SOME BASE-CATALYZED CONDENSATIONS OF SYSTEMS OF THE FORM $R_1R_2C{=}C(CN)_2$

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ABSTRACT

We have investigated the condensations of the systems $\phi CH_3C{=}C(CN)_2$, $\phi HC{=}C(CN)_2$, and $CH_3HC{=}C(CN)_2$ in the presence of organic bases. Proton nuclear magnetic resonance (n.m.r.) spectral evidence is presented in support of the suggested structures of the condensation products, and an attempt has been made to present diagrammatically the interrelation between these condensations and other known reaction pathways for condensations of this type.

INTRODUCTION

The reactive nature of methylenemalononitrile systems of the type $R_1R_2C{=}C(CN)_2$ in the presence of base has been known for some time (1, 2). In particular the tendency of such compounds to undergo condensations and dimerizations in the presence of base has been the subject of several recent investigations (3–7). The general mechanism of the base-catalyzed dimerizations of several alkylidenemalononitriles of the type $R_1R_2C{=}C(CN)_2$ has been described previously (6). We have now extended this study to some other methylenemalononitriles whose behavior under the basic reaction conditions appears to be somewhat more complex. Table I represents an attempt to show the interrelationships between the different reaction pathways, which we believe to be possible under various basic reaction conditions, leading to both carbocyclic and heterocyclic products.

Path A (Table I). Cyclodimerization of Alkylidenemalononitriles in the Presence of Organic Bases

When both R_1 and R_2 are alkyl groups, the critical first step is base abstraction of a proton from one of these groups. This is followed by attack of the anion so formed on a second monomer molecule, and then ring closure (4, 6). The same pathway is followed when $R_1 = \phi$ and $R_2 = CH_3$, the base abstracting a proton from the CH_3 group in the initial step.

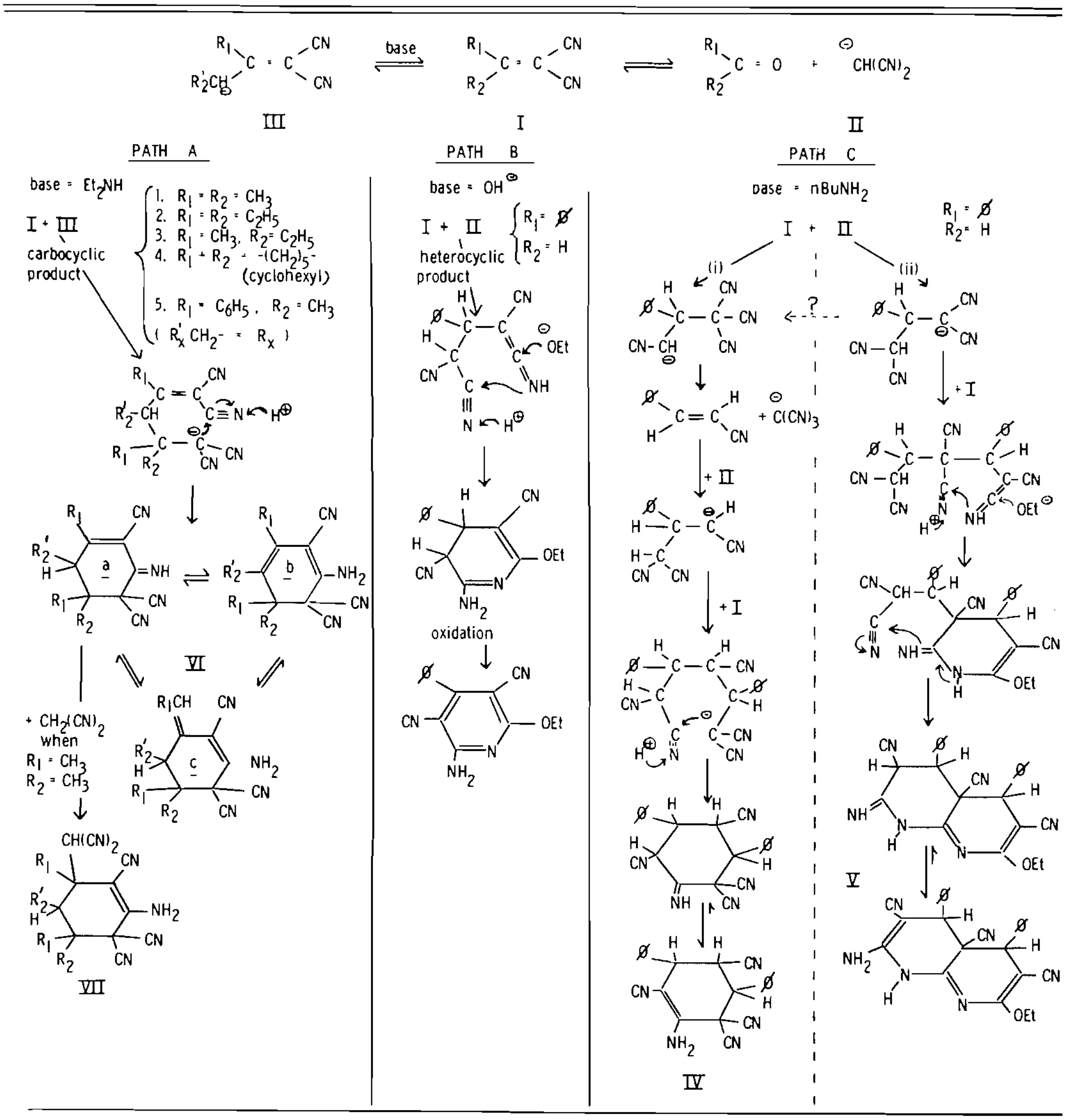
Path B (Table I). Condensation of Benzalmalononitrile in Ethanolic Potassium Hydroxide Solution

The formation of substituted pyridines by the action of ethanolic potassium hydroxide solution on benzalmalononitrile has been reported previously (7). The reaction was shown to proceed via a reverse aldol cleavage of the diene to benzaldehyde and malononitrile anion, followed by attack on the β-carbon atom of a second diene molecule by the $^{(-)}CH(CN)_2$ anion, and subsequent ring closure.

Path C (Table I). Condensation of Benzalmalononitrile in the Presence of Organic Bases

In contrast to its behavior in ethanolic potassium hydroxide solution benzalmalononitrile appears to undergo more complex condensations in the presence of *n*-butyl amine in aqueous ethanol. The initial step here again seems to be cleavage to benzaldehyde, or the corresponding anil with the organic base, and malononitrile anion, followed by attack of the latter on a molecule of monomer. In this case, however, there is further

TABLE I



incorporation of a second monomer molecule into the products. Also, under conditions which are as nearly identical as possible, *two* products of m.p.'s 210–213 °C, IV, and 155–158 °C, V, are obtained, IV being produced in some cases and V in others. Suggested structures for these products and possible pathways leading to them are outlined in Table I.

It may be noted that pathways A and B represent mechanistically the two simplest modes of condensation available to the alkylidene- and arylidene-malononitrile systems respectively. Thus, if the β-carbon carries a group (e.g. $C_2H_5CH_3C{=}C(CN)_2$) from which a proton may be readily extracted by base, then this abstraction is in fact the first step: if the system (e.g. $\phi HC{=}C(CN)_2$) does not contain such a group, then the condensation is forced to proceed via attack on the β-carbon by a $^{(-)}CH(CN)_2$ anion, i.e., via a Michael condensation.

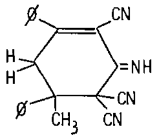
Special Case (Table II). Condensation of Ethylidenemalononitrile in the Presence of Organic Bases

Although ethylidenemalononitrile might have been expected to follow path A and give the dimeric product VI on treatment with base, we found no evidence for this material being formed. The spectral data strongly suggested that the product isolated was in fact VIII (although in the absence of solvent a second condensation product was also formed—see structure proof section).

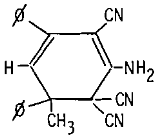
STRUCTURE PROOFS

1. β-Methylbenzalmalononitrile Dimer

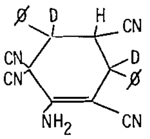
Of the compounds listed as reacting according to path A, the condensation products of 1–4 have been discussed (4, 6). β-Methylbenzalmalononitrile, (III, 5), appears to undergo dimerization in the presence of base by a similar pathway (Table I, Path A) leading to compound IX (special case of VI*a*). This reaction has been studied previously by Anderson, Bell, and Duncan (3) who isolated the bright-yellow crystalline dimer from the condensation of acetophenone and malononitrile in the presence of base. They reported its infrared spectrum and noted that it "did not agree with the expected 4-amino-1,1,5-tricyano-2,6-diphenylhepta-1,3,5 triene" (3), but they did not suggest an alternative structure. The n.m.r. spectrum (Fig. 1.1) of the dimer is consistent with the cyclic imino structure shown, IX. The AB quartet at 6.8 τ rules out the possibility of the previously proposed (3) triene structure $\phi(CH_3)C{=}C(CN){-}C(NH_2){=}CH{-}C(\phi){=}C(CN)_2$, and its tautomer $\phi(CH_3)C{=}C(CN){-}C({=}NH){-}CH_2{-}C(\phi){=}C(CN)_2$. The CH_2 group in the latter would be expected to give rise to a singlet signal rather than to an AB quartet. The large coupling constant (17 c.p.s.) of this quartet is similar to that noted by Calvin and co-workers (8) for the geminal coupling in the cyclic system XIII when the conformation of the molecule was fixed by cooling to −65 °C. The amino form of the cyclic dimer, X, is also inconsistent with the observed spectrum, since it again would not give rise to an AB quartet. The position of the CH_3 signal at 8.2 τ seemed somewhat low for a CH_3 on a saturated carbon. However, comparison of the two systems $CH_3CH{=}C(CN)_2$ and $\phi(CH_3)C{=}C(CN)_2$ indicated that the presence of a phenyl group on the carbon carrying the CH_3 significantly lowered the position of the CH_3 signal, the one in ethylidenemalononitrile appearing at 7.9 τ and that in β-methylbenzylmalononitrile at 7.5 τ.



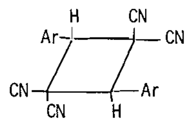
IX



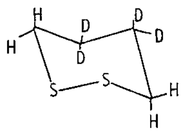
X



XI



XII



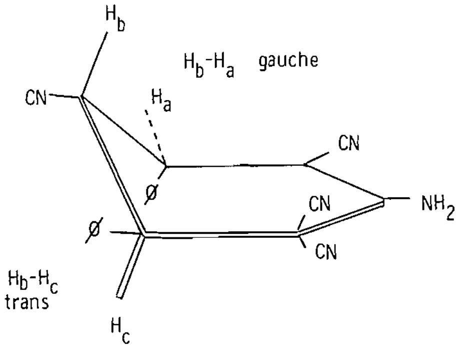
XIII

Apart from the apparently exclusive formation of the imino form here the dimerization of β-methylbenzalmalononitrile fits the pattern recently described (4, 6) for several alkylidenemalononitriles where both R_1 and R_2 are alkyl groups. In the present case the imino structure is presumably favored over the amino since straight conjugation from the phenyl group through to the imino group is possible only in the former, IX, the amino form, X, involving a cross-conjugated system. Also an examination of molecular models indicates that the ring strain in the cyclic amino form with two endocyclic double bonds is greater than that in the imino form in which one double bond is outside of the ring.

2. Products from Benzalmalononitrile

Benzalmalononitrile, on treatment with *n*-butyl amine in ethanolic solution gave two crystalline products, of m.p.'s 210–213 °C and 155–158 °C respectively.

A. The structure which seems to best fit the n.m.r., infrared, and analytical data on the 210–213° compound is IV, Table I. The outstanding structural feature in the n.m.r. spectrum (Fig. 1.2) of this material is the partially split AB quartet with the superimposed split singlet centered around 5.8 τ. We have interpreted this as an ABC system (9), in which the A and B hydrogens are involved in mutual splitting while the C hydrogen is not split by A. Such a system is present in the structure proposed, hydrogens A and B being on adjacent carbons and the angle between the two C—H bonds being about 60°, while hydrogens B and C, also on adjacent carbons, are *trans* to each other, and the C—H bonds are at approximately 180°. (See diagram of model.) Consideration of the Karplus curve (10, 11, 12) indicates that the expected coupling constants for such a system would be small in the case of the A and B hydrogens and large for the B and C hydrogens: the observed J values are in fact as follows: $J_{AB} = 2$ c.p.s.; $J_{BC} = 13$ c.p.s.; $J_{AC} = 0$ c.p.s.



Projection drawing IV

The other compelling piece of evidence in favor of this structure was obtained from deuterium-labelling experiments. When benzalmalononitrile was replaced by $C_6H_5CD{=}C(CN)_2$ as starting material in the base-catalyzed condensation the 210–213° compound which was isolated had only 1 singlet at 5.1 τ (Fig. 1.2*b*) in the n.m.r., instead of the quartet with superimposed singlet. The rest of the spectrum was unchanged. This would fit the proposed structure if both carbons carrying phenyl groups were deuterated, the structure being XI: the 5.1 τ peak now lies *between* the two peaks in the quartet assigned to hydrogen B. On the other hand, if the reaction were run with unlabelled benzalmalononitrile but in C_2H_5OD as solvent we should expect to see two singlets (those due to hydrogens A and C) remaining in the quartet region of the spectrum. These in fact appear (Fig. 1.2*a*) at 5.5 τ (the position of the split singlet due to hydrogen A (Fig. 1.2)) and at 5.9 τ (between the two peaks in the AB quartet assigned to hydrogen C in Fig. 1.2). The nonexchangeability of the benzylic hydrogen of benzalmalononitrile under basic conditions was checked (see experimental section).

A possible mechanistic pathway leading to this product is outlined in Table I, Path C (i). Here, instead of the "normal" Michael addition of malononitrile to benzalmalononitrile, we suggest that an "abnormal" Michael addition (13) takes place, involving the intramolecular shift of a CN group; the system then undergoes a reverse Michael reaction to give cinnamonitrile plus $^{(-)}C(CN)_3$. Such rearrangement retrogression products are not unknown in the literature (14, 15). The subsequent steps in the mechanism, addition of a malononitrile anion, and then of a second molecule of benzalmalononitrile and final ring closure, are indicated in Table I. The compound appears to contain one molecule of ethanol of crystallization, readily removed by heating under vacuum to 90°, or by heating at atmospheric pressure to 160°. Ethanol, or methanol, of crystallization could be reintroduced into the compound by crystallization of the de-ethanolated material from the appropriate solvent. The n.m.r. spectra of the ethanolate and of the de-ethanolated material were identical, except for the signals due to ethanol. Alkaline permanganate oxidation of IV gave benzoic acid in a yield which suggested the presence of two phenyl groups per molecule. Hydrolysis of IV in 30% sulfuric acid gave a ketone.

B. Consideration of the analytical and spectral data have lead us to suggest V as a likely structure for the 155–158° compound. The infrared spectrum of the material shows C═C, C═N, N—H and a strong conjugated CN band. The n.m.r. spectrum includes two single peaks at 5.2 τ and 5.4 τ, each of area 1 (the hydrogens on the carbons carrying phenyl groups), a signal at 3.6 τ of area 1.8 (the amino hydrogens), and a signal at 1.5 τ of area 0.8 (the hydrogen on the ring nitrogen), as well as the phenyl and the ethanolic CH_3CH_2 hydrogen signals (Fig. 1.3). The mechanism is outlined in Table I, Path C (ii). Hydrolysis of V in 30% aqueous sulfuric acid gave a ketone. Oxidation of the 155–158° compound with alkaline permanganate solution, or with dichromate, gave benzoic acid in a yield which suggested that each molecule of starting material contained two phenyl groups.

As isolated from the reaction medium this material contains one molecule of ethanol of crystallization, in addition to the bonded EtO, removable by heating under vacuum to 90° for several hours. This ethanol is reincorporated into the molecule by recrystallization of the de-ethanolated material from 95% ethanol (or it may be replaced by methanol by a similar procedure). The n.m.r. spectra of the ethanolate and the de-ethanolated material are identical, except for the signals due to ethanol. Both of these products from the condensation of benzalmalononitrile using *n*-butyl amine as catalyst, appear to be quite different from the cyclobutane dimers of the type XII, described recently by Patai and Rappoport (16), who stated that these can be produced by treatment of alkylidenemalononitriles with malononitrile under conditions similar to those used in some of the experiments here. The cyclobutane dimer of benzalmalononitrile was readily prepared by irradiation of the solid monomer for a few days with a sun lamp according to the method of Baker and Howes (17), but we were not able to produce this compound in solution media, either by using malononitrile, or malononitrile plus base, as catalyst. However, as Patai and Rappoport also state (16), these condensations are extremely sensitive to experimental conditions, so that even when the procedures given in the experimental part are followed closely the results are irreproducible. In many cases we isolated only tars or starting materials.

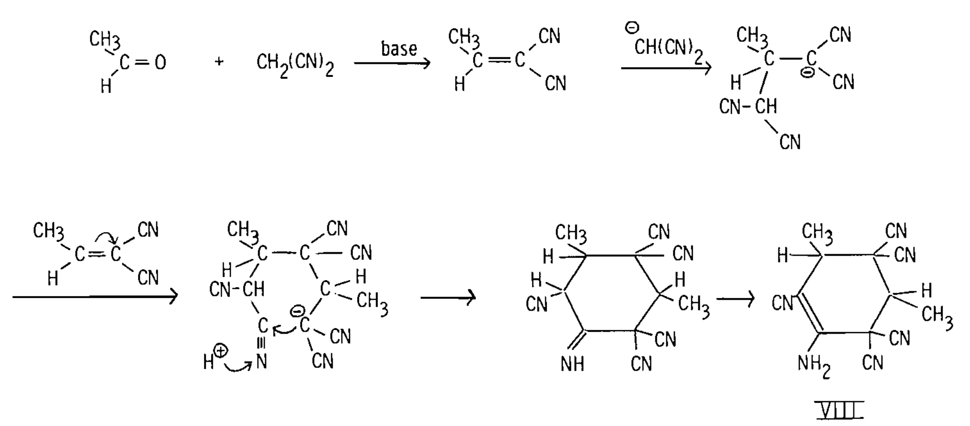
3. *Products from Ethylidenemalononitrile*

The extreme sensitivity of ethylidenemalononitrile to base is evident from the special precautions (20, 21) necessary in the preparation of the pure liquid. Contact with even the small amounts of alkali present in Pyrex glassware is sufficient to cause the liquid monomer to condense to a pale-yellow solid over a period of 1 or 2 days at room temperature. To determine whether this condensation of ethylidenemalononitrile followed the general pattern recently described (4, 6) for the base-catalyzed condensation of alkylidenemalononitriles (Table I, Path A), we have now investigated the reaction under more controlled conditions in dilute solution, in the presence of added base. By analogy to the base-catalyzed dimerization of isopropylidenemalononitrile (4) ethylidenemalononitrile might have been expected to form the dimeric product VI. Also by analogy to the isopropylidene system (4) the other expected product here would have been of type VII, formed by 1,4 addition of malononitrile to the imino form of the dimer (VI) (see Table I).

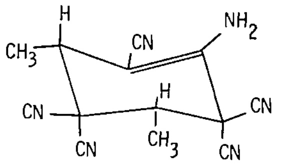
However, all of the spectral and analytical evidence we have obtained strongly suggests that the product isolated from the treatment of ethylidenemalononitrile with base in solution, or from acetaldehyde plus malononitrile (the precursors of ethylidenemalononitrile) and base in solution, was in fact VIII. Furthermore, this material (15) was not the same as the yellow solid formed by the action of base on the pure liquid ethylidenemalononitrile.

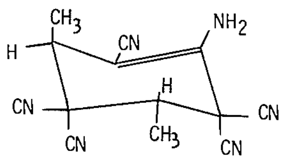
The reaction mechanism leading to VIII is outlined in Table II, and the n.m.r. spectrum is given in Fig. 1.4.

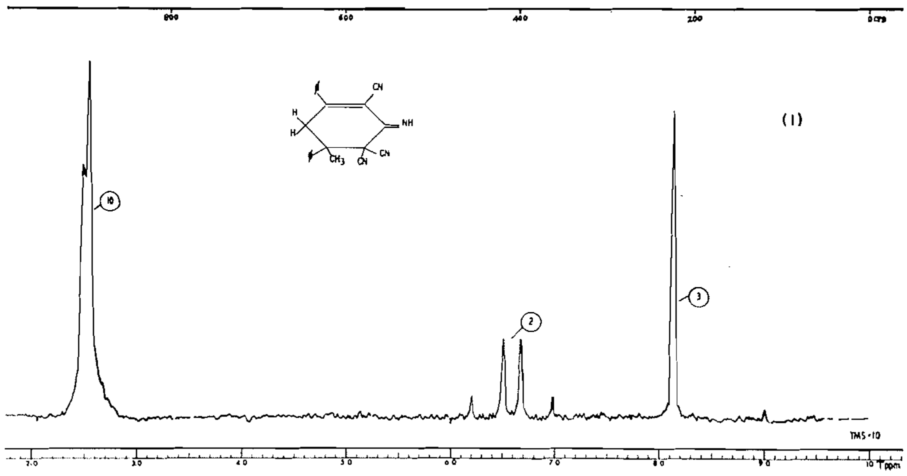
TABLE II



The area of the methyl doublets around 8.4 τ is in agreement with structure VIII and clearly indicates that the material is neither the simple dimer nor the dimer plus, malononitrile which might have been predicted by analogy to the isopropylidenemalononitrile system (4). Both the n.m.r. and the infrared spectra suggest that VIII is present almost exclusively in the amino form. Thus the infrared spectrum has a strong conjugated CN absorption which could not be accommodated in the imino structure; likewise the NH_2 signal of area 2 in the n.m.r. spectrum at 3.9 τ favors the amino form. The two sets of doublets centered around 8.4 τ and the overlapping quartets at 6.8 τ suggest that the compound exists as a mixture of two conformers.






800
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CN
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(1)
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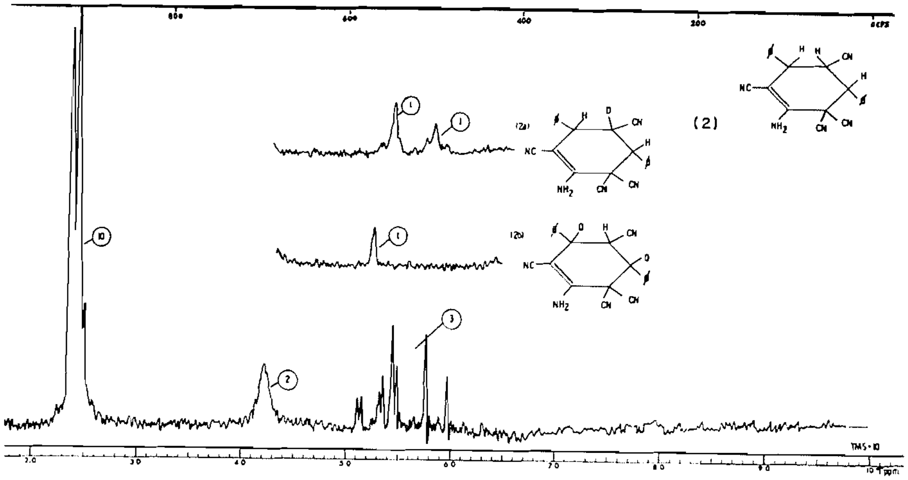
10 τ ppm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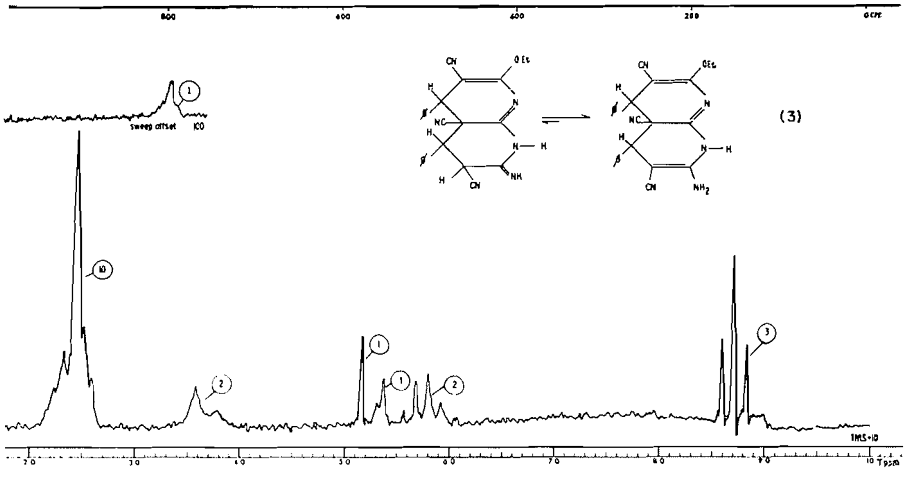
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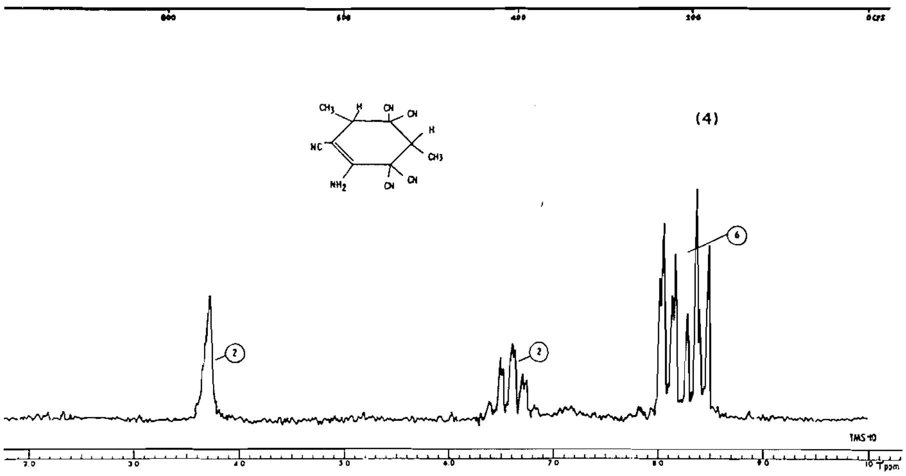

FIG. 1. (i) The spectra were run in the following solvents: (1) and (2) in acetonitrile and in benzonitrile; (3) in acetone and in benzonitrile; (4) in acetonitrile. All solutions approximately 10%. (ii) Relative peak areas are shown in the circled numbers. (iii) Tetramethylsilane internal standard.

The tendency of ethylidenemalononitrile to undergo condensation via attack on the β-carbon by a malononitrile anion in contrast to the pathway involving abstraction of a proton from a methyl in $(CH_3)_2C{=}C(CN)_2$ is possibly best explained on the basis of the inductive effects of the two methyl groups which reduce the effective polarization of the molecule and hence the net positive charge on the β-carbon, thereby making it less susceptible to attack by a malononitrile anion. Replacement of one of the CH_3 groups by a proton appears to diminish this effect sufficiently to favor condensation via initial attack on the β-carbon.

The other material isolated, the yellow solid formed by the action of base on liquid ethylidenemalononitrile, appears from the elemental analysis to be a simple polymer without any additional malononitrile incorporated into the structure. The infrared spectrum indicated that it did not contain any NH or conjugated CN. The n.m.r. spectrum showed two doublets around 8 τ and two shattered quartets between 6.5 and 7.5 τ. However, the low solubility of the material made good spectral determinations difficult. It seems possible that the yellow solid might be a mixture of cyclobutane dimers of the kind XII recently described by Patai and Rappoport (16) as being formed from systems of the type $ArCH{=}C(CN)_2$. However, molecular weight determinations were conflicting and failed to give clear evidence in favor of a dimeric structure.

General Remarks

Attempted base-catalyzed condensations of β-ethylbenzalmalononitrile, β-phenylbenzalmalononitrile, and β-naphthylmethylenemalononitrile, as well as of several ring-substituted benzalmalononitriles, have in our hands yielded only tarry products so far. It would appear that base-catalyzed condensations of arylmethylenemalononitriles are much more sensitive to reaction conditions than are those of the alkylidenemalononitriles studied here (with the exception of ethylidenemalononitrile). As we have already indicated, these condensations are not always reproducible even when the experimental procedures are followed closely. Also, when, as in the case of the arylmethylenemalononitriles, the first step in the reaction involves a Michael addition, in contrast to abstraction of a proton from an alkyl group as in the alkylidenemalononitrile cases, the number of subsequent mechanistic pathways available to the system is greatly increased; hence the greater variety of products obtained from benzalmalononitrile under basic conditions.

EXPERIMENTAL

Preparation of β-Methylbenzalmalononitrile (18)

Acetophenone (60 g, 0.50 mole) and malononitrile (33 g, 0.50 mole) were added to 4 g (0.057 mole) of ammonium acetate plus 12 ml of glacial acetic acid in 200 ml of benzene. The mixture was heated to reflux with stirring and the water evolved was collected in a Dean-Stark trap. Refluxing overnight produced 14 ml of water. The benzene was then removed under vacuum leaving a yellow solid, which was crystallized from 50% ethanol. The product was obtained in the form of pale-yellow prisms of m.p. 93–94°. (Lit. (18) 94 °C.) Yield 75 g, 90%.

Preparation of Ethylidenemalononitrile

Two recent patent references (19, 20) are available for the preparation of this material. We found, however, that the following method worked for the preparation of the quantities we required.

Malononitrile (3.3 g, 0.05 mole) and acetaldehyde (3.0 g, 0.07 mole) were dissolved in 50 ml of benzene, and a few drops of diethylamine were added. The solution was left at room temperature for 2 h, and then washed with dilute hydrochloric acid and water, and dried over "Drierite". Removal of the solvent gave a clear liquid, which was vacuum distilled from glassware previously well washed with dilute hydrochloric acid. $n_D^{20} = 1.4571$; infrared (smear) 3.2, 3.3, 4.4, 6.2, 6.95, 7.25, 7.50, 8.35, 9.20, 9.50, 10.20, 11.50, in μ; n.m.r. in CCl_4, doublet, relative area 3, centered on 7.75 τ, quartet, relative area 1, centered on 2.25 τ.

Base-catalyzed Condensation of β-Methylbenzalmalononitrile

β-Methylbenzalmalononitrile (4 g) was dissolved in 95% ethanol with slight warming, and a few drops of diethylamine added. On standing overnight a solid was deposited from the mixture. On crystallization from ethanol this gave 2.9 g of bright-yellow needles of m.p. 206–207 °C. (Yield 72%.)

Anal. Calcd. for $C_{22}N_{10}N_4$: C, 78.57; H, 4.76; N, 16.65; molecular weight, 336. Found: C, 78.42; H, 5.02; N, 16.50; molecular weight, 330.

The main infrared peaks (in KBr) are 2.92, 4.43, 6.23, 6.32 (shoulder), 6.45, 6.70, 6.90, 7.00, 7.95, 13.10, 13.50, 14.40, in μ. λ_{max} values in the ultraviolet: 324 mμ and 250 mμ. This compound may also be prepared from acetophenone and malononitrile plus base by the method of Anderson, Bell, and Duncan (3).

Base-catalyzed Condensation of Benzalmalononitrile

Benzalmalononitrile (1 g, 0.0065 mole) was dissolved in 50 ml of 95% ethanol, and 0.2 g (0.0033 mole) of malononitrile added. The flask was then swept with nitrogen, and 0.4 g (0.0055 mole) of *n*-butylamine was added. After stirring in a stream of nitrogen gas for about 24 h the solid product was collected, washed with 95% ethanol, and recrystallized from ethanol. This reaction was not reproducible, an intractable tar being the only product on many occasions. Also the crystalline product formed was sometimes the material of m.p. 155–158 °C, and sometimes that of m.p. 210–213 °C. Average yields were 0.10 g for the 210–213° compound, and 0.1–0.2 g for the 155–158° material. The difficulty of drying the samples thoroughly without removal of some of the ethanol of crystallization complicated the analyses in both the 210–213° and the 155–158° compounds.

210–213° Melting Compound

Analyses: (a) ethanolate.—Calcd. for $C_{24}H_{19}N_5O$: C, 73.40; H, 4.84; N, 17.80; molecular weight, 393. Found: C, 73.25; H, 5.26; N, 17.52; molecular weight, 406.

(b) De-ethanolated sample.—Calcd. for $C_{22}H_{13}N_5$: C, 76.02; H, 3.75; N, 20.06. Found: C, 76.08; H, 3.69; N, 19.63.

Main bands in the infrared spectrum of the de-ethanolated compound (KBr): 2.80, 2.89, 3.00, 3.20, 3.24 (weak), 4.50, 6.08, 6.20 μ. There was also a broad absorption between 13.7 and 14.4 with peaks at 13.72, 13.99, and 14.32, in μ.

Permanganate Oxidation of Solid, M.P. 210–213°

The material (0.1 g) was refluxed overnight in a mixture of 0.3 g of potassium permanganate, 1 small pellet of sodium hydroxide, and 10 ml of water. After cooling, the mixture was acidified with dilute sulfuric acid and refluxed for a further 30 min. The manganese dioxide was then taken up with sodium bisulfite, and the aqueous solution cooled and extracted with ether; 0.05 g of benzoic acid was obtained from the ether extracts; m.p. 121–122 °C, mixed melting point with an authentic sample of benzoic acid, 122–124 °C.

Hydrolysis of Solid, M.P. 210–213°

The solid (0.1 g) was heated with 20 ml of 30% aqueous sulfuric acid overnight. The resulting white powder was washed with distilled water till free from acid and dried. Attempted recrystallization led to discoloration. A strong ketone absorption was now present in the infrared spectrum, whose main peaks (KBr) were at 3.35, 5.68, 6.69, 6.82, 13.73 (shoulder at 13.9), and 14.28 μ.

155–158° Melting Compound

Analyses: (a) ethanolate.—Calcd. for $C_{27}H_{26}N_6O_2$: C, 69.50; H, 5.58; N, 18.00; molecular weight, 466. Found: C, 69.81; H, 5.54; N, 18.54; molecular weight, 419.

(b) De-ethanolated sample.—Calcd. for $C_{25}H_{20}N_6O$: C, 71.50; H, 4.76; N, 20.00. Found: C, 71.18; H, 4.79; N, 20.13.

Main absorptions in the infrared spectrum of de-ethanolated compound (KBr): 2.90 (shoulder at 2.80 and 3.00), 3.30–3.40 (weak), 4.50, 6.10, 6.25 (shoulders at 6.00 and 6.32), 6.70, 6.90, 14.00, and 14.30 (shoulders at 3.76), in μ. The permanaganate oxidation and the sulfuric acid hydrolysis were carried out in the same manner as for the other compound described above. The main infrared peaks (KBr) in the hydrolysis product were at 2.90 (shoulder at 2.85), 3.20–3.40 (broad and weak), 4.50, 5.70, 6.15, 6.25, 7.73, 6.90, 13.80 (shoulder at 13.95), and 14.30 μ.

Base-catalyzed Condensation of Ethylidenemalononitrile in Solution

Ethylidenemalononitrile (1 g) was dissolved in 25 ml of benzene and a small amount of malononitrile and 3 drops of diethylamine were added. The mixture was left at room temperature for 2 h, washed with dilute hydrochloric acid and then with water, and dried over Drierite. Removal of the benzene left a glass which crystallized to a white solid overnight. On recrystallization from chloroform this yielded a finely crystalline white powder of m.p. 173–174 °C. The main absorptions in the infrared were at 2.79, 2.86, 2.98, 3.25, 4.47, 6.04, 6.16, and 6.83, in μ.

Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.40; H, 4.00; N, 33.60; molecular weight, 250. Found: C, 62.50; H, 4.33; N, 33.40; molecular weight, 229.

This compound could also be prepared by the following method: 2.4 g (0.055 mole) of acetaldehyde and 6.6 g (0.050 mole) of malononitrile were dissolved in 100 ml of benzene and 6 drops of diethylamine were added to the mixture. After standing at room temperature for 2 h the benzene solution was washed with dilute hydrochloric acid, and then with water. Removal of the solvent and crystallization from chloroform as above gave the white crystalline product.

Base-catalyzed Condensation of Ethylidenemalononitrile in Absence of Solvent

Ethylidenemalononitrile on standing in contact with glass for 1 or 2 days condensed to a yellow solid, which on crystallization from 95% ethanol gave a pale-yellow powder of m.p. 166–168°.

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.30; H, 4.35; N, 30.41; molecular weight, 184. Found: C, 64.95; H, 4.53; N, 30.72; molecular weight, 180, 270 (on two separately prepared samples of material).

Preparation of Benzalmalononitrile-d_1

Ethyl benzoate was reduced with lithium aluminium deuteride to $C_6H_5CD_2OH$ (21) which was then oxidized with activated manganese dioxide to C_6H_5CDO (22). The benzaldehyde-d_1 was condensed with malononitrile following the method already described for the preparation of benzalmalononitrile.

1. To 1.7 g (0.041 mole) of lithium aluminium deuteride in 500 ml of dry ether was added, dropwise, 10 g (0.067 mole) of ethyl benzoate. After addition of the ester the mixture was refluxed for a further hour, the excess deuteride destroyed with wet ether, and the mixture poured into ice-cold 10% sulfuric acid. Extraction with ether and removal of the solvent gave 6.5 g (88%) yield of alcohol. The infrared spectrum of the product showed strong C—D absorptions at 4.5 and 4.7 μ. No ester absorption was apparent at this stage.

2. Activated manganese dioxide (22 g, 0.26 mole) was added to 250 ml of benzene and the mixture refluxed till no more water appeared to be coming off. The water evolved was collected in a Dean-Stark trap. $C_6H_5CD_2OH$ (6.5 g, 0.059 mole) was then added, and the refluxing continued till a further 1 ml (approximately) of water was collected. The mixture was then cooled and filtered and the solvent removed under vacuum. Benzaldehyde-d_1 (3.8 g, 67% yield) was isolated. This was distilled through a Nester/Faust micro spinning band column. The final product showed a strong carbonyl absorption in the infrared at 5.9 μ, and C—D absorptions at 4.5 and 4.7 μ. No alcohol or ester absorptions were apparent.

Control Experiment on Base-catalyzed Exchange of the Benzylic Hydrogen in Benzalmalononitrile

Benzalmalononitrile was dissolved in methanol-d_1 and the n.m.r. spectrum recorded. The benzylic hydrogen, appearing downfield from the aromatic hydrogens, is readily distinguishable from the latter. The addition of a drop of *n*-butyl amine or of ethanolic potassium hydroxide to the solution caused no appreciable change in the relative areas of the benzylic and aromatic hydrogens. Addition of several drops of base eventually caused the benzylic hydrogen peak to almost disappear, but not before the aromatic hydrogen absorptions had also decreased in intensity and sharpness, and the solution had turned brown, the latter presumably being due to condensation and tar formation.

Notes

Molecular weights were determined osmometrically. Melting points are uncorrected.

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