2-Methyl-8-phenyl-1,4-(2′-isopropylethano)-1,4-dihydropyrazolo[1,2-*a*]pyridazin-6-one (14).—From a mixture of 0.1 mole each of freshly distilled α-phellandrene (**1b**) and lead tetraacetate was obtained 24.3 g (82%) of crude solid (14). Recrystallization from cyclohexene yielded pure **14**, mp 176–178°.

Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.55; H, 7.48; N, 9.52. Found: C, 77.59; H, 7.50; N, 9.56.

An excess of α-phellandrene will cause the crude product to come out as an oil.

7,8-Diphenyl-1,4-methano-1,4-dihydropyrazolo[1,2-*a*]pyridazin-6-one (15).—From a mixture of 0.004 mole each of freshly distilled cyclopentadiene (**1c**) and lead tetraacetate was obtained 0.8 g (65%) of **15**. Recrystallization from cyclohexane gave pure **15**, mp 150–153° (lit.[15] mp 149–151°).

Attempted Reaction of Other Dienes with 3a.—In the reactions where **1a** was oxidized in the presence of anthracene, 1,3-cyclooctadiene, and *trans*-muconic acid no adduct was observed. The lead tetraacetate reacted with **1a** presumably for **3a** which decomposed without addition to the dienes. In each case a large fraction of the unreacted diene was recovered, no **1a** being isolated.

Reaction of Bicycloheptadiene with Lead Tetraacetate.—From a mixture of 0.1 mole each of freshly distilled bicycloheptadiene (**1a**) and lead tetraacetate was obtained 9 g (30%) of 2-*exo*-7-*syn*-norbornane-2,7-diacetate: bp 92–96° (0.5 mm); $n^{25}D$ 1.4700 (lit.[21] bp 96–98° (3.0 mm); $n^{20}D$ 1.4690). Some nonvolatile material could not be distilled. Ninety per cent of the unreacted **1a** was recovered. Concurrent addition of bicycloheptadiene and lead tetraacetate in a methylene chloride solution to **1a** was unsuccessful in causing preferential oxidations of **1a**.

3,3,6-Trimethyl-2-isobutenyl-2-hydropyrazolo[2,3-*b*]-1,3-oxazole (18).—From a mixture of 0.05 mole each of 2,5-dimethyl-2,4-hexadiene (**1a**) and lead tetraacetate was obtained 7.0 g (70%) of (**18**). Distillation at 49° (0.1 mm) gave **18**, $n^{30}D$ 1.4410, in an over-all yield of 63%.

Anal. Calcd for $C_{12}H_{18}N_2O$: C, 69.87; H, 8.80. Found: C, 69.98; H, 8.97.

Catalytic hydrogenation of 0.3 g of **18** over 5% platinum on charcoal led to the absorption of 2.3 equiv of hydrogen at 1 atm pressure and 33°. A 66% yield of **19** was obtained. The spectrum of the product was consistent with the above structure (*vide infra*).

8-Methyl-1,4-ethano-1,2,3,4-tetrahydropyrazolo[1,2-*a*]pyridazin-6-one (22).—To a slurry of 0.1 g of 5% platinum on carbon in 25 ml of 95% ethanol was added a solution of 3.0 g (0.017 mole) of **11** in 25 ml of 95% ethanol. The slurry was stirred under hydrogen at 1 atm and 23° for 20 hr. After uptake ceased at 410 ml, the catalyst was filtered and the solvent evaporated off to give 3.0 g (98%) of **22**. Sublimation at 70° (0.05 mm) yielded pure **22**, mp 61–62°.

Anal. Calcd for $C_{10}H_{14}N_2O$: N, 15.72. Found: N, 15.38.

8-Phenyl-1,4-methano-1,2,3,4-tetrahydropyrazolo[1,2-*a*]pyridazin-6-one (23).—To a slurry of 0.1 g of 5% palladium on carbon in 25 ml of benzene was added a solution of 5.0 g (0.022 mole) of **13** in 100 ml of benzene. The slurry was stirred under hydrogen at 1 atm and 25° for 20 hr. After uptake ceased at 527 ml, the catalyst was removed by filtration and the solvent evaporated to give 5.0 (98%) of **23**. Crystallization from benzene–cyclohexane gave 3.0 g (70%) of pure **23**, mp 148–149°.

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.34; H, 6.29; N, 12.39. Found: C, 74.05; H, 6.34; N, 12.19.

3,4-Diphenylpyrazolidin-5-one (24).—Ethyl α-phenylcinnamate was prepared by the method of Sudborough and Loyd.[28] A 50% yield was obtained after distillation: bp 70–75° (75 μ) (lit.[28] bp 163–165° (1 mm)). The ethyl α-phenylcinnamate was converted to **24** by the method of Carpino.[29] A 70% yield was obtained which may be crystallized from benzene to give a white solid (**24**), mp 136–137° (lit.[29] mp 139–141°).

Oxidation of 24 with Lead tetraacetate in the Presence of Cyclopentadiene.—The procedure of the previous oxidation was used herein and from a mixture of 0.009 mole each of freshly distilled cyclopentadiene (**24**) and lead tetraacetate was obtained 1.2 g of *trans*-stilbene, mp 125°. The infrared spectrum of the crude product obtained from the evaporation of the methylene chloride showed peaks for *trans*-stilbene.

Registry No.—**7**, 14181-54-5; **8**, 14181-55-6; **9**, 14181-56-7; **10**, 14264-76-7; **11**, 14264-77-8; **12**, 14264-78-9; **13**, 14181-57-8; **14**, 14271-47-7; **15**, 1162-74-9; **18**, 14181-59-0; **22**, 14319-53-0; **23**, 14181-60-3.

Acknowledgment.—The authors wish to acknowledge the assistance of the National Science Foundation in providing for departmental use a Cary 14 spectrophotometer, upon which the ultraviolet spectra contained herein were obtained.

(28) S. S. Sudborough and L. L. Loyd, *J. Chem. Soc.*, **73**, 81 (1898).
(29) L. A. Carpino, *J. Am. Chem. Soc.*, **80**, 601 (1958).

The Cyclization of Nitriles by Halogen Acids. II. A New Synthesis of Substituted 3H-Azepines

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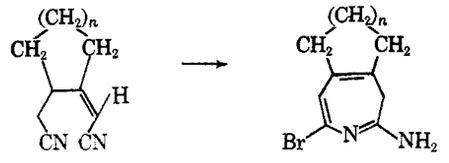
Received May 8, 1967

The treatment of 2-aryl- (or alkyl-) 1,4-dicyano-1-butenes (III) having *syn*-nitrile groups with hydrogen bromide in anhydrous media leads to 2-amino-5-aryl- (or alkyl-) 7-bromo-3H-azepines in good yield. However, a new attempt to obtain the corresponding azepine from *cis*-1,4-dicyano-1-butene was once again unsuccessful, despite the fact that 1,4-dicyano-2-methylbutene-1 did give the expected azepine derivative. The dinitriles required for the cyclization studies were synthesized by conventional methods and their stereochemistry was assigned by comparing their nmr spectra with those of suitable model compounds. The previous geometrical assignments of the *cis*- and *trans*-1,4-dicyano-1-butenes were found to be incorrect.

The synthesis of a series of azepine derivatives represented by II ($n = 1, 2, 3,$ or 4) was described in the preceding paper of this series.[1] These compounds



I II

were obtained by treating the corresponding dinitriles (I) with hydrogen bromide under anhydrous conditions, followed by neutralization of the initially formed hydrobromide salts. The success achieved in these cyclizations encouraged us to attempt the cyclization of some purely acyclic dinitriles despite the fact that neither adiponitrile, 2,5-diphenyladiponitrile, nor yet a mixture of *cis*- and *trans*-1,4-dicyano-1-butenes had led to azepine derivatives[2] under the conditions used for the preparation of II.

(1) W. A. Nasutavicus and F. Johnson, *J. Org. Chem.*, **32**, 2367 (1967).
(2) F. Johnson and W. A. Naustavicus, *J. Heterocyclic Chem.*, **2**, 26 (1965).

Apart from the *syn* relationship of the nitrile groups of I, other possible structural features required for cyclization of a dinitrile to an azepine were unknown. It seemed possible that the failure of 1,4-dicyanobutene-1 to provide the desired product upon treatment with hydrogen bromide was due to fast irreversible addition of the acid to the double bond. On this basis the most logical step seemed to be to depress the reactivity of the double bond to the point where cyclization would take complete precedence over addition. The simplest way of accomplishing this appeared to be to locate an aryl group at the β position of the unsaturated nitrile. To this end several such nitriles were synthesized and their stereochemistry was determined.

Synthesis and Stereochemistry of the Dinitriles.—The first two nitriles chosen (IIIa and IIIb) were synthesized according to eq 1. Addition of hydrogen

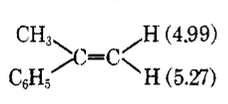
$$CH_2{=}CHCOAr \longrightarrow \underset{\text{IV}}{NCCH_2CH_2COAr} \longrightarrow NCCH_2CH_2C(Ar){=}CHCN \quad (1)$$

IIIa, Ar = C_6H_5
b, Ar = p-$C_6H_4C_6H_5$

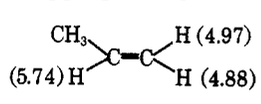
cyanide to the aryl vinyl ketone[3] followed by treatment of the cyano ketone IV with the sodium salt of diethyl cyanomethylphosphonate[4] gave in each case a good yield of a single crystalline product. The stereochemistry of both of these compounds was assigned on the basis of nmr spectral evidence using the method of substituent additivity effects on ethylenic protons.[5,6]

The nmr spectrum of IIIa shows a sharp singlet vinyl proton resonance[7] at 5.64 ppm and a single sharp phenyl proton resonance at 7.45 ppm. The $-CH_2CH_2-$ hydrogens absorb as two approximate triplets (with further splitting) at ~3.25 and ~2.51 ppm.

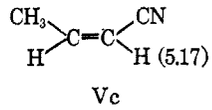
The simplest method of approximating the expected positions for the vinyl protons of the *cis* and *trans* forms (with reference in this and other cases to the CN and cyanoalkyl groups) of IIIa is to treat the molecules as cyano-substituted α-alkylstyrenes, making the assumption that $-CH_2CH_2CN$ will have approximately the same effect as CH_3 or a small alkyl group. Suitable models for this calculation are shown and the the resonance positions of the appropriate protons are



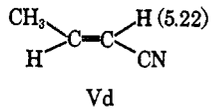
Va



Vb

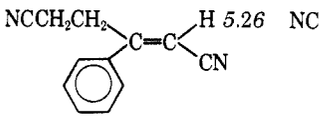


Vc

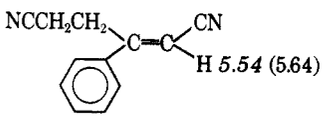


Vd

given in parentheses.[8] By comparing Vc with Vb we see that introduction of the cyano group into the propene backbone shifts the resonance position of the proton geminal to the cyano group *downfield* 0.29 ppm. Comparison of Vd with Vb yields a similar value of 0.25 ppm for this same geminal cyano effect. Presuming that introduction of a cyano group into the double bond in α-methylstyrene (or α-2-cyanomethylstyrene) would cause a similar geminal proton resonance shift, the vinyl proton in *trans* IIIa would be predicted to absorb at 5.26 ppm (4.99 + 0.27 ppm), as shown in italics. Similarly, the vinyl proton in *cis*



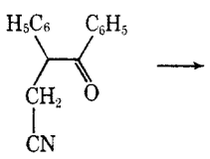
trans IIIa



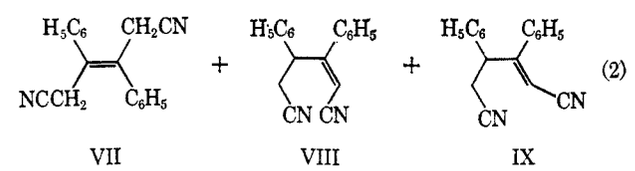
cis IIIa

IIIa is predicted to absorb at 5.54 ppm (5.27 + 0.27 ppm). Since the observed vinyl proton resonance for IIIa (5.64 ppm) is in close agreement only with this latter value, we assign IIIa the *cis* structure. By analogy, IIIb is assigned the same stereochemistry since its vinyl proton also absorbs at 5.64 ppm.

The third nitrile chosen was 1,4-dicyano-2,3-diphenylbutene-1. For the preparation of this material, we followed the pathway used for III. Addition of hydrogen cyanide to 2-phenylacrylophenone[9] proceeded in good yield to give VI. However, treatment of VI with sodium diethyl cyanomethylphosphonate did not lead to a single product. Crystallization of the resulting oil gave a small quantity of a high melting material (mp 215–217°) having the correct elemental analysis for the expected product, while chromatography of the residue led to two additional isomers of mp 109–110° (41% yield) and 85° (15% yield). The high melting material was assigned the completely symmetrical structure VII since its nmr spectrum shows a very simple pattern having aromatic proton absorption at 7.2–7.5 ppm and a CH_2 band at 3.36 ppm, which integrated in the ratio of 10:4. In addition, its infrared spectrum shows only a very weak absorption at 6.24 μ for the double-bond stretching vibration, in accord with the proposed *trans* geometry of the molecule. Further chemical evidence for this assignment is given in the subsequent section.



VI



(2)

VII VIII IX

The geometries of VIII and IX were assigned by nmr, taking advantage of the similarity of these compounds to IIIa. Since to a good approximation the chemical shielding effects of $-CH_3$, $-CH_2CH_2CN$, and $-CH(C_6H_5)(CH_2CN)$ on nearby vinyl protons may be taken to be the same, the vinyl proton resonance po-

(3) C. F. H. Allen, M. R. Bilbert, and D. M. Young, *J. Org. Chem.*, **2**, 227 (1937).

(4) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(5) B. S. Reddy and J. H. Goldstein, *ibid.*, **83**, 2045 (1961).

(6) C. Pascual, J. Maier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(7) Measured downfield relative to TMS (internal), in 10% w/v in deuteriochloroform.

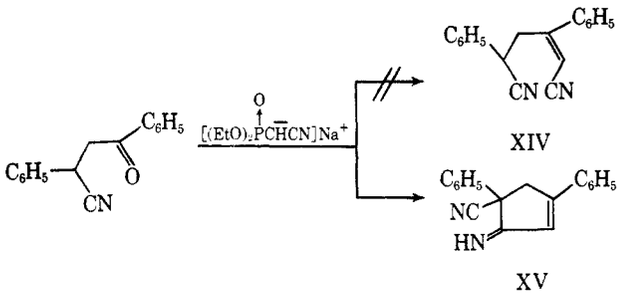
(8) We thank A. W. Douglas of The Chemical Physics Laboratory, The Dow Chemical Co., Midland, Mich., for the data on α-methylstyrene. The values for the other three compounds were taken from ref 5.

(9) H. Fiesselmann and J. Ribka, *Chem. Ber.*, **89**, 27 (1956).

sition for VIII can be predicted to be about the same as for *cis* IIIa, namely 5.54 ppm. Similarly, the vinyl proton resonance for IX is predicted to be approximately the same as that for *trans* IIIa, *i.e.*, 5.26 ppm. Of the two isomers under consideration, the higher melting compound (VIII) shows vinyl proton absorption at 5.54 ppm and the lower melting material (IX) absorbs at 5.33 ppm, in good agreement with the predicted values.

An attempt was made to synthesize the dinitrile XIV from 3-benzoyl-2-phenylpropionitrile[10] using the procedure given in Scheme I. Under all conditions tried

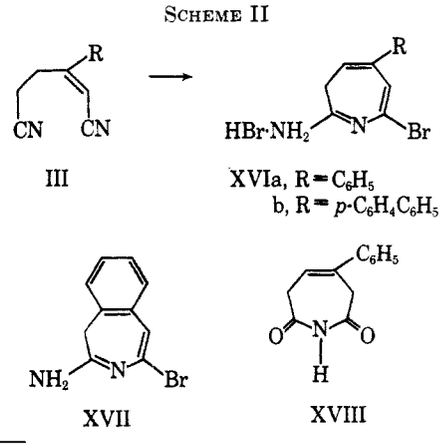
SCHEME I



the only product obtained was the iminonitrile XV. The reaction undoubtedly proceeds through XIV, but the acidity of the benzylic hydrogen of this substance would lead to proton exchange with the phosphonate anion. Such exchange, followed by a Ziegler–Thorpe condensation, would give XV. The structure XV is assigned on the basis of its infrared spectrum which shows bands at 4.43 (–CN) and 3.08 μ (imine) and its nmr spectrum which shows the methylene protons as two coupled unsymmetrical doublets at 3.42 and 3.92 ppm (J = 19 cps), a pattern which is due to the magnetic nonequivalence of these hydrogens. These peaks, in addition, are coupled with the vinyl proton at 6.77 ppm ($J \sim 1.5$ ppm). Phenyl hydrogen absorption occurs at 7.4 and 7.5 ppm.

Cyclization of the Dinitriles.—Treatment of IIIa with hydrogen bromide in methylene chloride–ether led to a tan crystalline product (67% yield). Recrystallization afforded the colorless azepine hydrobromide (XVIa) (Scheme II). The structure of the compound is in little doubt as its nmr spectrum (Figure 1A) shows bands which integrate correctly and are highly characteristic of this system. The coupled doublet at 3.40 and triplet centered at 5.97 ppm (J = 7 cps) represent the protons in the group $-CH_2CH=$, whereas the singlet at 6.89 ppm is due to the $-CH=CBr-$ proton. The remaining peak at 7.37 ppm is due to the aromatic protons of the phenyl ring. Evidence that the double-bond tautomer represented by XVIa is correct comes from a comparison of the infrared spectrum of the free base (easily obtained by neutralization with mild alkali) of XVIa with that of XVII.[11] The NH_2 absorption patterns in the 3-μ region are all but identical for the two compounds. In addition both spectra also contain the very intense band in the region of 12.6–13.3 μ which appears to be characteristic of this particular azepine system.[1,2] Further proof of the cyclic nature of XVIa comes from its conversion to the cyclic imide XVIII when heated with aqueous dimethylformamide. The nmr spectrum of this compound is in agreement with structure XVIII. It shows a doublet (CH_2) at 3.56 ppm coupled ($J \sim 6.5$ cps) with a triplet at 6.13 ppm (vinyl hydrogen). The second CH_2 and phenyl protons absorb as singlets at 3.87 and 7.35 ppm, respectively, whereas the imide proton displays a broad peak at 8.25 ppm.

SCHEME II



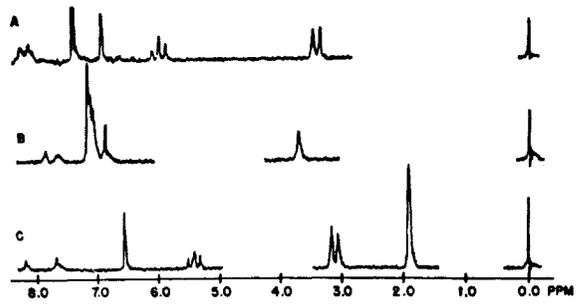
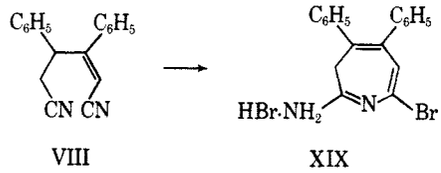


Figure 1.—Nmr spectra of (A) XVIa, (B) XIX, and (C) XXI.

Returning to the cyclization of the dinitriles, the reaction of IIIb with hydrogen bromide gave better results than were obtained with IIIa. Here the product XVIb formed in 90% yield and neutralization afforded the free base in 83% yield. Both of these compounds were too insoluble for solution spectral studies and their structures were assigned by analogy with XVIa.

Cyclization of VIII proceeded in a similar manner and yielded XIX in 80% yield (eq 3). Subsequent neutralization gave its free base in 83% yield. The



(3)

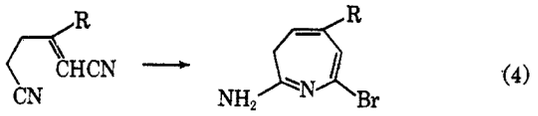
structure XIX is assigned on the basis of its nmr spectrum (Figure 1B) and the infrared spectrum of its free base, which was again very similar to that of XVII. Of great interest was the fact that neither of the other isomeric dinitriles (VII or IX) led to a cyclic product when treated with dry hydrogen bromide. In fact only starting material was obtained from either reaction, after work-up in the usual fashion. This

(10) A. C. O. Hamm and A. Lapworth, *J. Chem. Soc.*, **85**, 1358 (1904); A. Lapworth and E. Wechsler, *ibid.*, **97**, 41 (1910).

(11) The structure of XVII has been proved rigorously as reported in an earlier paper.[2]

finding adds weight to the stereochemical assignments made to the three isomeric dinitriles VII, VIII, and IX. In addition, it seems to set a limit on the versatility of the cyclization, confining it to compounds in which the nitriles are *syn* oriented and perhaps to those *anti* related dinitriles whose double bond may undergo a fairly easy isomerization under the reaction conditions.

Encouraged by the cyclizations accomplished thus far, a mixture of the *cis* and *trans* isomers of 1,4-dicyano-2-methyl-1-butenes (XX, R = CH_3) obtained from the condensation of sodium diethyl cyanomethylphosphonate with levulinonitrile[12] was treated with dry hydrogen bromide. After the normal isolation procedure, including neutralization of the acid salt, a 30% yield of the desired azepine compound XXI (R = CH_3) was obtained (eq 4). Its structure was



(4)

XX XXI

again assigned on the basis of the usual nmr (Figure 1C) and infrared spectral data. It cannot be stated with certainty but a good case could be made for the supposition that only the *cis* isomer in XX (R = CH_3) gives rise to XXI (R = CH_3). Integration of the methyl hydrogen doublet absorptions in the nmr spectrum of XX (R = CH_3) at 1.98 ($J \sim 1.5$ cps) and 2.08 ppm ($J \sim 1.2$ cps) showed the former to be present to the extent of 30% and, if this is the *cis* isomer of XX (R = CH_3), it might account for the low yield of XXI (R = CH_3).

Since the cyclization of XX (R = CH_3) proved successful, it seemed strange that a mixture of the *cis* and *trans* isomers of 1,4-dicyano-1-butenes (XX, R = H) had not given any of the parent azepine (XXI, R = H) under these reaction conditions.[2] Repetition of the experiment under a variety of conditions gave no better result. The *cis* and *trans* isomers were separated, therefore, by fractional distillation and each was individually subjected to the cyclization procedure. Again none of the desired product (XXI, R = H) could be obtained in either case and experiments in this direction have been abandoned.

One last point is worth noting and this concerns the geometry of the isomers of XX (R = H). The *cis* and *trans* structures were assigned[13] originally to the high and low boiling forms, respectively. However, the infrared spectrum of the former contains a strong absorption at 10.3–10.5 μ, whereas the latter has a strong peak at 13.3–13.5 μ and none in the 10.4-μ region. These characteristics are consistent only with the opposite assignments [14] given above and the higher boiling isomer must now be regarded as the *trans* and the low boiling as the *cis* isomer. This is now consistent with the boiling point relationship expected for such pairs of isomers.

Further reactions of the azepines described in this paper are under investigation and will be reported in a separate publication.

(12) Obtained from the Aldrich Chemical Co.

(13) G. F. Hager, U. S. Patent 2,451,386 (Oct. 12, 1948).

(14) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 34.

Experimental Section

Nmr spectra were recorded using a Varian A-56/60 instrument downfield relative to TMS. Where not stated, deuteriochloroform was the solvent. All infrared spectra were obtained in Nujol mull on a Baird spectrophotometer, model N°4-55. Melting points were determined on a Fisher-Johns melting point block and are not corrected.

***cis*-1,4-Dicyano-2-phenylbutene-1 (IIIa).**—A cooled solution of sodium hydride (3 g), diethyl cyanomethylphosphonate (20 g), and 1,2-dimethoxyethane (75 ml) was added dropwise to a cooled, dry solution of 3-benzoylpropionitrile (14 g) in the same solvent (50 ml). The mixture was allowed to warm to room temperature, stirred for 4 hr, then cautiously quenched by addition of water (500 ml). The total liquid was extracted with three 150-ml portions of ether. This ether extract was washed with a little water, and dried over anhydrous magnesium sulfate, then evaporated to dryness. The residual material was crystallized from methylene chloride–ethyl ether and afforded IIIa as a colorless crystalline solid (8.5 g): mp 65–66°; yield, 53%. Its infrared spectrum shows bands at 4.43, 4.47, 6.20, 7.02, 7.69, 8.22, 9.28, 9.80, 11.35, 11.88, 13.10, and 14.44 μ.

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.1; H, 5.5; N, 15.4. Found: C, 79.3; H, 5.5; N, 15.3.

***cis*-1,4-Dicyano-2-(*p*-biphenylyl)butene-1 (IIIb)** was prepared by precisely the same method as was used for IIIa (*vide supra*). In this instance, sodium hydride (1.2 g), diethyl cyanomethylphosphonate (8.35 g), and *p*-biphenylyl 3-cyanoethyl ketone (6.5 g) were used together with the proportionate amount of solvent. The product was crystallized from methylene chloride–ether and gave IIIb as colorless crystals (4.6 g): mp 112°; yield, 64%. Its infrared spectrum showed absorptions at 4.49, 6.22, 7.10, 9.95, 12.06, 12.22, 13.01, 13.70, and 14.35 μ.

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.7; H, 5.5; N, 10.9. Found: C, 83.6; H, 5.6; N, 10.7.

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3-Benzoyl-3-phenylpropionitrile (VI).—To 2-phenyl-acrylophenone (35 g) in ethanol (200 ml) there was added solid potassium cyanide (13.2 g). Hydrochloric acid was added dropwise until the pH of the solution dropped to about 8.0. The mixture was stirred for 3 hr and poured into a large excess of water; the product was isolated by ether extraction. Crystallization of the crude substance from ether–petroleum ether (bp 30–60°) then afforded pure VI (26 g), mp 84–85°. Its infrared spectrum showed bands at 4.42 (CN) and 5.94 μ (C=O).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.7; H, 5.6; N, 5.9. Found: C, 82.1; H, 5.8; N, 5.6.

Condensation of VI with Sodium Diethyl Cyanomethylphosphonate.—Sodium hydride (1.10 g) was stirred with diethyl cyanomethylphosphonate (8.5 g) in 1,2-dimethoxyethane (50 ml) for 1 hr. This was then added dropwise to a solution of VI (9 g) in the same solvent (50 ml). After standing for 2.5 hr, the reaction mixture was processed as for IIIa above. The crude syrup deposited a small amount of a highly crystalline solid (1.0 g) when triturated with ether. This was recrystallized from methylene chloride–ether and afforded pure VII as needles, mp 215–217°. Its infrared spectrum showed bands at 4.43, 6.24 (w), 6.70, 6.92, 7.10, 7.90, 9.29, 10.44, 10.92, 12.72, 13.00, 14.02, and 14.17 μ. Its ultraviolet spectrum in ethanol had λ_{max} 231 mμ (ϵ 13,670).

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.7; H, 5.5; N, 10.9. Found: C, 83.8; H, 5.6; N, 10.7.

The mother liquors from the isolation of VI were taken to dryness under reduced pressure. The residue was dissolved in methylene chloride–petroleum ether and chromatographed over silica gel (100 g). Elution with the same solvent pair (800 ml) afforded a colorless solid which, when crystallized from ether, gave VIII as white prisms (4 g), mp 109–110°. Its infrared spectrum had absorption at 4.41, 4.48, 5.92 (s), 6.26, 6.34, 6.70, 7.05, 7.50, 7.83, 7.95, 8.32, 10.23, 10.58, 12.03, 13.05, 13.23, 13.53, 13.95, 14.36–14.53, and 15.34 μ.

Anal. Found: C, 84.1; H, 5.6; N, 10.6.

Further elution of the above column with methylene chloride afforded a mixture (1.5 g) of the dinitriles VIII and IX. This was rechromatographed over fresh silica gel (100 g) exactly as before. The early fractions eluted by methylene chloride–petroleum ether gave small amounts of VIII, while later fractions, using only methylene chloride as the eluent, yielded rela-

tively pure IX. These were combined and crystallized from methylene chloride–ether to give pure IX (1.3 g) as white prisms, mp 85°. Its infrared spectrum had bands at 4.43, 4.48, 6.17 (w), 6.69, 7.01, 7.35, 9.29, 9.71, 10.70, 12.11, 12.60, 12.79, 13.10, 13.52, and 14.40 μ.

Anal. Found: C, 84.0; H, 5.5; N, 10.6.

5-Cyano-3,5-diphenyl-2-cyclopentenimine-1 (XV).—Following the procedure used for IIIa, an attempt was made to condense the sodium salt of diethyl cyanomethylphosphonate (from 1.4 g of NaH and 12 g of diethyl cyanomethylphosphonate) with 3-benzoyl-2-phenylpropionitrile (11.8 g). Ether extraction afforded a solid which was recrystallized twice from ethyl acetate to give the crude cyclic imine XV. Two further crystallizations from methylene chloride–petroleum ether afforded the pure material, mp 146–148° (softening at 143°). Its infrared spectrum showed bands at 3.07, 4.43, 6.13, 6.24, 10.63, 10.98, 13.05–13.25, 14.20, 14.43, and 14.66 μ.

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.7; H, 5.5; N, 10.9. Found: C, 83.6; H, 5.5; N, 11.2.

1,4-Dicyano-2-methylbutene-1. (Mixture of *cis* and *trans* Forms) (XX, R = CH_3).—Levulinic nitrile (12.6 g) was added dropwise to a solution prepared from sodium (3.1 g), diethyl cyanomethylphosphonate (25 g), and 1,2-dimethoxyethane (75 ml). After 2 additional hr of stirring, the reaction mixture was worked up in the usual way. The resulting crude oil (19 g) was distilled under reduced pressure. The fraction (11 g) boiling at 90° (58 mm) was collected and since it still appeared to contain starting material (infrared evidence) it was dissolved in a 1:1 mixture of methylene chloride and petroleum ether and then chromatographed over silica gel. Elution with the same solvent mixture (300 ml) gave fractions containing starting material, but subsequent elution with methylene chloride alone (2:1) gave only the desired product (6 g) as a colorless liquid, $n^{25}D$ 1.4745. Its infrared spectrum showed bands at 4.43, 4.49, 6.12, 6.85–7.05, 7.24, 9.38, 11.85–12.65, and 13.12 μ.

Anal. Calcd for $C_7H_8N_2$: C, 70.0; H, 6.7; N, 23.3. Found: C, 70.1; H, 7.0; N, 23.0.

2-Amino-7-bromo-5-phenyl-3H-azepine Hydrobromide (XVIa) and Its Free Base.—The dinitrile IIIa (5.5 g) was dissolved in a mixture of methylene chloride (20 ml) and ether (200 ml) and purged at ~0° for 1.5 hr with a stream of anhydrous hydrogen bromide. The volatile materials were removed *in vacuo* and the resulting solid was triturated with ether to give crude product. The latter was twice recrystallized from methanol–acetone–ethyl ether to give pure XIVa (7.0 g), mp 210–230° dec. Its infrared spectrum showed bands at 3.0–3.7, 6.01, 6.37, 8.34, 8.75, 13.22, and 14.34 μ.

Anal. Calcd for $C_{12}H_{12}Br_2N_2$: C, 41.9; H, 3.5; Br, 46.5; N, 8.1. Found: C, 41.9; H, 3.4; Br, 46.3; N, 8.1.

The free base of this salt (and the others mentioned below) was obtained by dissolving a specimen of XIVa (3.4 g) in dimethylformamide followed by pouring the solution into saturated sodium bicarbonate solution. The precipitated solid was removed by filtration, washed with water, and then dried and recrystallized from methylene chloride to give 2-amino-7-bromo-5-phenyl-3H-azepine (2.7 g) as white needles, mp 173–175° dec. The infrared spectrum had bands at 2.89, 3.04, 3.19, 6.10, 6.40, 6.54, 7.69, 8.33, 9.80, 10.26, 11.20, 11.33, 12.04, 12.17, 13.00–13.50, and 14.38 μ.

Anal. Calcd for $C_{12}H_{11}BrN_2$: C, 54.8; H, 4.2; Br, 30.4; N, 10.6. Found: C, 54.8; H, 4.0; Br, 30.5; N, 10.5.

2-Amino-7-bromo-5-(*p*-biphenylyl)-3H-azepine Hydrobromide (XVIb) and Its Free Base.—Using exactly the same method as above, IIIb (2.6 g) was cyclized with hydrogen bromide. The product (3.8 g) was obtained pure in 90% yield simply by triturating the residue, after removal of the volatiles, with ether. It had mp 245–250° dec and its infrared showed absorption at 3.04–3.60, 6.02, 12.24, 13.00, 13.65, and 13.90–14.55 μ (w).

Anal. Calcd for $C_{18}H_{16}Br_2N_2$: C, 51.5; H, 3.8; Br, 38.0; N, 6.7. Found: C, 51.2; H, 3.8; Br, 37.9; N, 6.8.

Its free base was obtained in 83% yield, mp 195–200° dec, and had bands in the infrared spectrum at 2.88, 3.03, 3.20, 6.10, 6.42, 6.55, 7.64, 7.70, 8.36, 9.78, 11.20, 11.34, 11.84, 12.33, 13.03, 13.76, and 14.40 μ.

Anal. Calcd for $C_{18}H_{15}BrN_2$: C, 63.7; H, 4.5; Br, 23.6. Found: C, 63.8; H, 4.8; Br, 23.5.

2-Amino-7-bromo-4,5-diphenyl-3H-azepine Hydrobromide (XIX) and Its Free Base.—A sample (1.3 g) of the dinitrile VIII in methylene chloride (50 ml) was cyclized with hydrogen bromide as described for IIIa above. The product XIX was obtained in 80% yield (1.7 g) and had, after crystallization from methanol, mp 275 dec. Its infrared spectrum showed bands at 3.10–3.60, 6.00, 6.24, 6.44, 8.31, 8.64, 9.72, 10.99, 11.54, 12.31, 12.92, 13.11, and 14.10–14.75 μ.

Anal. Calcd for $C_{18}H_{16}Br_2N_2$: C, 51.5; H, 3.8; Br, 38.0; N, 6.7. Found: C, 51.6; H, 3.8; Br, 38.0; N, 6.7.

2-Amino-7-bromo-4,5-diphenyl-3H-azepine obtained in 83% yield had mp 212–215° dec and showed bands in the infrared spectrum at 2.90, 3.05, 3.19, 6.14, 6.43, 6.10, 7.23, 8.32, 9.79, 11.07, 11.42, 11.95, 12.48, 13.10, and 14.35 μ.

Anal. Calcd for $C_{18}H_{15}BrN_2$: C, 63.7; H, 4.5; Br, 23.6; N, 8.3. Found: C, 63.4; H, 4.3; Br, 23.4; N, 8.2.

2-Amino-7-bromo-5-methyl-3H-azepine (XXI, R = CH_3).—A sample (1.2 g) of dinitrile XX (R = CH_3) was dissolved in dry ether (150 ml) and hydrogen bromide gas was passed through the resulting solution for 20 min. The mixture was kept at ~0° for 1 hr more and the volatile materials were then removed under reduced pressure. The pale yellow syrup was dissolved in methanol and poured into saturated sodium bicarbonate solution. The resulting solid (0.6 g) was removed by filtration, dried, and recrystallized from ethanol to give pure XXI (R = CH_3) as shiny platelets, mp 160–165° dec. Its infrared spectrum showed peaks at 2.91, 3.03, 3.20, 6.06, 6.40, 6.48, 6.56, 7.71, 8.25, 11.30, and 12.55–12.90 μ.

Anal. Calcd for $C_7H_9BrN_2$: C, 41.8; H, 4.5; Br, 39.7; N, 13.9. Found: C, 41.7; H, 4.3; Br, 39.7; N, 13.8.

4-Phenyl-2,7-dioxo-2,3,6,7-tetrahydro-1H-azepine (XVIII).—A specimen of XVIa (1.0 g) was heated with dimethylformamide (5 ml) and water (10 ml) on a steam bath for 2.5 hr. The reaction mixture was cooled and the solid product filtered off and dried. This solid (0.42 g, 76% yield) was recrystallized once from tetrahydrofuran–petroleum ether to provide pure XVIII as platelets, mp 157–158°. The infrared spectrum showed bands at 3.10, 3.22, 5.86, and 5.97 μ characteristic of the imide function.

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.6; H, 5.5; N, 6.9.

Registry No.—IIIa (*cis*), 13970-28-0; IIIb (*cis*), 13866-35-8; VI, 13866-36-9; VII, 13970-29-1; VIII, 13866-37-0; IX, 13866-38-1; XV, 13866-39-2; XVIa, 13866-40-5; XVIa, free base, 13866-41-6; XVIb, 13866-42-7; XVIb, free base, 13866-43-8; XVIII, 13866-44-9; XIX, 13866-45-0; XIX, free base, 13866-46-1; XX, R = Me (*cis*), 13866-47-2; XX, R = Me (*trans*), 13866-48-3; XXI, R = Me, 13866-49-4.

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