μ that are characteristic of the derivative of the *trans* amine.

A mixture of 0.46 g. of the nitro compound, 25 ml. of methanol, 10 drops of sulfuric acid, and 0.1 g. of 10% palladium on charcoal was hydrogenated for 250 min. (72% hydrogen uptake). The catalyst was collected and washed and the filtrate was neutralized with 20% sodium hydroxide solution. Extraction with ether followed by drying and preparation of the phenylthioureide gave 45% recovery of material melting at 115–124° whose spectrum contained no bands characteristic of the *trans* phenylthioureide. After crystallization from ethanol this material melted at 137–138°.

On hydrogenation of the *cis* nitro compound in ethanol using platinum oxide catalyst there was obtained 68% of a mixture consisting of *cis* and *trans* amines (judging from the melting point of the phenylthioureide derivative, 140–167°, and from the presence of relatively strong bands at 9.35, 10.27, and 13.19 μ in its spectrum).

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# Ring Closure of Ylidenemalononitriles

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*Contribution No. 1088 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana*

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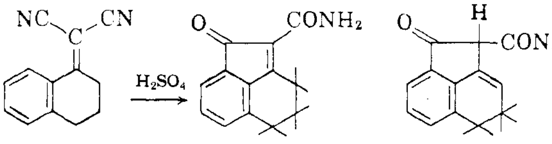
Ylidenemalononitriles are readily available by the reaction of aldehydes or ketones with malononitrile. Treatment of aromatic aldehyde derivatives in concentrated sulfuric acid, followed by quenching the reaction mixture over ice, results in hydrolysis of one nitrile group to produce α-cyanocinnamamides. Similar treatment of ketone derivatives may result in cyclization to form indenones and/or indanones. The rate of ring closure is increased by increase of size of group R in III. When R is incapable of prototropic rearrangement with the endocyclic double bond, as *t*-butyl or phenyl, only the indenones V are formed. When R carries a hydrogen on the α-carbon, mixtures of the endocyclic and exocyclic isomers V and VI may be obtained. Ring closures to produce three fused-ring systems are also possible, starting with two-ring ketones like α-tetralone. A series of cyclized compounds derived from III (R = H, $CH_3$, $C_2H_5$, *i*-$C_3H_7$, *t*-$C_4H_9$, $C_6H_5$) have been prepared, and the separation, identification, ultraviolet spectral characteristics, and certain reactions of derivatives V and VI are discussed.

The observation that sulfuric acid treatment of α-tetrylidenemalononitrile (I) led to a five-membered cyclized product[3] suggested further study of this facile ring closure to determine the scope and limitations of the reaction. The structure of the keto amide was reported as IIa,[3] but we have now established that the compound actually is 2-carbamoyl-3,4-trimethylene-1-indenone (IIb). I was prepared from α-tetralone using a method described by Mowry.[4] Although he named the product 1,2,3,4 - tetrahydro - 1 - naphthylidenemalonitrile, Mowry presented no evidence favoring either the structure having the exocyclic double bond I or the isomer having the endocyclic double bond, 1-dicyanomethyl-3,4-dihydronaphthalene.



I IIb IIa

Ring closure of *cis*-cinnamic acid derivatives are known[5] in Stobbe condensation products, but have not been reported with simple cinnamic acids or with arylidenemalonic acids or esters. Cyclization of aromatic derivatives of nitriles to form six-membered rings are known.[6,7] The present report deals with the formation of five-membered ring ketones.

A series of ylidenemalononitriles III was synthesized in which the group R in the β-position was H, $CH_3$, $C_2H_5$, *i*-$C_3H_7$, *t*-$C_4H_9$, or $C_6H_5$ (Table I). This series of α-cyano-β-substituted cinnamonitriles was designed to help prove the structure of I by a comparison of the ultraviolet absorption spectra and to shed light on two important aspects of the ring closure; one, the influence of the steric effect of bulky groups; and two, the possibility that prototropy, with concommitant rearrangement of the double bond so as to be exocyclic to the ring being formed, might play a role in ring formation. This latter possibility cannot be ruled out in previous reports of the ring closure of cinnamic acid derivatives.[5]

A comparison of the ultraviolet spectral data of the ylidenemalononitriles III served as a method of locating the double bond in I; that is, whether endo-or exocyclic to the six-membered ring. If the olefinic bond is in the endocyclic position, the chromophore should have a $\lambda_{max}$ value corresponding to a 1-substituted 3,4-dihydronaphthalene. An example is 1-methyl-3,4-dihydronaphthalene, which exhibits a $\lambda_{max}$ at 258 mμ ($\epsilon$ = 6,300).[8] If, however, the double bond is exocyclic, then the $\lambda_{max}$

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[1] Bristol Postdoctoral Fellow, 1960–1961.

[2] Taken in part from a thesis submitted to Indiana University in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1962, by D. M., Bristol Predoctoral Fellow, 1960–1962. This work was presented before the Organic Division at the 140th National Meeting of the American Chemical Society in Chicago, Ill., September, 1961.

[3] E. Campaigne and G. Bulbenko, *J. Org. Chem.*, **26**, 4703 (1961).

[4] D. T. Mowry, *J. Am. Chem. Soc.*, **67**, 1050 (1945).

[5] *Cf.* W. S. Johnson and G. H. Daub, "Organic Reactions," Vol. 4, John Wiley & Sons, Inc., New York, N. Y., 1951, p. 23.

[6] C. K. Bradsher, D. J. Beavers, and E. D. Little, *J. Am. Chem. Soc.*, **76**, 948 (1954); **78**, 2153 (1956).

[7] Donald R. Maulding, Ph.D. thesis, Indiana University, June, 1962.

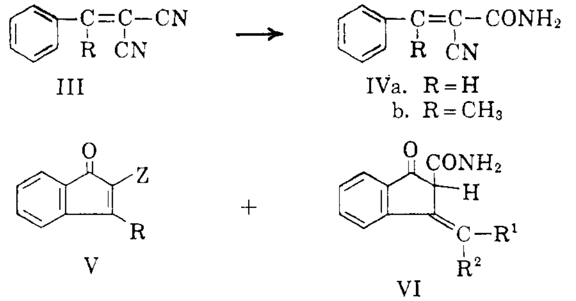
[8] M. P. Ramart and M. J. Hoch, *Bull. soc. chim. France*, **5**, 860 (1938).

Table I

Preparation and Properties of Ylidenemalononitriles

| Compound | Reaction time, hr. | Yield, % | M.p. | Molecular formula | % N Calcd., Found |
|---|---|---|---|---|---|
| I | 6 | 81 | 110–111 | $C_{13}H_{10}N_2$ | [a] |
| III (R = H) | 6 | 95 | 86.5–87 | $C_{10}H_6N_2$ | [b] |
| III (R = $CH_3$) | 6 | 61 | 93–94 | $C_{11}H_8N_2$ | [a,c] |
| III (R = $C_2H_5$) | 5 | 65 | 69–70 | $C_{12}H_{10}N_2$ | [d] |
| III (R = $i$-$C_3H_7$) | 6 | 93[e] | 60–62[f] | $C_{13}H_{12}N_2$ | 14.28, 14.38 |
| III (R = $t$-$C_4H_9$) | 12 | 88[e] | 114.5–115 | $C_{14}H_{14}N_2$ | 13.33, 13.18 |
| III (R = $C_6H_5$) | 48 | 68 | 140–141[g,c] | $C_{16}H_{10}N_2$ | 12.17, 12.09 |

[a] D. T. Mowry, *J. Am. Chem. Soc.*, **67**, 1050 (1945). [b] G. J. Ostling, *Chem. Zentr.*, I, 613 (1921). [c] D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, 4705 (1961). [d] Calcd.: C, 79.09; H, 5.53. Found: C, 78.93; H, 5.85. [e] Yields based on unrecovered ketone. [f] The product distilled at 120°/0.4 mm. [g] R. Schenck and H. Finken, *Ann.*, **462**, 267 (1928). A melting point of 136° was reported.


III

IVa. R = H
b. R = $CH_3$

V

VI

a) Z = $CONH_2$, R = $CH_3$
b) Z = $CONH_2$, R = $C_2H_5$
c) Z = $CONH_2$, R = $CH(CH_3)_2$
d) Z = CN, R = $C(CH_3)_3$
e) Z = CN, R = $C_6H_5$
f) Z = $CONH_2$, R = $C_6H_5$

a) $R^1$ = H, $R^2$ = H
b) $R^1$ = H, $R^2$ = $CH_3$
c) $R^1$ = $R^2$ = $CH_3$

should agree with that obtained for α-cyano-β-substituted cinnamonitriles, in the range 282–320 mμ (Table II). The $\lambda_{max}$ value of 313 mμ ($\epsilon$ = 13,300) for I clearly indicates that the double bond is exocyclic to the six-membered ring.

Table II

Ultraviolet Spectra of Ylidenemalononitriles[a]

| Compound | $\lambda_{max}$, mμ | $\epsilon$ | Other peaks | |
|---|---|---|---|---|
| I | 313 | 13,300 | 237 | 5,600 |
| | | | 231 | 5,800 |
| III (R = H) | 309 | 20,400 | 231 | 7,800 |
| | | | 224 | 8,300 |
| III (R = $CH_3$) | 292 | 12,800 | 232 | 7,600 |
| | | | 228 | 7,300 |
| III (R = $C_2H_5$) | 292 | 12,800 | 232 | 8,400 |
| | | | 229 | 8,200 |
| III (R = $i$-$C_3H_7$) | 283 | 5,400 | 232 | 10,900 |
| III (R = $t$-$C_4H_9$) | 282 | 614 | 236 | 20,200 |
| III (R = $C_6H_5$) | 320 | 1,900 | 227 | 14,400 |

[a] The ultraviolet absorption spectra were determined in 95% ethanol with either a Cary Model 14 or a Beckman Model DK-1 recording spectrophotometer.

The steric hindrance associated with the group in the β-position correlates with a systematic decrease in $\lambda_{max}$ and $\epsilon$ values for R = H to R = $t$-$C_4H_9$. Although the shift in wave length is only 1 mμ in comparing R = $i$-$C_3H_7$ with R = $t$-$C_4H_9$, the $\epsilon$ value is changed from 5400 to 614. The $\epsilon$ value of 614 for III (R = $t$-$C_4H_9$) indicates that the phenyl group and the double bond have been distorted so much by the considerable steric hindrance created by the tertiary butyl group, that they no longer are coplanar. The chromophore corresponding to the peaks in the region of 224–236 mμ becomes intensified as the size of the R group increases. Again, the greatest change in $\epsilon$ values is that from R = $i$-$C_3H_7$ (10,900) to R = $t$-$C_4H_9$ (20,200).

Treatment of the ylidenemalononitriles with concentrated acid did not give a cyclized product in every case. When a solution of benzylidenemalononitrile (III. R = H) in concentrated sulfuric acid was heated on a steam bath for ten minutes, then poured over ice, only α-cyanocinnamamide (IVa) was obtained.

When the dinitriles having a group larger than hydrogen in the β-position were treated with strong acid, ring closure did occur. For example, α-cyano-β-methylcinnamonitrile (III. R = $CH_3$) yielded a bicyclic product, 2-carbamoyl-3-methyl-1-indenone (Va) in low yield, as well as α-cyano-β-methylcinnamamide (IVb). The isomeric keto amide, 2-carbamoyl-3-methylene-1-indanone (VIa), was not isolated, although it probably was formed and subsequently polymerized, since much polymeric material was present after hydrolysis. It is possible to have *cis* and *trans* isomers of the cyano amide and both were isolated. The ratio of the isomers (m.p. 179–181° and 128–130°) depended upon the reaction conditions. While treatment of the lower melting isomer with alumina caused isomerization, thereby giving a mixture, silica gel produced no isomerization. The formation of the least hindered cyano amide would be expected from the condensation of acetophenone with cyanoacetamide. When this reaction was carried out, only the higher melting isomer was obtained, which suggests that the isomer melting at 179–181° is probably the one having the phenyl and amide groups *trans*.

Although the ring closure of III (R = $CH_3$) gave Va in only 12% yield, the yields of cyclized products from the other ylidenemalononitriles were much better. Treatment of α-cyano-β-ethylcinnamonitrile (III. R = $C_2H_5$) in sulfuric acid at 55° for two hours led to the formation of a mixture of two ketones in 72% yield. With silica gel, chromatographic separation of these ring-closed products, each having similar elemental analysis and infrared spectrum, afforded a low melting yellow isomer identified as 2-carbamoyl-3-ethyl-1-indenone (Vb) and a higher melting white isomer, 2-carbamoyl-3-ethylidene-1-indanone (VIb). Similarly, α-cyano-β-isopropylcinnamonitrile (III. R = $i$-$C_3H_7$) yielded the isomers, yellow 2-carbamoyl-3-isopropyl-1-indenone (Vc), and colorless 2-carbamoyl-3-isopropylidene-1-indanone (VIc).

The white products were readily soluble in dilute base, indicating the presence of an acidic hydrogen, while the yellow compounds dissolved in base only after heating. The colored products melted around 150°, solidified and melted again at the temperature corresponding to the melting point of the white isomers, disclosing the possibility of a tautomeric rearrangement. Solution of the yellow compounds in base, followed by acidification gave the white isomer, while the white indanone did not change when subjected to the same treatment. It is also interesting to note that dissolving the white compounds in concentrated sulfuric acid and pouring on ice gave mixtures of the *exo–endo* isomers. Finally, the yellow indenone Vb has $\lambda_{max}$ values at 249 and 244 mμ and the white indanone VIb has a single peak at 239 mμ, (See Table III) but a hypsochromic shift was observed ($\lambda_{max}$ 249 and 244 mμ going to $\lambda_{max}$ 236 mμ) when 10 ml. of an ethanol solution of 2-carbamoyl-3-ethyl-1-indenone ($6.5 \times 10^{-5}$ $M$) was treated with three drops of 10% sodium hydroxide ($[OH^-] = 3.8 \times 10^{-3}$). This shift to a lower wave length indicates the conversion of the yellow indenone to the conjugate base of the white isomer.

TABLE III

ULTRAVIOLET SPECTRA OF INDENONES AND INDANONES[a]

| Compound | $\lambda_{max}$ | $\epsilon$ | Other peaks | |
|---|---|---|---|---|
| IIb | 252 | 39,400 | [b] | |
| | 259 | 38,700 | | |
| Va | 247 | 41,600 | [b] | |
| | 252 | 40,900 | | |
| Vb | 244 | 36,300 | [b] | |
| | 249 | 35,300 | | |
| Vc | 247 | 36,300 | [b] | |
| | 252 | 34,100 | | |
| Vd | 244 | 35,000 | [b] | |
| Ve | 249 | 29,400 | 310 | 11,700 |
| | 254 | 29,700 | | |
| Vf | 248 | 37,200 | [b] | |
| VIb | 239 | 31,900 | [b] | |
| | | | 272 | 13,500 |
| | | | 262 | 16,200 |
| VIc | 242 | 34,400 | [b] | |
| | | | 278 | 16,300 |
| | | | 269 | 17,900 |

[a] The ultraviolet absorption spectra were determined in 95% ethanol with either a Cary Model 14 or a Beckman Model DK-1 recording spectrophotometer. [b] Indicates a very broad peak having a $\lambda_{max}$ between 340 and 310 mμ and an $\epsilon$ value less than 3000.

Ring closure of α-cyano-β-$t$-butylcinnamonitrile (III. R = $t$-$C_4H_9$) afforded only the yellow product, 2-cyano-3-$t$-butyl-1-indenone (Vd.). The lack of hydration of the nitrile to the amide can be attributed to the steric hindrance of the tertiary butyl group. Treatment of α-cyano-β-phenylcinnamonitrile (III. R = $C_6H_5$) in sulfuric acid for five to ten minutes yielded a yellow product, 2-cyano-3-phenyl-1-indenone (Ve), but when the reaction time was increased to twenty-four hours, a second deeper yellow product, 2-carbamoyl-3-phenyl-1-indenone (Vf) was obtained.

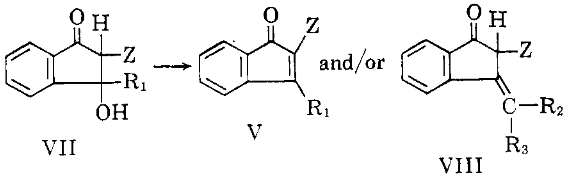
Table IV lists the yields in the ring closure of the ylidenemalononitriles. This table is helpful in drawing some conclusions concerning the effect produced by the steric hindrance of the β-substituent. These results suggest the steric hindrance has an effect on the initial rate of ring closure as evidenced by the increase in yields when a reaction time of ten to fifteen minutes is maintained. There seems to be no steric control on the formation of cyclized products, however, when the reaction time is extended to two hours, providing R is greater than methyl. The yields for R = $C_2H_5$, $i$-$C_3H_7$, $t$-$C_4H_9$ and $C_6H_5$ are about the same (72–80%).

TABLE IV

PRODUCTS FROM ACID TREATMENT OF α-CYANO-β-SUBSTITUTED CINNAMONITRILES

| III, R = | Reaction time, min. | Temp., °C. | Yield of IV, % | Total yield of cyclized product(s) V and/or VI % |
|---|---|---|---|---|
| H | 10–15 | 95 | 50 | 0 |
| $CH_3$ | 10–15 | 95 | 8 | 3 |
| $C_2H_5$ | 10–15 | 95 | 0 | 27 |
| $i$-$C_3H_7$ | 10–15 | 95 | 0 | 37 |
| $t$-$C_4H_9$ | 10–15 | 95 | 0 | 54 |
| $C_6H_5$ | 10–15 | 95 | 0 | 65 |
| H | 2 hr. | 50–55 | 55 | 0 |
| $CH_3$ | 2 hr. | 50–55 | 14 | 12 |
| $C_2H_5$ | 2 hr. | 50–55 | 0 | 72 |
| $i$-$C_3H_7$ | 2 hr. | 50–55 | 0 | 75 |
| $t$-$C_4H_9$ | 2 hr. | 50–55 | 0 | 75 |
| $C_6H_5$ | 2 hr. | 50–55 | 0 | 80 |

Further support for the proposed structures of the cyclized products may be found in the work reported by Frank, *et al.*,[9] and Koelsch.[10] Frank and co-workers[9] prepared some 2,3-disubstituted 1-indenones by a route synthetically different from ours. In their reaction sequence the final step was the dehydration of the tertiary alcohol VII (Z = $C_6H_5$) which Frank realized could conceivably lead to structures V or VIII. To establish the position of the double bond in 3-ethyl-2-phenyl-1-indenone, ozonolysis was performed and the product isolated



VII V VIII

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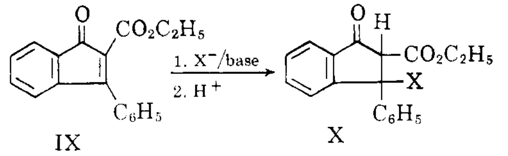
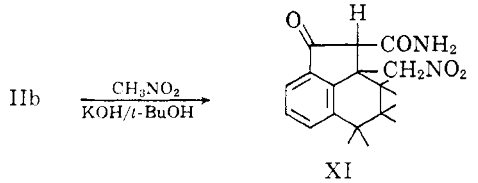
(9) R. L. Frank, H. Eklund, J. W. Richter, C. R. Vanneman, and A. N. Wennenberg, *J. Am. Chem. Soc.*, **66**, 1 (1944).

(10) C. F. Koelsch, *J. Org. Chem.*, **25**, 2088 (1960); **26**, 1003 (1961).

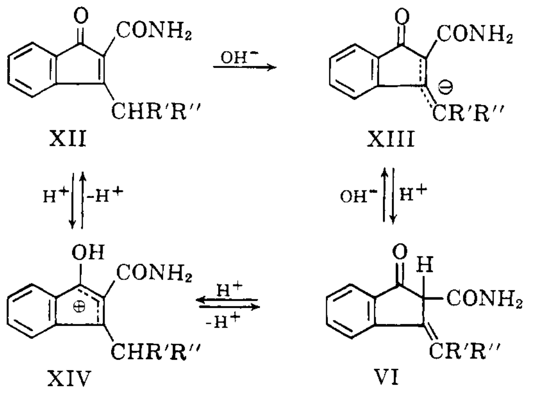
was *o*-propionylbenzoic acid, indicating the double bond was endocyclic to the five-membered ring and not exocyclic. It should also be noted that each of the eight indenones Frank prepared was colored and melted below 165°.

Koelsch[10] demonstrated that the 2,3-double bond in ethyl 3-phenyl-1-indenone-2-carboxylate (IX) was quite reactive to Michael addition in base by such nucleophilic reagents as aqueous cyanide, aqueous acetone, cyclohexanone, ethyl malonate, ethyl cyanoacetate, nitromethane and thioglycollate. In this system the double bond has to be endocyclic, since a phenyl group is in the 3-position. Similarly, we were able to demonstrate the electrophilic character of IIb by the addition of nitromethane, thus corroborating the assignment of the double bond endocyclic to the five-membered ring.





In addition to the evidence already presented, the ultraviolet spectra of the indenones and indanones (See Table III) support the assigned structures. The colored compounds have $\lambda_{max}$ values higher than the white, and each indenone, with two exceptions, has a characteristic doublet, which is separated by approximately 5 mμ. The width of the peaks of the two exceptions, Vd and Vf, is approximately 5 mμ, and it seems likely that a doublet is present, but the peaks are not distinct. The single peaks observed for the indanones are much sharper compared to those found for Vd and Vf. Thus a study of the ultraviolet spectra indicates the colored compounds IIb, Va, Vb, Vc, Vd, Ve, and Vf are indenones and the white products VIb and VIc are indanones. These data also favor IIb as the structure of the keto amide, previously reported[3] as IIa.



The series of reactions shown helps rationalize the behavior of our isomeric pairs in acid and base. The yellow indenone XII is slowly soluble in base, probably forming the resonance-stabilized carbanion, XIII. The white indanone VI could then be formed from the intermediate XIII by protonation. The indanone VI dissolves readily in base to form XIII, and is reprecipitated with acid. Protonation of VI in concentrated acid presumably gives the resonance-stabilized carbonium ion XIV, which is partially converted to XII by loss of a proton.

## Experimental

All melting points reported are corrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. All infrared spectra were recorded by a Perkin–Elmer Model 137 Infracord. The ultraviolet spectra were determined in 95% ethanol with either a Cary Model 14 or a Beckman Model DK-1 recording spectrophotometer. Molecular weights were determined in specified solvents on a Mechrolab Vapor Pressure Osmometer, Model 301A.

**Preparation of the Ylidenemalononitriles.**—The method described by Mowry[4] was used for the preparation of the ylidenemalononitriles. Using the suggestion made by Cope and co-workers[11] an additional amount of catalyst was used for the condensation of malononitrile with hindered ketones. The general procedure for the condensation of nonhindered carbonyl compounds with malononitrile used in these experiments is described in the following. For every 0.5 mole of carbonyl compound, 0.6 mole of malononitrile, 4 g. of anhydrous ammonium acetate, and 12 ml. of glacial acetic acid were used. Anhydrous benzene was added and the benzene solution was refluxed on a steam bath until the amount of water in the Dean-Stark water trap remained constant (4–12 hr.). For sterically hindered carbonyl compounds the reflux time was longer and two to eight times the required amount of catalyst was added. After refluxing, the benzene solution was washed with water and dried with sodium sulfate. Evaporation of the solvent yielded either a crystalline dinitrile or an oil. The latter was distilled at reduced pressure. The conditions and physical properties of the dinitriles are listed in Table I.

**Ring Closure of α-Tetrylidenemalononitrile (I) in Concentrated Sulfuric Acid.**—Using the procedure described by Campaigne and Bulbenko,[3] IIb was obtained in 77% yield.

**Attempted Cyclization of Benzylidenemalononitrile (III. R = H).**—Two grams of benzylidenemalononitrile was dissolved in 20 ml. of concentrated sulfuric acid and heated on a steam bath for 10 min. (until the solution turned bright red). The solution was cooled and poured into a beaker containing 200 g. of cracked ice. After 24 hr., the solid was collected by filtration and recrystallized from 95% ethanol. The yield of white crystalline α-cyanocinnamamide(IVa), m.p. 122–123° (lit.,[12] 123°) was 1.1 g. or 53%.

**Treatment of α-Cyano-β-methylcinnamonitrile (III. R = $CH_3$) with Concentrated Sulfuric Acid.**—Two grams of III (R = $CH_3$) was dissolved in 20 ml. of concentrated sulfuric acid and heated at 50–55° for 30 min. The red acid solution was poured over 200 g. of ice. Extraction with several portions of chloroform afforded a yellow oil, which was dissolved in benzene and put on a column packed with silica gel. The first fraction was obtained by elution with benzene–

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[11] A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenberg, *J. Am. Chem. Soc.*, **63**, 3452 (1944).

[12] J. N. E. Day and J. F. Thorpe, *J. Chem. Soc.*, **117**, 1473 (1920).

ethyl acetate. Recrystallization of the solid from benzene–petroleum ether produced 566 mg. (12%) of yellow needles of Va, m.p. 192–193°. The infrared spectrum showed peaks at 3553 (NH), 3257 (H-bonded NH), 1718 (CO) and 1681 cm.$^{-1}$ (amide CO). The ultraviolet spectrum contained two strong peaks at 247 m$\mu$ ($\epsilon$ = 41,600) and 252 m$\mu$ ($\epsilon$ = 40,900).

*Anal.* Calcd. for $C_{11}H_9NO_2$: C, 70.59; H, 4.82; N, 7.48. Found: C, 70.50; H, 5.02; N, 7.32.

The second chromatographic fraction was eluted with ethyl acetate. Recrystallization from benzene–hexane yielded 75 mg. of white crystals of the cyano amide IVb, m.p. 179–181°, and 500 mg. of a mixture of the *cis* and *trans* isomers of IVb. The mixture consisted predominately of the higher melting isomer. The infrared spectrum of each product contained peaks at 3505 (NH), 3275 (H-bonded NH), 2225 (CN) and 1655 cm.$^{-1}$ (amide CO). The mother liquors from recrystallization of the mixture from ethanol yielded a small amount of crystals melting at 128–130°.

*Anal.* Calcd. for $C_{11}H_{10}N_2O$: N, 15.04. Found: N, 15.02.

The chromatographic separation also gave 125 mg. of acetophenone.

**Isomerization of α-Cyano-β-methylcinnamonitrile (IVb).**—One hundred fifty milligrams of IVb (melting at 128–130°) was dissolved in a minimum amount of anhydrous benzene and put on a column of alumina. Elution with benzene gave 70 mg. of a mixture of the *cis* and *trans* isomers of IVb, m.p. 176–179°. Further elution with benzene–ethyl ether (4:1) yielded only the lower melting isomer, m.p. 128–130°.

**Condensation of Acetophenone with Cyanoacetamide.**—Refluxing 2.4 g. of acetophenone, 1.7 g. of cyanoacetamide, 0.5 g. of ammonium acetate and 2 g. of glacial acetic acid in 100 ml. of absolute ethanol for 6 hr. produced 1.6 g. of IVb (R = $CH_3$), m.p. 178–180°. The infrared spectrum showed peaks at 3505 (NH), 3275 (H-bonded NH), 2225 (CN) and 1655 cm.$^{-1}$ (amide CO). A mixed melting point with the higher melting product isolated above was undepressed.

*Anal.* Calcd. for $C_{11}H_{10}N_2O$: N, 15.04. Found: N, 15.02.

**Cyclization of α-Cyano-β-ethylcinnamonitrile (III. R = $C_2H_5$).**—Two grams of the dinitrile was dissolved in 20 ml. of concentrated sulfuric acid and heated at 50–55° for 2 hr., then poured over 200 g. of ice. The solid was collected, dried and dissolved in chloroform. Column chromatography using silica gel afforded 0.43 g. (20%) of Vb, m.p. 148–150° (solidified and melted again at 189–194°), upon elution with chloroform. The yellow solid showed peaks in the infrared 3480 (NH), 3220 (H-bonded NH), 1710 (CO) and 1640 cm.$^{-1}$ (amide CO) and exhibited $\lambda_{max}$ values 244 m$\mu$ ($\epsilon$ = 36,300) and 249 m$\mu$ ($\epsilon$ = 35,300).

*Anal.* Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51. Found: C, 71.80; H, 5.91.

Further elution with 2% methanol–chloroform gave 1.05 g. (52%) of colorless VIb, m.p. 199–200°; infrared, similar to Vb; $\lambda_{max}$ 239 m$\mu$ ($\epsilon$ = 31,900).

*Anal.* Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; mol. wt., 201. Found: C, 71.79; H, 5.77; mol. wt. ($CHCl_3$), 203.

The two isomers were also separated by making use of their difference in solubility in ethyl ether. Treating the crude product with ether dissolved all of Vb and very little of VIb. Crude extracts were then recrystallized from alcohol.

**Cyclization of α-Cyano-β-isopropylcinnamonitrile (III. R = i-$C_3H_7$).**—Two grams of the dinitrile was dissolved in 20 ml. of concentrated sulfuric acid and heated at 50–55° for 2 hr., then poured over 200 g. of ice. Using the same separation procedure as described for Vb and VIb, 0.49 g. (22%) of yellow Vc, m.p. 155–156° (solidified and melted again at 203–208°), was obtained after recrystallization from cyclohexane. The infrared spectrum contained peaks at 3500 (NH), 3240 (H-bonded NH), 1705 (CO) and 1640 cm.$^{-1}$ (amide CO), and the ultraviolet spectrum had a doublet at $\lambda_{max}$ 247 m$\mu$ ($\epsilon$ = 36,300) and 252 m$\mu$ ($\epsilon$ = 34,100).

*Anal.* Calcd. for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.05; N, 6.51. Found: C, 71.97; H, 6.55; N, 6.67.

The white isomer VIc, 1.06 g. (53%), m.p. 214–215°, had a similar infrared spectrum and also had a strong peak in the ultraviolet at 242 m$\mu$ ($\epsilon$ = 34,400).

*Anal.* Calcd. for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.05; mol. wt., 215. Found: C, 72.16; H, 6.10; mol. wt. ($CHCl_3$), 214.

**Ring Closure of α-Cyano-β-*t*-butylcinnamonitrile (III. R = *t*-$C_4H_9$).**—Two grams of III (R = *t*-$C_4H_9$) dissolved in 20 ml. of concentrated sulfuric acid was heated at 60° for 2 hr., the poured over 200 g. of ice. The red solid was collected, dried, and recrystallized from ethanol and gave 1.52 g. (75%) of yellow Vd, m.p. 197–198°; infrared, 2940 (aliphatic CH), 2250 (CN) and 1720 cm.$^{-1}$ (CO); ultraviolet, $\lambda_{max}$ 251 m$\mu$ ($\epsilon$ = 19,300).

*Anal.* Calcd. for $C_{14}H_{13}NO$: N, 6.63. Found: N, 6.55.

**Ring Closure of α-Cyano-β-phenylcinnamonitrile (III. R = $C_6H_5$).**—A. Five grams of the dinitrile was heated in 50 ml. of concentrated sulfuric acid for 5–10 min. on a steam bath. The red solution was poured over ice and a yellow solid precipitated. Recrystallization from 95% ethanol gave 4.1 g. (80%) of Ve, yellow crystals, m.p. 165–167°. Peaks at 2250 (CN) and 1724 cm.$^{-1}$ (CO) were present in the infrared. The ultraviolet spectrum had a doublet at $\lambda_{max}$ 249 m$\mu$ ($\epsilon$ = 29,400) and $\lambda_{max}$ 254 m$\mu$ ($\epsilon$ 29,700).

*Anal.* Calcd. for $C_{16}H_9NO$: C, 83.12; H, 3.90; N, 6.06. Found: C, 82.27; H, 4.10; N, 6.26.

B. Two grams of III (R = $C_6H_5$) was heated at 40° in 20 ml. of concentrated sulfuric acid for 24 hr., then poured over 200 g. of ice. Recrystallization of the crude product from ethanol gave 1.7 g. (84%) of yellow-orange crystals, Vf, m.p. 183–184°. The infrared showed peaks at 3500 (NH), 3240 (H-bonded NH), 1722 (CO) and 1650 cm.$^{-1}$ (amide CO). The ultraviolet spectrum had a $\lambda_{max}$ at 248 m$\mu$ ($\epsilon$ = 37,300).

*Anal.* Calcd. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.16; H, 4.56; N, 5.50.

**Addition of Nitromethane to 2-Carbamoyl-3,4-trimethylene-1-indenone (IIb).**—Using the method described by Koelsch,[10] 3 g. of IIb and 3 g. of nitromethane were dissolved in 40 ml. of *t*-butyl alcohol and treated dropwise with 10% potassium hydroxide. The solution was stirred at room temperature for 4 hr. Acidification with 20% sulfuric acid and dilution to 200 ml. gave 1.3 g. (42%) of XI, colorless crystals, m.p. 174–175°, after recrystallization from aqueous methanol.

*Anal.* Calcd. for $C_{14}H_{14}N_2O_4$: C, 61.29; H, 5.15, N, 10.21. Found: C, 61.55; H, 5.25; N, 10.18.

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