption only in the uv region; nmr spectrum very similar to that of the epoxide of **1b**.

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.35; H, 9.64. Found: C, 73.21; H, 9.59.

Elution with ether gave a colorless crystalline solid (1.0 g): mp 115°; λ_{max} 249 mμ (ε 12,750); ν_{max} 1730 (ester C=O), 1660, and 1610 cm^{-1} (α,β-unsaturated C=O); glpc gave a major peak, *t* 5.5 min, identical with that of the product **4** from CrO_3 oxidation of **1b**.

Registry No.—**1b**, 19206-15-6; **1b** (8,9-epoxy), 19206-20-3; **3a**, 19206-16-7; **3b**, 19206-17-8; **4**, 19206-18-9; **4** (2,4-dinitrophenylhydrozone), 19237-74-2; **5**, 19206-19-0; **7**, 19203-28-2.

Acknowledgments.—The authors wish to thank Mr. G. S. Fisher of the Naval Stores Station and Dr. Werner Herz, Florida State University, for helpful discussions, and to thank Mr. Robert T. O'Conner, Southern Utilization Research and Development Division, New Orleans, La., for the provision of mass spectra.

Conformational Studies. II. Consequences of the Conjugate Addition of Cyanide Ion to Rigid Bicyclic Systems. A. Hexahydro-1,4a-dimethyl-2-naphthalenone[1]

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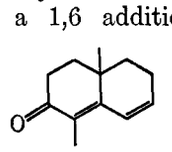
The unsaturated ketone named in the title underwent conjugate addition when treated with potassium cyanide in ethanol. In the absence of ammonium chloride, the main products were two isomeric lactamols, while in the presence of this salt the reaction yielded two epimeric ketonitriles. The structure proofs of the products entailed the use of dipole moment measurements, infrared intensity studies, and nuclear magnetic resonance spectroscopy, as well as classical chemical correlations.

Several years ago a series of publications appeared describing the introduction of a nitrile group at an angular position by the conjugate addition of potassium cyanide to an α,β-unsaturated ketone system.[2,3] In studies originally directed toward the total synthesis of certain sesquiterpenes, this reaction was likewise encountered in our laboratory at that time. The potential synthetic applications of such a cyanation procedure encouraged us to examine it in some detail as to yield, stereoselectivity, and reversibility. Our initial studies were concerned with the addition of potassium cyanide to dienone **1** for the purpose of effecting a 1,6 addition, yielding adduct **2**. The



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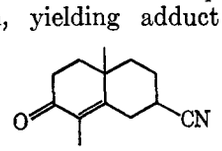


2

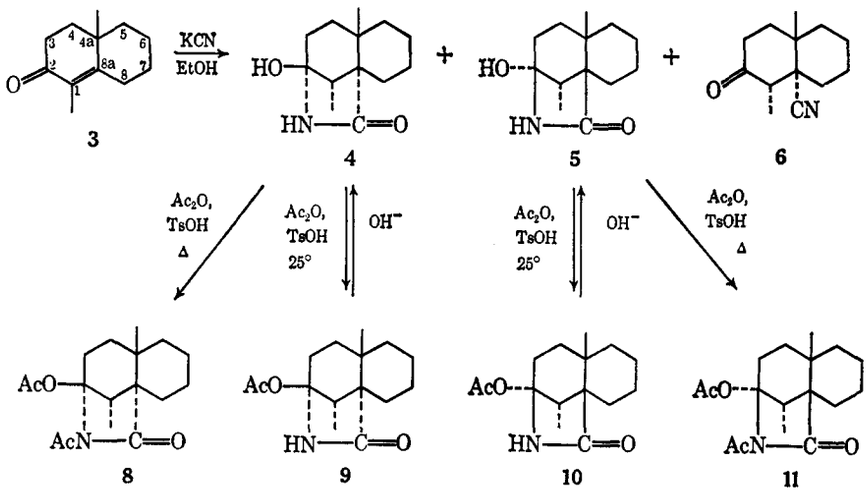
products obtained from this reaction were sufficiently complex, however,[4] that the elucidation of their struc-

(1) (a) Taken in part from the dissertation of Norman J. Johnston submitted for the Doctor of Philosophy Degree, University of Virginia, 1963. (b) This is part of a series of conformational studies; for earlier work, see O. R. Rodig and L. C. Ellis, *J. Org. Chem.*, **26**, 2197 (1961).

(2) Some of the more influential contributions in this field have been made by Nagata and coworkers. For a lead reference to their work, see W. Nagata, M. Narisada, and T. Sugasawa, *J. Chem. Soc., C*, 648 (1967). We wish to thank W. Nagata for sending us prior to their publication copies of some of the papers describing the work of the Shionogi group.

(3) Some other significant references are (a) A. Bowers, *J. Org. Chem.*, **26**, 2043 (1961); (b) J. A. Marshall and W. S. Johnson, *J. Amer. Chem. Soc.*, **84**, 1485 (1962); (c) W. L. Meyer and N. G. Schnautz, *J. Org. Chem.*, **27**, 2011 (1962); (d) W. L. Meyer and J. F. Wolfe, *ibid.*, **29**, 170 (1964).

(4) This reaction is described in detail in the following paper: O. R. Rodig and N. J. Johnston, *J. Org. Chem.*, **34**, 1949 (1969).



SCHEME I

tures was greatly facilitated by studying the addition reaction on the simpler α,β-unsaturated ketone **3**. Our findings on this phase of the work are discussed in this paper.

When ketone **3** was treated with ethanolic potassium cyanide (Scheme I), the main products were lactamols **4** (20%) and **5** (55%), together with a small amount of cyano ketone **6** (1%) and a compound (**7**) of unknown structure (1% by weight).[5] To determine the structures of lactamols **4** and **5**, attempts were made to hydrolyze the lactam ring. However, this function was found to be stable even under the most severe hydrolytic conditions, including 10 and 50% aqueous sulfuric acid at reflux temperatures, concentrated sulfuric acid at room temperature and 85°, and refluxing 10 and 40% aqueous potassium hydroxide.[6] When the hydrolysis method of Hauser and Hoffenberg[7] using boron trifluoride in glacial acetic acid was tried, lactamol **5** yielded 45% of monoacetate **10** whereas, interestingly enough, lactamol **4** failed to react.

Nevertheless, the assigned lactamol structures are supported by spectroscopic data. The substances exhibited no significant ultraviolet absorption above 220 mμ and lacked the $n \rightarrow \pi^*$ transitions at 270–285 (unconjugated) or 300–350 mμ (conjugated) characteristic of the ketone group. The infrared spectrum confirmed the lack of ketone carbonyl absorption and also contained no amide II bands at 1570–1515 cm^{-1}.[8a]

Selected solid state infrared absorption bands of the lactamols are shown in Table I. The assignments given in the first column are supported by dilution studies in chloroform,[8b,9] and by acetylation experiments described below.

When the two lactamols were heated at reflux in acetic anhydride containing molar quantities of *p*-toluenesulfonic acid, diacetylation occurred to yield

TABLE I
SELECTED INFRARED ABSORPTION BANDS OF LACTAMOLS 4 AND 5

Assignment	Lactamol 5	Lactamol 4	Ref
Bonded OH	3284 b[a]	3257 b	8b
Bonded NH	3189 b		8c
Lactam	3086 sh[a]	3096 sh	8c
Bonded lactam C=O	1658 b	1664 b	8d

[a] b = broad, sh = shoulder.

products **8** and **11**. The replacement of two hydrogens with acetyl groups was confirmed by the lack of infrared absorption in the N–H and O–H regions at 3300–3000 cm^{-1}. The two acetyl groups showed carbonyl absorption which overlapped into one broad band at 1736–1734 cm^{-1} and the original lactam carbonyl was shifted from 1658–1664 cm^{-1} to 1705 cm^{-1} due to the elimination of intermolecular hydrogen bonding.

Room temperature acetylation of the lactamols **4** and **5** by the acetic anhydride–*p*-toluenesulfonic acid method[10] yielded monoacetyl derivatives **9** and **10**, respectively. The infrared spectra of these compounds confirmed that O acetylation had occurred because of the retention of the 3086–3096-cm^{-1} lactam absorption which now appeared as a defined peak[8c] along with the expected bonded NH absorption. Saponification equivalents of both monoacetates were in excellent agreement with the theoretical values, the parent lactamols being recovered from the hydrolysis media.

Proofs of structure for lactamols **4** and **5** came largely from their preparations through the hydrolyses of ketonitriles **6** and **12** (Scheme II).[11] The latter were obtained in 42 and 18% yields, respectively, when ammonium chloride was added to the cyanide addition reaction and a shorter reaction time was employed.[12]

(5) The yields given are those obtained before final purification.

(6) The lack of hydrolysis under these conditions is in keeping with the observations on the reported stabilities of similar lactamol structures; for example, see W. Nagata, S. Harai, H. Itazaki, and K. Takeda, *Ann.*, **641**, 184, 196 (1961); W. Nagata, S. Hirai, T. Aoki, and K. Takeda, *Chem. Pharm. Bull. Jap.*, **9**, 837 (1961).

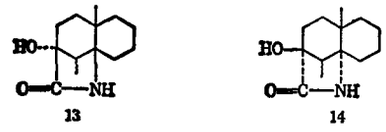
(7) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1448 (1955).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958: (a) p 216 ff; (b) p 96; (c) pp 205, 208; (d) p 213.

(9) Dilution in chloroform is accompanied by the appearance of a band in the 1600-cm^{-1} region which might be a primary amide II band arising from lactam ring opening;[8a] also *cf.* ref 3c.

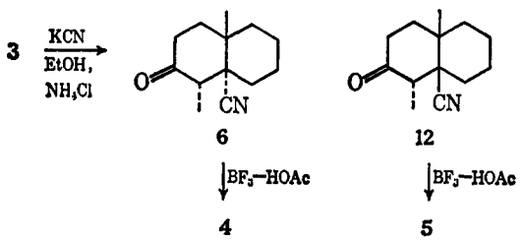
(10) Huang-Minlon, E. Wilson, N. L. Wendler, and M. Tishler, *J. Amer. Chem. Soc.*, **74**, 5394 (1952).

(11) This sequence thus ruled out the alternate, but less likely, structures **13** and **14**. Such products could arise by 1,2 addition of cyanide ion, yielding epimeric cyanohydrins, followed by hydrolysis to amidohydrins in the basic media and cyclization with the $\Delta^{1(8a)}$-double bond. The latter would be analogous to the cyclization of β,γ-unsaturated acids to γ-lactones.



(12) W. Nagata, *Tetrahedron*, **13**, 278 (1961).

SCHEME II



In addition, small amounts of lactamols **4** and **5** as well as some starting ketone **3** were obtained.

Hydrolysis Studies.—A number of hydrolysis conditions were tried to convert ketonitriles **6** and **12** into the corresponding lactamols. Interestingly, lactamol formation could be effected under mildly basic conditions, a fact which has also been affirmed by other workers.[13] However, in every case employing basic media, an appreciable quantity of ketone **3** was formed, presumably by β elimination of hydrogen cyanide. This result obviously vitiated the use of such hydrolyses in a structure proof sequence since cyanide ion could re-add to give the alternate isomer.

Actually, the conditions in the cyanide addition reaction in the absence of ammonium chloride are sufficiently basic to cause this reversibility.[14] This was nicely demonstrated by heating *trans* epimer **6** at reflux for 48 hr in a 2% solution of potassium cyanide in aqueous ethanol. Careful chromatography of the reaction mixture yielded a trace of ketone **3**, lactamol **4** (30%), lactamol **5** (25%), ketonitrile **6** (13%), ketonitrile **12** (6%), and the compound of unknown structure **7** (4% by weight).

To avoid side reactions arising from the reversal of the cyanide addition reaction, acidic hydrolysis conditions were investigated. Boron trifluoride in acetic acid[7] afforded good yields of the lactamols without the observed formation of ketone **3**, and these reactions therefore unequivocally established the structures of **4** and **5**.

Each ketonitrile contains three asymmetric centers (C-1, C-4a, and C-8a); however, if the C-1 methyl group (and boat or twist forms) is ignored for the moment, the conformations possible are those shown in Figure 1. The *trans*-decalin ring system is rigid and so can exist in but one conformation, A. The *cis*-decalin system, on the other hand, is flexible and can have two different conformations, B and B′.[15] The structures of the two ketonitriles were determined by infrared, nuclear magnetic resonance and dipole moment studies.

The elegant method of using infrared intensity measurements recently reported by Nagata and coworkers[16] was used to determine the stereochemistry at the ring junctures. This method is based on the principle that the intensity of the stretching frequency of a nitrile group is directly related to the number of

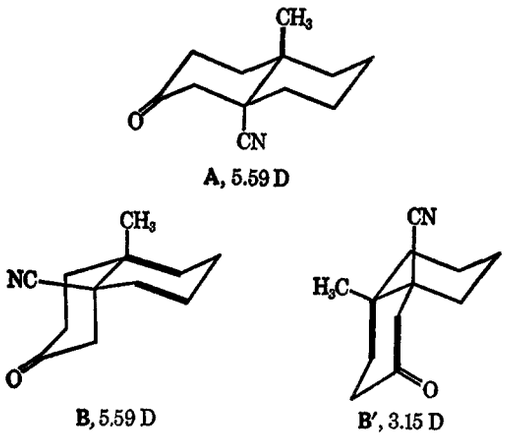


Figure 1.—Calculated dipole moments.

parallel β–γ carbon–carbon bonds. These bonds are shown as heavy lines in Figure 1, *cis* structures B and B′ having two such bonds while *trans* structure A has only one. The observed molar extinction coefficients for ketonitriles **6** and **12** are 19.9 and 33.8, respectively, which clearly indicate that **6** possesses the *trans* structure while **12** has the *cis* configuration. Still, these studies do not allow a distinction between *cis* conformations B and B′.

Inspection of molecular models shows, however, that *cis* form B should have the same dipole moment as *trans* form A (the two strong dipoles, the keto and nitrile groups, have equivalent mutual spacial orientations in each), whereas *cis* form B′ should possess a smaller dipole moment (the two dipoles are oriented at a dihedral angle approximately twice as great as that in A or B). Theoretical dipole moments for the three forms were calculated by a vector analysis method, employing the Corey and Sneen cartesian coordinate values for the cyclohexylidene ring,[17] and the carbonyl and nitrile vector moments of Lehn, Levisalles, and Ourisson.[18a] These values, which are expressed in Debye units, are shown in Figure 1.[18b] The experimentally determined dipole moments for the two ketonitriles **6** and **12** were 5.59 ± 0.06 and 3.08 ± 0.03 D, respectively, which confirm the *trans* assignment of ketonitrile **6** and establish the B′ conformation for compound **12**. In addition, they tend to rule out any appreciable distortion of the ketone-containing ring from the normal chair form. It has been suggested that such distortions, a result of dipole–dipole repulsions, may be present in 5-cyano-3-keto steroids.[19]

Theoretically, a differentiation between structures A and B or B′ should also be possible by observing the chemical shift of the C-4a methyl group protons in the nuclear magnetic resonance spectrum. In conformations B and B′ the nitrile groups are identically oriented with respect to the C-4a methyl groups, the dihedral angle being nearly 60° in each case. In *trans* structure A, however, the dihedral angle between these two groups is approximately 180°. Thus, one might anticipate a significant difference in the chemical shifts of the C-4a methyl groups in A and B or B′.[20] As seen from Table II the C-4a methyl group in ketonitrile **6**

(13) *Cf.* W. Nagata, S. Hirai, H. Itayaki, and K. Takeda, *J. Org. Chem.*, **26**, 2413 (1961).

(14) The reversible nature of this reaction has also been noted by other investigators: for example, W. Nagata, M. Yoshioka, and S. Hirai, *Tetrahedron Lett.*, 461 (1962), and ref 13.

(15) *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 231 ff.

(16) W. Nagata, M. Yoshioka, M. Narisada, and H. Watanabe, *Tetrahedron Lett.*, 3133 (1964).

(17) E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **77**, 2505 (1955).

(18) (a) J. M. Lehn, J. Levisalles, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1096 (1963). (b) For the theoretical and experimental dipole moment calculations, see ref 4.

(19) A. D. Cross and I. T. Harrison, *J. Amer. Chem. Soc.*, **85**, 3223 (1963).

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA FOR THE KETONITRILES AND LACTAMOL ACETATES[a]

Compound	C-4a methyl,[c] ppm	(angle, deg)	C-1 methyl,[b] ppm	(angle, deg)	C-1 hydrogen,[b] ppm	(angle, deg)
Ketonitrile **6**	1.24	(180)	1.16	(60)	2.50	(180)
Ketonitrile **12**	1.48	(60)	1.16	(60)	3.05	(60)
Lactamol acetate **9**	1.07	(180)	0.88	(60)	2.40	(180)
Lactamol acetate **10**	1.03	(60)	0.95	(180)	2.63	(60)

[a] The absorption spectra were determined at 60 Mc in deuteriochloroform solutions using tetramethylsilane as an internal reference. The chemical shifts are reported in parts per million measured from TMS (0 ppm) in the direction of decreasing field. [b] The geometrical center positions of the C-1 methyl doublet and the C-1 hydrogen quartet are reported. [c] The angle reported in each parenthesis is the approximate dihedral angle between that respective atom or group and the C-8a nitrile group in the ketonitriles or the bond at C-8a in the lactamol acetates.

exhibits a 0.24 ppm upfield shift from its position observed in the spectrum of **12**. Since this trend was also observed for the cyano steroid C-19 methyl groups,[19] the nmr evidence provides further support for the configurational assignments made for **6** and **12**.[21]

The configurations of the C-1 methyl groups were also determined from the nmr spectra. The two possible structures for *cis*-ketonitrile **12** are shown in Figure 2 as C and D (compare with structure B'). Of these, one might expect that structure C should be the less stable since it contains a severe 1,3-diaxial interaction between the two methyl groups.[22-24] Nonetheless, both C and D must be considered since the conditions of the reaction are not necessarily equilibrating, and it is well known that reactions of this type may yield the less stable isomer.[25]

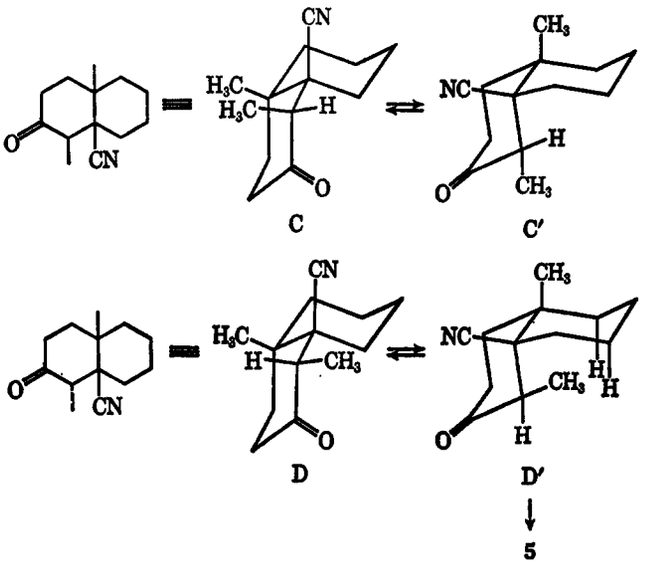
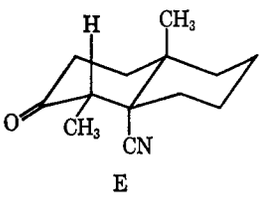


Figure 2

Since structures C and D have the flexible *cis*-decalin ring system, each can exist in the alternate conformations C' and D'. Fairly accurate estimates of the energy differences between these conformers can be obtained by considering the 1,2 and 1,3 interactions present in each. By applying values reported previously for such interactions,[24] it can be calculated that form C' should be about 2.2 kcal more stable than C, a value of sufficient magnitude to ensure almost complete exclusion of the latter conformation in an equilibrium mixture.[23] Thus, if C were the end product of the reaction, it would adjust itself to the more stable conformer C'. But C' (compare with structure B) has been ruled out by the dipole moment data; therefore, ketonitrile **12** must be represented by D.

Once the stereochemistry of ketonitrile **12** was established, it was possible to use this compound as a model to determine the shielding effects of the nitrile and carbonyl groups on the C-1 methyl and hydrogen substituents.[26] This information aided in the elucidation of stereochemistry of the *trans*-ketonitrile **6** as well as of compounds described in the subsequent publication.[4]

The fact that the C-1 methyl groups for both ketonitriles have essentially the same chemical shift (Table II) suggests that these groups probably lie in closely similar environments. Only if the C-1 methyl group in **6** is in an equatorial position as shown in E are such environmental conditions met with respect to the strongly anisotropic keto and nitrile groups.



E

These arrangements, on the other hand, necessarily place the two axial C-1 hydrogen atoms in different environments (compare D and E). Their relationships to the respective carbonyl groups remain the same, but in **6** the dihedral angle between the C-1 hydrogen atom and the nitrile group is 180°, while in **12** it is 60°. Consequently, the hydrogen atoms might reasonably be expected to exhibit different chemical shifts. A downfield shift of the C-1 hydrogen quartet in *cis*-ketonitrile

(20) Although it should be possible to calculate the magnitude of this difference from the known anisotropic shielding characteristics of the nitrile group [G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961)], recent work with 5-cyano steroids of established structure showed that additional factors of as yet undetermined origin are apparently involved.

(21) The observed chemical shift for the C-4a methyl group in the *cis* structure is also supported by dipole moment measurements on compounds discussed in the following paper (ref 4).

(22) The energy of a 1,3-diaxial dimethyl interaction has been reported to be about 3.7 kcal/mol [N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **83**, 2145 (1961)]. Since structure D contains a 1,3 interaction between the C-1 methyl group and the equatorial C-8 hydrogen atom which is absent in C, the actual energy difference involved will be 3.7 kcal minus one 1,3-diaxial methyl–hydrogen interaction, or about 2.9 kcal. The 2-alkyl ketone effect was assumed to be negligible (see references cited in ref 23).

(23) It can be likewise calculated that D is about 0.6 kcal more stable than C'. In these treatments, the 2- and the 3-alkyl ketone effects were considered to be negligible [B. Rickborn, *J. Amer. Chem. Soc.*, **84**, 2414 (1962); N. L. Allinger and H. M. Blatter, *ibid.*, **83**, 994 (1961), and ref 24a], as was possible dipole interaction between the nitrile and keto groups.

(24) (a) N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **84**, 2201 (1962). (b) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962); B. Rickborn and F. R. Jensen, *ibid.*, 4606 (1962).

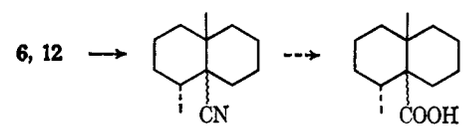
(25) For example, see (a) H. E. Zimmerman and T. W. Cutshall, *J. Amer. Chem. Soc.*, **81**, 4305 (1959); H. E. Zimmerman and A. Mais, *ibid.*, **81**, 3644 (1959); (b) E. J. Corey and R. A. Sneen, *ibid.*, **78**, 6269 (1956).

(26) The C-1 hydrogen is easily identified because it is split into a quartet having the same J value as the C-1 methyl doublet.

12 as compared with that in the *trans* isomer is indeed observed in the spectra of these compounds (Table II).

With respect to the lactamols, the equatorial C-1 methyl group in ketonitrile **6** would be expected to retain this configuration during the hydrolysis to **4**.[27] On the other hand, ketonitrile **12** which also has the C-1 methyl group equatorial (structure D in Figure 3) must shift to conformer D′ in order to cyclize to the lactam. In doing so, however, severe interactions between the C-1 methyl group (which has now become axial) and the C-5 and C-7 hydrogen atoms arise. Should the methyl group epimerize before lactam formation takes place, then such interactions would be alleviated. Nevertheless, the conformation of the C-1 methyl group in lactamol **5** appears to be axial. Evidence for this assignment comes from the nuclear magnetic resonance spectra of lactamol acetates **9** and **10**, wherein the C-1 hydrogen peak in the former appears further upfield than does its counterpart (Table II). These hydrogens thus appear to be in different magnetic environments in the two compounds. Molecular models show that the only way that this condition is fulfilled ensues when the C-1 methyl group of **10** (and therefore of **5**) assumes an axial position.

In the course of this work, an attempt was made to elucidate the structures of ketonitriles **6** and **12** by converting them into the isomeric carboxylic acids **16a** and **b** and determining the structures of the latter by the method of Sommer and coworkers.[28] Although it was possible to remove the keto groups by Clemmensen reduction, subsequent hydrolysis of nitriles **15a** and **b** was unsuccessful, even under rather drastic conditions.



15a, b **16a, b**

These results, contrasted with the mild conditions required for the hydrolysis of the nitrile group in the ketonitriles themselves, demonstrate the importance of carbonyl participation in the hydrolysis reaction.[3c]

Experimental Section[29]

Potassium Cyanide Addition to 4,4a,5,6,7,8-Hexahydro-1,4a-dimethyl-2(3H)-naphthalenone (3). A. In Aqueous Ethanol.—A solution of 20.0 g (0.11 mol) of enone **3**[30] (n^{26}D 1.5250), 40.0 g (0.62 mol) of potassium cyanide, 800 ml of 95% ethanol and 80 ml of water was heated at reflux with stirring for 12 hr.[31] The reaction rate was monitored by periodic sampling and observing the decrease of the 248-mμ peak in the uv spectrum of **3**. The solvent was removed *in vacuo* and water was added to the remaining yellow semisolid. This mixture was extracted with ether and ethyl acetate, and the aqueous layer was acidified and further extracted in like manner. The combined extracts were dried and concentrated *in vacuo*, yielding 22.6 g of a colorless solid which was chromatographed on 600 g of florisil.[32]

Elution with benzene and benzene–ether (10:1, 5:1) afforded 0.63 g (3%) of enone **3** followed by 0.05 g (0.2%) of *trans*-ketonitrile **6** as colorless crystals, mp 90–100°, further raised to 100.5–102° by recrystallization from benzene–petroleum ether. Continued elution yielded an additional 0.21 g (0.9%) of impure ketonitrile **6** as an oil.

Benzene–ether (1:1) eluents gave 0.25 g (1% by weight) of solid **7** of unknown structure which was recrystallized from benzene, yielding colorless crystals, mp 203.5–204.5°, ir 3441, 3195, 3080, 1718, 1705 and 1685 cm^{-1}, the latter three bands as a broad triplet. Substance **7** was readily soluble in dilute sodium hydroxide solution but insoluble in hot water; it did not react with dinitrophenylhydrazine reagent[33a] on standing for 3 days.

Anal. Found: C, 67.90, 68.04; H, 8.48, 8.49; N, 5.81, 6.10; mol wt, 332 (Rast).[34]

Further elution with benzene–ether (1:1) gave 0.35 g of a mixture of compounds **4** and **7**, followed by a series of fractions totaling 4.9 g (20%) of lactamol **4** with melting points in the range 175–185°. Recrystallization of this product from benzene furnished colorless crystals: mp 191.5–192.5°, ir (chloroform) 3534 (OH), 3378 (NH), 1701 (sh) and 1689 (b, associated lactam C=O) and 1597 cm^{-1} (weak, $CONH_2$ amide II).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.79; H, 9.25; N, 6.25.

Continued elution with benzene–ether (1:1), ether and ether–ethyl acetate (9:1) afforded 2.09 g (8%) of a mixture of lactamols **4** and **5**, mp 148–167°, which could not be separated by recrystallization from benzene.

Additional elution with ether–ethyl acetate mixtures yielded fractions containing 13.7 g (55%) of lactamol **5** in various states of purity, most of which had mp 170–173°. Recrystallization of this material from benzene readily afforded colorless crystals, mp 172–173.5°, ir (chloroform) 3584 (OH), 3425 (NH), 1701 (sh) and 1686 (b, associated lactam C=O) and 1592 cm^{-1} (weak, $CONH_2$ amide II).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.08; H, 9.30; N, 6.54.

Lactamols **4** and **5** were insoluble in cold water, cold dilute sodium bicarbonate and hydrochloric acid solutions but soluble in hot water and cold aqueous sodium hydroxide. They gave negative tests for unsaturation.[33b] Lactamol **5** gave a negative xanthydrol test for primary amides[33c] and failed to absorb hydrogen at 60 psi with 10% palladium–carbon. Lactamol **5** could not be hydrolyzed with concentrated sulfuric acid at 25 and 85°, refluxing 10 and 50% aqueous sulfuric acid, refluxing 10 and 40% aqueous sodium hydroxide and 20% sodium hydroxide in ethylene glycol–water (6:1). With nitrous acid at 0°, lactamol **5** afforded a nitrogen-containing solid of unknown structure in 31% yield, having a melting point of 245–248° (decomposes with gas evolution) after several recrystallizations from ethyl acetate: ir 3125 (b), 3008, 1763 (b), 1700 (b) and 1683 cm^{-1} (sh, b).

Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.81, 61.45; H, 7.71, 7.51; N, 5.40.

Treatment of lactamols **4** and **5** with polyphosphoric acid at 180° gave a vigorous evolution of hydrogen cyanide and produced enone **3**, 29% from **5** and 17% from **4**, as well as a mixture of unsaturated hydrocarbons resulting from the action of the reagent on **3**.

A solution of lactamol **5** and 2,4-dinitrophenylhydrazine reagent,[33a] upon standing 2 days at room temperature, deposited yellow needles (54%) which were recrystallized from ethyl acetate: mp 221–223° (dec); uv max (chloroform) 276, 383 mμ (log ε = 4.294, 3.449) inflex 315 mμ (log ε = 3.214); ir 3311, 3086, 1721, 1613, 1589 (sh), 1526 (NO_2), 1493, 1464 and 1343 cm^{-1} (NO_2). The elemental analysis is in agreement with a

(27) D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 44 (1956); D. H. R. Barton, *Chem. Ind.* (London), 664 (1953); *J. Chem. Soc.*, 1027 (1953).

(28) P. F. Sommer, C. Pascual, V. P. Arya, and W. Simon, *Helv. Chim. Acta*, 1734 (1963).

(29) All melting points were determined in a heated oil bath and are corrected, while boiling points are uncorrected. The nmr spectra were determined in deuteriochloroform solution (unless specified otherwise) on a Varian A-60 spectrometer and chemical shift values are given in parts per million (ppm) measured downfield from tetramethylsilane used as an internal standard. The infrared spectra were determined in the solid state in a potassium bromide matrix (unless indicated otherwise) on a Perkin-Elmer Model 21 spectrophotometer. The ultraviolet absorption spectra were obtained with a Perkin-Elmer Model 4000A Spectracord. Magnesium sulfate was usually employed to dry organic extracts, and the microanalyses were performed by Mrs. D. Ellis and Mrs. W. Coyne of this laboratory.

(30) M. Yanagita, M. Hirakura and F. Seki, *J. Org. Chem.*, **23**, 841 (1958).

(31) No reaction was observed when the solution temperature was maintained at 30° for 12 hr or when the water was omitted from a solution which was heated at reflux for 21 hr.

(32) Floridin Co., Talahassee, Fla., 60–100 mesh.

(33) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley & Sons, Inc., New York, N. Y. 1964: (a) p 126; (b) pp 121, 149; (c) p 256; (d) p 292.

(34) Althouhg the observed molecular weight value is low, the elemental analysis conforms to a dimer, $C_{26}H_{38-40}N_2O_5$. Dimeric species also have been isolated by other workers.[3,6,13]

TABLE III

HYDROLYSIS CONDITIONS FOR KETONITRILES 6 AND 12

		Hydrolysis conditions				Yields[a]		
			Media, ml		Reflux	Recovered	Ketone 3,	Lactamol	
Nitrile	Wt, mg	Reagent	EtOH (95%)	H_2O	time, hr	nitrile, mg (%)	mg (%)	mg (%)	Total %
6	261	3% KOH	32	1	1		110 (49)	43 (15)	64[b]
	250	3% $KHCO_3$	24	9	23		68 (31)	92 (34)	65[c]
	251	3% K_2CO_3	19	14	2	63 (25)	20 (9)	51 (19)	53[d]
	251	Concd. H_2SO_4[e]	0	0	0.7	182 (73)		40 (15)	88[c]
	251	3% HCl[f]	33	0	20	227 (91)			91[c]
	250	BF_3-HOAc[g]	0	0.8	2			168 (62)	62[b]
12	253	3% KOH	32	1	1		60 (27)	83 (30)	57[d]
	207	3% K_2CO_3	19	15	2	95 (46)	17 (9)	73 (32)	87[d]
	253	BF_3-HOAc[g]	0	0.8	2	34 (13)		225 (82)	95[c]

[a] Blanks indicate that none of that compound could be detected. Yields reported are those obtained before final purification. [b] Products isolated by chromatography on florisil. [c] Products isolated by fractional crystallization. [d] Products isolated by a combination of fractional crystallization and florisil chromatography. [e] 1.5 ml of concentrated sulfuric acid containing one drop of concentrated hydrochloric acid. Reaction conducted at 90°. [f] 3 ml of concentrated hydrochloric acid. [g] 7 ml of glacial acetic acid saturated with gaseous boron trifluoride.

formula obtained by combining **5** and 2,4-dinitrophenylhydrazine with the loss of 2 mol of water.

Anal. Calcd for $C_{19}H_{23}N_5O_4$: C, 59.21; H, 6.01; N, 18.17; mol wt, 385. Found: C, 58.99, 59.10; H, 6.01, 6.13; N, 18.04; mol wt, 383 (Rast).

No reaction was observed when the experiment was repeated with lactamol **4**.

One other reaction served to distinguish lactamol **5** from lactamol **4**. Only the former reacted with hot absolute ethanol containing a trace of concentrated sulfuric acid. The 3α-ethoxy derivative was formed in 60% yield and was recrystallized from ether: mp 158.5–160°; ir 3165 (NH), 3058 (lactam), 1686 (C=O) and 1078 cm^{-1} (C–O–C).

Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.03; N, 5.57. Found: C, 71.62; H, 9.87; N, 5.61.

This substance was separated from unreacted lactamol **4** (30% recovery) by chromatography on florisil[32] and could be quantitatively hydrolyzed to the parent lactamol **5** in acetic acid containing a trace of concentrated hydrochloric acid.

B. In Aqueous Ethanol with Ammonium Chloride.[12]—A solution of 7.3 g (0.11 mol) of potassium cyanide and 5.3 g (0.098 mol) of ammonium chloride in 38 ml of water was added to 10.0 g (0.056 mol) of enone **3** in 35 ml of ethanol. The mixture was heated at reflux for 4 hr with stirring, the rate of the reaction being monitored by periodic ultraviolet sampling as described above for the untempered reaction. The solvent was removed *in vacuo* and the red residue was extracted with ethyl acetate then diluted with water and further extracted with ethyl acetate. The combined extracts were dried and concentrated, yielding 11.2 g of orange oil which was only partly resolved when chromatographed on Woelm[35] neutral or acidic alumina.

Nevertheless, separation was sufficient to allow the isolation of 0.04 g of starting material **3**, 1.70 g of *trans*-ketonitrile **6**, mp 99–101°, and 0.04 g of epimeric *cis*-ketonitrile **12**, mp 106.5–108°, by the fractional crystallization of certain fractions. The remaining fractions and mother liquors were combined and rechromatographed in two equal portions on florisil.[32] Elution with petroleum ether–benzene (9:1) gave 0.57 g of **3** (total recovery, 0.61 g, 6%) while petroleum ether–benzene (4:1, 1:1) eluted 2.01 g of *cis*-ketonitrile **12** for a total yield of 2.05 g (18%). Recrystallization from petroleum ether–benzene afforded colorless crystals: mp 107–108.5°; uv max 286 mμ (ε 20), ir 2232 (C≡N) and 1710 cm^{-1} (C=O); nmr[36] δ 1.16 (d, 3, J = 7 Hz, C-1 CH_3), 1.48 (s, 3, C-4a CH_3), 3.05 (qr, 1, J = 7 Hz, C-1 **H**).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.19; H, 9.55; N, 6.79.

Continued elution with petroleum ether–benzene (1:1), benzene and benzene–ether (9:1) produced 3.09 g of *trans*-ketonitrile **6** (total yield 4.79 g, 42%). Recrystallization of this material from petroleum ether–benzene yielded colorless crystals: mp 101–102°; uv max 286–288 mμ (ε 18); ir 2227 (C≡N) and 1706 cm^{-1} (C=O); nmr[36] δ 1.16 (d, 3, J = 7 Hz, C-1 CH_3), 1.24 (s, 3, C-4a CH_3), 2.50 (qr, 1, J = 7 Hz, C-1 **H**).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.28; H, 9.29; N, 6.58.

Final eluents composed of ethyl acetate and ethanol afforded 0.47 g (4%) of a mixture of lactamols **4** and **5**.

Hydrolyses of *cis*- and *trans*-Ketonitriles 6 and 12. General Procedures.—Table III presents the pertinent data for nine hydrolyses of two ketonitriles **6** and **12**. The reaction mixtures were processed as follows. The aqueous ethanol solutions were evaporated to dryness under reduced pressure and water was added to the residues prior to extraction. The concentrated sulfuric acid solution was diluted sevenfold with cold water before being extracted, while the boron trifluoride–acetic acid mixtures were made basic with 8 ml of 6 *N* sodium hydroxide solution prior to extraction. All extractions were made with both ether and ethyl acetate; the extracts were dried and concentrated *in vacuo* and the resulting residues were fractionated by either crystallization, chromatography on florisil[32] or by a combination of these two methods. The products of each reaction were carefully identified by comparison of their infrared spectra with those of authentic samples and by mixture melting points.

The Reaction of *trans*-Ketonitrile 6 with Potassium Cyanide in Ethanol.—A clear solution of 138 mg of ketonitrile **6**, 280 mg of potassium cyanide, 11.2 ml of absolute ethanol and 2.1 ml of water was heated at reflux with stirring for 48 hr. To follow the hydrolysis, infrared spectra were taken of aliquots removed from the reaction mixture at periodic intervals. The reaction mixture was extracted with ether and ethyl acetate and the combined extracts were dried and evaporated to dryness under reduced pressure. The colorless residue was chromatographed on florisil.[32] Benzene eluents afforded initially a trace of the enone **3**, then 7 mg (6%)[37] of *cis*-ketonitrile **12** contaminated with a trace of **3**. Further elution with benzene–ether (20:1) gave 15 mg (13%) of starting material **6**, also containing a trace of **3**. Benzene–ether (5:1) then furnished 6 mg (4% by weight) of the dimeric substance **7** of unknown structure. Continued elution with ether gave 38 mg (30%) of lactamol **4** and, finally, elution with ethyl acetate afforded 31 mg (25%) of the corresponding lactamol **5**.

Isomeric Naphthalenecarbonitriles 15a and b.—To 10 g of washed zinc amalgam, made from 10 g of granulated zinc, 15 ml of water, 0.5 ml of concentrated hydrochloric acid and 1.0 g of mercuric chloride,[38] were added in order 7.5 ml of water, 17.5 ml of concentrated hydrochloric acid, 10 ml of toluene and 0.93 g of a mixture consisting of approximately two parts of **6** and three parts of **12** (infrared). The reaction mixture was heated at reflux for 25 hr with the addition of 5-ml portions of concentrated hydrochloric acid after 13, 19 and 23 hr. The aqueous layer was separated from the cooled reaction mixture and extracted with ethyl acetate, saturated with sodium chloride and again extracted with ethyl acetate. These extracts were combined with the toluene layer and washed with 5% sodium

(35) Alupharm Chemicals, New Orleans, La.

(36) The chemical shift values for all doublets and quartets were measured at the geometrical midpoint between the peaks.

(37) The yields in this experiment are adjusted to correct for the removal of 21 mg of solid from the reaction medium during the infrared sampling. All products were identified by comparing their infrared spectra with those of authentic samples.

(38) E. L. Martin, *J. Amer. Chem. Soc.*, **58**, 1438 (1936).

hydroxide solution until the washings remained basic. The organic phase was dried and concentrated *in vacuo*, affording 0.82 g (95%) of a mixture of epimeric nitriles **15a** and **b** as a semisolid which showed strong nitrile absorption in the infrared spectrum and which readily dissolved in petroleum ether (bp 30–60°). No further purification was attempted.

Attempted Hydrolyses of Nitriles 15a and b.—Seven unsuccessful attempts were made to hydrolyze nitrile mixture **15a** and **b**. Hydrolysis conditions included 5% potassium hydroxide in ethanol–water (3:1), 29 hr reflux; concentrated hydrochloric acid, 25 hr reflux; 40% aqueous potassium hydroxide solution, 49 hr reflux; concentrated sulfuric acid, 15 min at 75°, then diluted with ethanol–water (1:4) to 10% acid concentration, followed by 34 hr reflux; anhydrous boron trifluoride–glacial acetic acid, 10 min at 120°, also 90 min at 120° followed by 30 min at 135°;[7] and 75% aqueous sulfuric acid, 1 hr at 155–180°. From each run only unreacted nitrile (infrared identification) was obtained in 82% average recovery. None of the procedures afforded acidic products.

Treatment of Lactamol 5 with Acetic Anhydride. A. At Room Temperature.[10]—A solution of 7 ml of acetic anhydride, 130 mg of *p*-toluenesulfonic acid monohydrate and 157 mg of lactamol **5** was stirred for 21 hr at 35°, then poured onto crushed ice and allowed to warm to room temperature. The resultant clear solution was extracted with ether, saturated with sodium chloride and again extracted with ether. The combined extracts were washed with saturated sodium bicarbonate solution until evolution of gas had ceased, dried and evaporated to dryness *in vacuo*. The colorless residue was chromatographed on florisil[32] whereby benzene–ether (20:1 to 1:1) eluents yielded 127 mg (68%) of lactamol acetate **10**, mp 160–162.5°, raised to 162–163° by one recrystallization from benzene. The product from a similar reaction exhibited mp 164–164.5°; ir 3205 (N–H), 3077 (lactam), 1744 ($CH_3C{=}O$), 1692 (lactam C=O), 1268 and 1229 cm^{-1} (b, –COO–); nmr[36] δ 0.95 (d, 3, J = 6.5 Hz, C-1 CH_3), 1.03 (s, 3, C-4a CH_3), 2.05 (s, 3, CH_3CO), 2.63 (qr, 1, J = 6.5 Hz, C-1 **H**).

Anal. Calcd for $C_{15}H_{23}NO_3$: C, 67.87; H, 8.74; N, 5.28. Found: C, 68.05; H, 8.57; N, 5.18.

Further elution with ether and ethyl acetate gave 23 mg (15% recovery) of starting material **5**, mp 135–160°, raised to 167.5–170.5° by one recrystallization from benzene.

The hydrolysis of acetate **10** was effected by refluxing 105.4 mg for 12 hr in 25.13 ml of 0.0393 *N* potassium hydroxide solution. Titration of the cooled mixture with 11.82 ml of 0.0488 *N* hydrochloric acid solution to a phenolphthalein end point furnished a saponification equivalent of 252 (theoretical 265). To isolate the reaction product, the solution was further acidified and extracted with ether and ethyl acetate prior to and after some concentration of the aqueous phase under reduced pressure. The combined extracts were washed with saturated sodium bicarbonate solution, dried and evaporated *in vacuo*. The residual oil crystallized when triturated with benzene–petroleum ether and afforded 52 mg (59%) of lactamol **5**, mp 169–172°, the ir spectrum of which was identical with that of an authentic sample.

Monoacetate **10** was also obtained during an attempt to hydrolyze lactamol **5** by heating it with anhydrous boron trifluoride–glacial acetic acid for 10 min at 120–125°.[7] The reaction mixture was processed as described above for the similar hydrolyses of ketonitriles **6** and **12**. Accordingly, from 109 mg of **5**, 58 mg (45%) of colorless monoacetate **10** was obtained, mp 150–156°, raised to 163–164.5° after two recrystallizations from benzene. A mixture melting point of this product with an authentic sample, mp 164–164.5°, was undepressed, and the infrared spectra of the two samples were identical.

B. At Reflux Temperature.—A mixture of 25 ml of acetic anhydride, 800 mg of *p*-toluenesulfonic acid monohydrate and 507 mg of lactamol **5** was heated at reflux for 24 hr. The resulting deep red reaction mixture was processed in the manner described above for the room temperature acetylation and yielded a brown oil which solidified on standing. The solid was chromatographed on florisil[32] whereby elution with benzene and benzene–ether (4:1) yielded 642 mg (92%) of lactamol diacetate **11** in several fractions having melting points in the range 119–125°. The fractions were combined and recrystallized from petroleum ether–benzene, yielding an analytical sample: mp 126–127°, ir 1751 (sh, CH_3CON–), 1736 (b, CH_3COO–), 1705 (lactam C=O), 1276, 1260, 1239 and 1217 cm^{-1} (b, –COO–); nmr[36] δ 0.89 (d, 3, J = 7 Hz, C-1 CH_3), 1.03 (s, 3, C-4a CH_3), 2.22 (s, 3, CH_3COO), 2.66 (s, 3, CH_3CON), 3.33 (qr, 1, J = 7 Hz, C-1 **H**).

Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.42; H, 8.20; N, 4.56. Found: C, 66.47; H, 7.92; N, 4.52.

Treatment of Lactamol 4 with Acetic Anhydride. A. At Room Temperature.—By employing the same conditions described above for the monoacetylation of lactamol **5**, 149 mg of lactamol **4** yielded 154 mg of monoacetate **9** as colorless crystals, mp 143–150°. On recrystallization from benzene, 133 mg (76%) of **9**, mp 155–160°, was recovered. Two additional recrystallizations from benzene raised the melting point to 158.5–160°: ir 3185 (NH), 3067 (lactam), 1736 ($CH_3C{=}O$), 1689 (lactam C=O), 1275, 1254 and 1229 cm^{-1} (b, –COO–); nmr[36] δ 0.88 (d, 3, J = 6.5 Hz), 1.07 (s, 3, C-4a CH_3), 2.08 (s, 3, CH_3CO), 2.40 (qr, 1, J = 6.5 Hz, C-1 **H**).

Anal. Calcd for $C_{15}H_{23}NO_3$: C, 67.87; H, 8.74; N, 5.28. Found: C, 68.12; N, 8.68; N, 5.43.

Another run employing 404 mg of **4** afforded 393 mg (82%) of **9**, mp 154–157°, which gave 306 mg (64%), mp 157.5–159.5°, when recrystallized from benzene.

The hydrolysis of monoacetate **9** was effected by the same procedure employed for monoacetate **10**. Thus, 101.5 mg of **9**, when heated at reflux for 12 hr in 25.12 ml of 0.0393 *N* potassium hydroxide solution and titrated with 12.35 ml of 0.0488 *N* hydrochloric acid solution to a phenolphthalein end point, furnished a saponification equivalent of 259 (theoretical 265). From this solution, 67 mg (78%) of lactamol **4** was recovered, mp 191–192.5°, which gave an undepressed mixture melting point with an authentic sample of **4**. The infrared spectra of the two were identical.

When lactamol **4** was treated with anhydrous boron trifluoride–glacial acetic acid[7] in the same manner described above for lactamol **5**, no acetylated products were obtained and the starting material was recovered.

B. At Reflux Temperature.—Under the same conditions employed for the diacetylation of lactamol **5**, 511 mg of lactamol **4** gave a dark oil which solidified on standing and was chromatographed on florisil.[32] Elution with benzene yielded a combined 620 mg (88%) of diacetate **8** as colorless crystals, mp 74–81°. When recrystallized from petroleum ether–benzene, this material afforded 496 mg (71%) of **8**: mp 82–85°; ir 1751 (sh, CH_3CON–), 1734 (b, CH_3COO–), 1706 (lactam C=O), 1282, 1264, 1247 (sh), 1233 (b) and 1214 cm^{-1} (b, –COO–); nmr δ 0.83 (d, 3, J = 7.5 Hz, C-1 CH_3), 1.19 (s, 3, C-4a CH_3), 2.20 (s, 3, CH_3COO), 2.65 (s, 3, CH_3CON), 3.01 (qr, 1, J = 7.5 Hz, C-1 **H**).

Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.42; H, 8.20; N, 4.56. Found: C, 66.62; H, 8.08; N, 4.36.

Further elution with benzene–ether (1:1) yielded no additional identifiable material.

TABLE IV

INFRARED INTENSITY MEASUREMENTS

Compd	Concn, mol/l. of $CHCl_3$	I_0	I	ϵ
6	1.226	89.2	45.9	18.7
6	0.768	93.1	59.7	19.9
6	0.360	95.1	76.3	21.1
12	1.292	91.9	29.2	30.6
12	0.813	91.2	40.3	34.6
12	0.380	96.1	64.6	36.1

Infrared Intensity Measurements.—Molar extinction coefficients were obtained for the C≡N stretching vibration of the two ketonitriles **6** and **12** using the data presented in Table IV. For each compound, three concentrations in chloroform were measured using a Perkin-Elmer Model 521 infrared spectrophotometer and a 0.0126-cm sodium chloride cavity cell[39] matched against a cavity cell containing chloroform in the reference beam. The region from 2300–2200 cm^{-1} was scanned at 14 cm^{-1}/min using a 10:1 scale expansion. The $\nu_{max}^{C\equiv N}$ for **6** and **12** is 2231 cm^{-1}.

Registry No.—Cyanide ion, 57-12-5; **3**, 878-55-7; **4**, 19292-09-2; **5**, 19292-10-5; 3α-ethoxy derivative of **5**, 19291-70-4; **6**, 19292-04-7; **8**, 19292-13-8; **9**, 19292-14-9; **10**, 19292-15-0; **11**, 19292-16-1; **12**, 19292-17-2.

(39) Connecticut Instrument Corp., Stamford, Conn.