probably dimorphic, the low melting variety tending to change into the higher melting form.

Anal. Calcd. for $C_{44}H_{46}O_{10}$: C, 71.90; H, 6.31; $COCH_3$, 11.72. Found: C, 72.00; H, 6.54; $COCH_3$, 11.60.

The crude dehydrogenation product of dehydrodiisoeugenol was hydrogenated at room temperature in ethanol over palladium–carbon. The product was practically identical to that formed by the dehydrogenation of dihydrodehydrodiisoeugenol in respect to analytical values and ultraviolet spectra and it gave an identical crystalline fraction.

Dehydrogenation of Pinoresinol.—To a solution of 1.00 g. of pinoresinol diacetate in 10 ml. of ethanol, 10 ml. of 1 *N* sodium hydroxide was added and the mixture refluxed 1 hr. The cooled solution was diluted with 6.5 ml. of 1 *N* hydrochloric acid and 3.5 ml. of water and then, with vigorous stirring, 2.0 ml. of 1% hydrogen peroxide (50% of theoretical) added dropwise over a 30-min. period. The resin which separated was dried, triturated with absolute ether, the ether decanted, and the residue extracted with boiling benzene. The benzene solution was allowed to stand at room temperature for several hours, the benzene decanted, and the residue recrystallized several times from benzene. The crystals after drying 3 days at 80° under vacuum (yield 6.8% based on pinoresinol) melted at 120–122° (lit.,[6] m.p. 119–121°). The acetylated material had m.p. 193–195° (lit.,[6] m.p. 195.5–197°).

Dehydrogenation of Dihydroconiferyl Alcohol.—To the compound (0.25 g.) in 5 ml. of ethanol was added 5 ml. of water containing 2.5 mg. of peroxidase and dropwise over a 30-min. period 20 drops of 3% hydrogen peroxide. A precipitate formed on keeping the solution at +2° for several hours. Recrystallization twice from ethanol gave a small yield of colorless crystals, m.p. 148–150°. The ultraviolet spectra closely agreed with that of the 4,4′-dipropyl-6,6′-biguaiacol.

Anal. Calcd. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 65.98; H, 7.29.

Dehydrogenation of Eugenol.—Using the general methods described above, 1.00 g. of eugenol produced a resin which gave 0.42 g. of crystals from hexane, m.p. 96–100°. Recrystallization from ethanol gave pure dehydrodieugenol, m.p. and m.m.p. 104–105° (lit.,[11] m.p. 106°).

Isoeugenol, using 67% of the theoretical amount of hydrogen peroxide, gave 26% of the expected dehydrodiisoeugenol.

Dehydrogenation of Vanillin.—To a solution of 1.00 g. of vanillin in 100 ml. of ethanol and 10 ml. of water containing 5 mg. of peroxidase, 5 ml. of 3% hydrogen peroxide was added dropwise over a period of 1 hr. The mixture was allowed to stand overnight, the precipitate filtered, washed with water, then washed with acetone which removed an orange-colored resin. The product, 0.88 g. melting at 306–312°, was recrystallized from acetic acid giving pure dehydrodivanillin, m.p. and m.m.p. 315–316° (lit.,[12] m.p. 315–316°).

Dehydrogenation of Acetovanillone.—This was carried out as with the vanillin to give 0.66 g. of crude product, m.p. 306–312°, and pure crystals, m.p. 310–312° (lit.,[13] m.p. above 300°). The ultraviolet spectra was quite similar to that of dehydrodivanillin.

One gram of the material as prepared above was dissolved in 10 ml. of *N* sodium hydroxide and 0.2 g. of sodium borohydride added. The solution was allowed to stand overnight, acidified with acetic acid, extracted with ethyl acetate, and the solution was dried, concentrated, and cooled to −20°. The crystals (0.42 g.) had m.p. of 133–136°, or 138–140° on repeated recrystallization. The ultraviolet spectra was identical with that of dehydrodivanillyl alcohol.

Anal. Calcd. for $C_{20}H_{21}O_4$: C, 73.82; H, 6.51; OCH_3, 19.08. Found: C, 73.70; H, 6.76; OCH_3, 19.03.

Dehydrogenation of Vanillyl Alcohol.—To a solution of 1.00 g. of vanillyl alcohol in 10 ml. of hot water was added 10 ml. of water containing 5 mg. of peroxidase. With vigorous stirring 7.4 ml. of 1% hydrogen peroxide was added dropwise over a period of 1 hr. The solution was extracted with ether and the ether evaporated to give 0.28 g. of vanillyl alcohol containing a little vanillin. The solution was next extracted with ethyl acetate, the ethyl acetate evaporated, and the residue rubbed with a mixture of alcohol and acetone. Crystals, 0.153 g., m.p. 188–190°, separated. Reworking the mother liquor gave an additional 0.019 g. and the evaporated extracted solution 0.013 mg. or a total of 0.185 g. Recrystallization gave a product melting at 192–194° (lit.,[14] m.p. 187–190°). None of the highly insoluble dehydrodivanillin was detected.

The dehydrogenation of apocynol was attempted as described for vanillyl alcohol. Only starting material, resin, and a considerable amount of acetovanillone was recovered. The difficultly crystallizable biphenyl compound may have been produced but not successfully isolated. No dehydrodiacetovanillone was detected.

5-Propylvanillyl Alcohol.—A solution of 0.50 g. of 4-propylvanillin and 0.05 g. of sodium borohydride in 10 ml. of methanol was allowed to stand several hours and the methanol removed at room temperature. The residue was taken up in water, the mixture extracted with ether, the ether evaporated, and the residue recrystallized twice from hexane at −20°. The yield was 0.41 g., m.p. 45–50°. Repeated recrystallization from hexane gave crystals melting at 70–72°.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33; H, 8.22; OCH_3, 15.82. Found: C, 67.23; H, 8.30; OCH_3, 15.71.

Acknowledgment.—The author is indebted to Professor E. Adler, Dr. J. A. F. Gardner, and Dr. I. A. Pearl for furnishing some of the model compounds investigated.

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[12] J. G. Pew, *J. Am. Chem. Soc.*, **77**, 2833 (1955).

[13] F. Tiemann, *Ber.*, **18**, 3493 (1885).

[14] E. Adler, *Acta Chem. Scand.*, **9**, 332 (1955).

The Structure and Some Reactions of Isopropylidenemalononitrile Dimer

J. K. WILLIAMS

Contribution No. 788 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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Isopropylidenemalononitrile dimer is shown to exist predominantly as the aminocyclohexadiene IVa, which is in equilibrium with the tautomer IVb. It undergoes addition of nucleophiles, such as methoxide, to give cyclohexenes such as IXb. These undergo a reverse Diels–Alder reaction on heating near 150° to form isobutylene and dienes such as Xb. Gentle acid hydrolysis of the cyclohexenes (IX) leads to 1,4-transannular transfer of alkoxide to a cyano group to form imino ethers that subsequently undergo hydrolysis to the esters XX.

Isopropylidenemalononitrile dimer has been obtained by the base-catalyzed reaction of acetone with malononitrile[1,2] and by the piperidine-catalyzed dimerization of isopropylidenemalononitrile (I).[3] It has been suggested that the dimer is the cyclobutane II,[2] the imino diene IIIa,[2] and the tautomeric amino triene IIIb.[4] We have studied the dimer and conclude

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[1] G. J. Ostling, *Oevers. Finska Vetenskaps-Soc. Forh.*, **57A**, No. 11, 1 (1915).

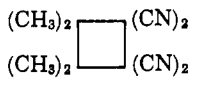
[2] R. Schenk and H. Finken, *Ann.*, **462**, 267 (1928).

[3] A. C. Cope and K. E. Hoyle, *J. Am. Chem. Soc.*, **63**, 733 (1941).

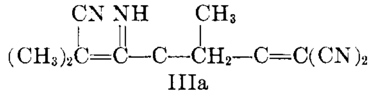
[4] D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, 4705 (1961). Professors Anderson and Bell have examined the manuscript of this publication and have graciously suggested that we include a note stating that they agree with our structures and conclusions.

$(CH_3)_2C{=}C(CN)_2$

I

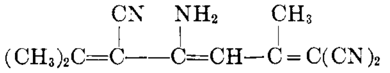


II



$(CH_3)_2C{=}\overset{CN}{\overset{|}{C}}{-}\overset{NH}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}H_2{-}C{=}C(CN)_2$

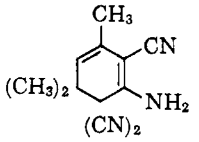
IIIa



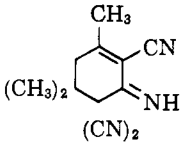
$(CH_3)_2C{=}\overset{CN}{\overset{|}{C}}{-}\overset{NH_2}{\overset{|}{C}}{=}CH{-}\overset{CH_3}{\overset{|}{C}}{=}C(CN)_2$

IIIb

that it is instead the cyclohexadiene IVa, probably mixed with the tautomeric compound IVb.



IVa



IVb

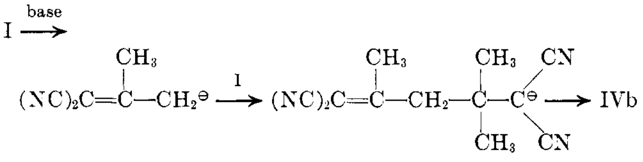
The cyclobutane structure (II) can be eliminated since it is incompatible with both the infrared spectrum, which shows absorption for NH_2 and C=C, and the ultraviolet spectrum (Table I) which shows a number of strong absorption maxima typical of conjugated unsaturated systems. Optical spectra did not serve to differentiate between structures III and IV; however, the proton n.m.r. spectrum of the dimer clearly indicated that it has the cyclic structure IV. A proton resonance was observed for one methyl group at low field assignable to a methyl group attached to unsaturated carbon. A resonance for two equivalent methyl groups occurred at high field, typical of methyl groups on saturated carbon. Resonances were also observed for the two NH_2 protons and for a single proton on unsaturated carbon. The positions of the methyl resonances are incompatible with structures IIIa or IIIb and support structure IV. The relative magnitudes of the resonances observed for the NH_2 and C=C—H protons indicate that the major component in solution is IVa. In addition, a number of weaker resonances were observed that can probably be attributed to the presence of the tautomer IVb.

TABLE I

ULTRAVIOLET SPECTRA OF ISOPROPYLIDENEMALONONITRILE DIMER AND DERIVATIVES

Compound	λ_{max}^{EtOH} mμ	(ε)	Compound	λ_{max}^{EtOH} mμ	(ε)
IV	217	(9,750)	Xc	232	(55,000)
	239	(4,700)		266(sh)	(4,760)
	321	(5,300)		316	(3,700)
IXa	281	(16,800)	Xd	240	(41,100)
				250(sh)	(30,000)
IXb	275	(7,080)		312	(5,660)
IXc	275	(7,740)	XI	263	(12,500)
IXd	226	(10,700)	XII	271	(12,500)
	276	(6,580)			
			XV	347	(32,200)
Xa in 0.1	252	(14,900)		457	(8,000)
N HCl	285	(23,300)			
	337	(28,600)	XVII	251	(10,300)
				295	(2,610)
Xa in 0.1	248	(1,600)			
N NaOH	282	(22,600)	XXb	251	(9,890)
	327	(19,500)		295	(2,260)
	352	(19,700)			
			XXc	249	(9,760)
Xb	232	(54,000)		295(sh)	(893)
	270	(4,720)			
	316	(3,760)			

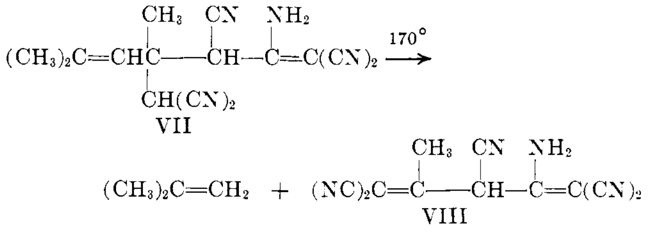
In addition to the spectral evidence for structure IV, we feel that it is reasonable to expect the course of the base-catalyzed dimerization of I to involve first the Michael addition of the anion V to a molecule of I to form VI which can then undergo Thorpe cyclization to IVb. An analogous sequence has been suggested by Kenner[5] for the base-catalyzed dimerization of mesityl oxide.



$I \xrightarrow{\text{base}}$

$(NC)_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2^{\ominus} \xrightarrow{I} (NC)_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C^{\ominus}(CN)_2 \longrightarrow IVb$

We have examined the chemistry of isopropylidenemalononitrile dimer and have found compelling chemical evidence to support structure IV. Ostling[1] found that when acetone was allowed to react with an excess of malononitrile in the presence of base he obtained a compound $C_{15}H_{14}N_6$. Later Anderson, Bell, and Duncan[4] examined Ostling's C_{15} compound, for which they suggest formula VII, and found that it decomposed near 170° with evolution of isobutylene to form a compound with the formula $C_{11}H_6N_6$, for which they proposed structure VIII. We have found that isopropylidenemalononitrile dimer reacts with malononitrile in the presence of base to give Ostling's C_{15} compound and that methanol, ethanol, and ammonia undergo similar addition to the dimer. This reaction can be interpreted as involving 1,4-addition to tautomer IVb of the dimer to give the 3-substituted 1-amino-2,6,6-tricyano-3,5,5-trimethylcyclohexenes, IXa, IXb, IXc, and IXd.

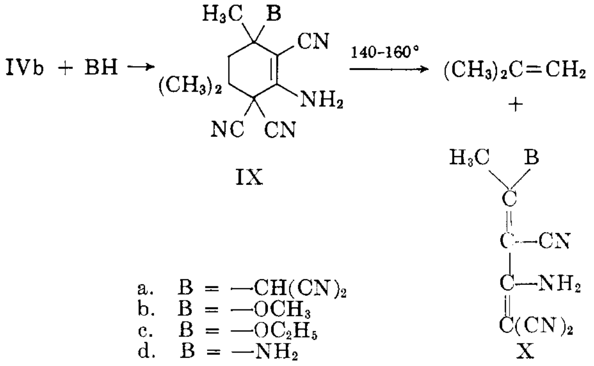


$(CH_3)_2C{=}CH\underset{CH(CN)_2}{\overset{CH_3}{C}}{-}\overset{CN}{CH}{-}\overset{NH_2}{C}{=}C(CN)_2 \xrightarrow{170°}$

VII

$(CH_3)_2C{=}CH_2 + (NC)_2C{=}\overset{CH_3}{C}{-}\overset{CN}{CH}{-}\overset{NH_2}{C}{=}C(CN)_2$

VIII



IX

a. B = —CH(CN)$_2$
b. B = —OCH$_3$
c. B = —OC$_2$H$_5$
d. B = —NH$_2$

X

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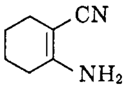
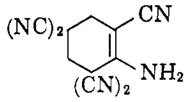
(5) J. Kenner, *Tetrahedron*, **8**, 350 (1960).

Compounds IXa–d undergo reverse Diels–Alder reaction near 150° to give isobutylene and the dienes[6] Xa–d in nearly quantitative yield. Addition of malononitrile, alcohols or ammonia to IIIa or IIIb cannot result in an adduct having a carbon skeleton suitable for ready loss of isobutylene, a fact that gives strong support to structure IV over structure III. Similarly structure VII is unlikely since it cannot be formed by addition of malononitrile to either III or IV. Thus Ostling's C_{15} compound has the cyclic structure IXa rather than the previously suggested linear structure VII. Additional support for the 1-amino-2-cyanocyclohexene structures IXa–d is the close similarity of their ultraviolet spectra to those of the known 1-amino-2-cyanocyclohexenes XI[7] and XII[8] (Table I). The infrared spectra of IXa–d are consistent with the proposed structures in that they all exhibit absorption for unconjugated $C\equiv N$ slightly below 4.50 μ and for conjugated $C\equiv N$ slightly above 4.50 μ. Baldwin's[9] study of the problem of the amine–imine tautomerism of compounds containing the 1-amino-2-cyanoethylene system provides additional infrared and ultraviolet spectral data to support structures IXa–d.

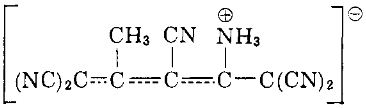


XI



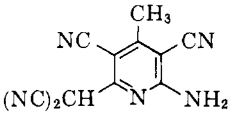
XII

The structure of the dienes Xa–Xd is based mainly on their mode of formation and is supported by their rich absorption in the ultraviolet (Table I) and their compatible infrared spectra. The pentacyano compound Xa differs from the other four dienes in that it is essentially insoluble in organic solvents, does not melt below 400°, is acidic and forms readily soluble salts. Its structural similarity to a number of cyanocarbon acids[10] suggests that its physical properties can be explained by assuming it exists in the delocalized zwitterion form, XIII. Another alternative structure for Xa is the pyridine XIV that could form by a cyclization involving addition of the amino group of Xa to a cyano group. However, the great difference between the ultraviolet spectra of salts of Xa and salts of the known pyridine, XV,[11,12] eliminates structure XIV.

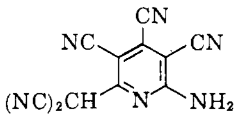


$\left[(NC)_2C\overset{CH_3}{\underset{}{\cdots C}}\cdots\overset{CN}{C}\cdots\overset{\overset{\oplus}{NH_3}}{C}-C(CN)_2\right]^{\ominus}$

XIII (Xa)

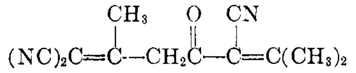


XIV



XV

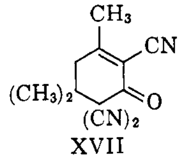
Coenen[13] has studied the gentle acid hydrolysis of isopropylidenemalononitrile dimer in methanol–water solution. Since he accepted structure III for the dimer, he formulated the hydrolysis product as the linear ketone XVI. Based on the cyclic structure IV



$(NC)_2C{=}\overset{CH_3}{C}{-}CH_2\overset{O}{\overset{\|}{C}}{-}\overset{CN}{C}{=}C(CH_3)_2$

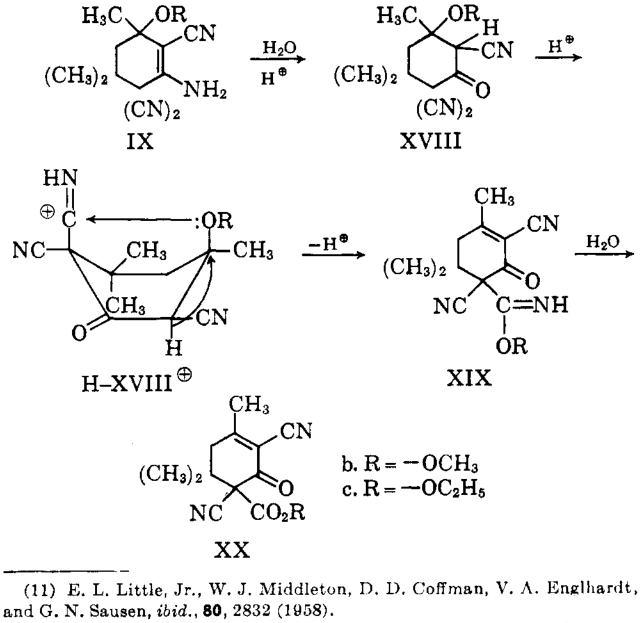
XVI

for the dimer it is clear that Coenen's hydrolysis product has structure XVII.



XVII

We investigated the hydrolysis of the alcohol adducts IXb and IXc under Coenen's conditions and were surprised to find that both IXb and IXc gave products having the same chromophore in the ultraviolet as XVII indicating that the alkoxy group had been removed. In both cases, however, the hydrolysis products had the same number of carbon atoms as the starting materials, but had lost two nitrogen atoms. The infrared spectra of the hydrolysis products showed absorption for an ester carbonyl group. That the alcohol in the solvent was not participating in the formation of the ester function was shown by parallel experiments in which a methyl ester was formed from the methoxy compound, IXb, in ethanol–water solvent and an ethyl ester was obtained from the ethoxy compound, IXc, in methanol–water. These results can be explained by a transannular transfer of alkoxide during the hydrolysis to give the keto esters XXb and XXc. The most likely sequence for this remarkable transformation



b. R = $-OCH_3$
c. R = $-OC_2H_5$

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(6) The pyrolysis product Xa is a tautomer of VIII and is thus equivalent to it.

(7) K. v. Auwers, T. Bahr, and E. Frese, *Ann.*, **441**, 91 (1925).

(8) (a) J. C. Westfahl and T. L. Gresham, *J. Org. Chem.*, **21**, 319 (1956); (b) O. Diels and B. Conn, *Ber.*, **56**, 2076 (1923).

(9) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961). In this paper only one $C\equiv N$ stretching vibration (4.53 μ) was reported for XII. We have found an additional, very weak, band at 4.41 μ that we assign to the stretching vibration of the four unconjugated $C\equiv N$ groups. It has been our experience that the $C\equiv N$ stretching vibration in compounds containing an unconjugated $C\equiv N$ group attached to a carbon atom bearing other electron withdrawing groups, such as additional $C\equiv N$ groups, can give rise to very weak absorption in the infrared. To observe this band in the spectrum of XII, we employed an unusually high concentration of the compound in our potassium bromide pellet.

(10) W. J. Middleton, E. L. Little, Jr., D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(11) E. L. Little, Jr., W. J. Middleton, D. D. Coffman, V. A. Englhardt, and G. N. Sausen, *ibid.*, **80**, 2832 (1958).

(12) The ultraviolet spectrum of the tetramethylammonium salt of XV was kindly supplied by Dr. W. J. Middleton.

(13) M. Coenen, German Patent 942,810 (1956).

involves initial hydrolysis of the enamines IXb or IXc to the keto compounds XVIIIb or XVIIIc. The boat conformation of XVIII places the oxygen of the alkoxy group approximately 2 Å. from the carbon of the opposite cyano group as estimated by measurement of Drieding Stereomodels. In the acidic reaction medium XVIII will be in equilibrium with the protonated form H-XVIII$^{\oplus}$. Migration of the alkoxy group to the nearby protonated cyano group with simultaneous loss of the proton α to the carbonyl group would form the imino ethers XIXb and XIXc. In the aqueous acid reaction medium, XIXb and XIXc would hydrolyze quickly to the esters XXb and XXc.

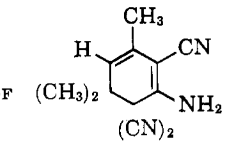
Support for structures XVII, XXb and XXc is supplied by their proton n.m.r. spectra. The most interesting feature of these spectra is that the ketone XVII shows a single resonance for the geminal hydrogens in the 4-position while in compounds XXb and XXc these protons are non-equivalent and give rise to a typical weak-strong-strong-weak pattern.

Experimental[14]

Proton N.m.r. Spectra.[15]—The proton n.m.r. spectrum of IV in 1.0 *M* solution in deuterioacetone at room temperature indicated that about 60% exists as IVa. Complete analysis of this n.m.r. spectrum has not been accomplished, but those resonances attributable to IVa can be analyzed in a straightforward way. Table II summarizes the n.m.r. data. One noteworthy feature of the spectrum is the coupling of 1.6 c.p.s. between the 3-methyl group and the adjacent ring proton. Coupling through a double bond would be expected to be greater than through a single bond, and thus coupling between the ring proton and the *gem*-dimethyl groups would be somewhat less than 1.6 c.p.s. and in fact is not observed. Additional weaker broad resonances with unresolved fine structure were observed, as well as a sharp resonance at 8.69 τ. Of these weaker resonances the strongest, at 8.69 τ, had an area of 0.6 of that at 8.63 τ and is probably the 5-*gem*-dimethyl group of tautomer IVb. That tautomers IVa and IVb are not in rapid equilibrium in neutral solution is indicated by the lack of incorporation of deuterium (by infrared) when solutions of IV in acetonitrile–D_2O were allowed to stand for 4 hr. at room temperature. Structure III should have a resonance for the two methyls of the $C{=}C(CH_3)_2$ group at considerably lower field than 8.63 τ.[17]

TABLE II

PROTON N.M.R. OF



Protons	τ, p.p.m.	Relative[a] area
NH_2	3.16	2
C=C—H	4.76 quadruplet, *J* = 1.6 c.p.s.	1
$C{=}C{-}CH_3$	8.11 doublet, *J* = 1.6 c.p.s.	3
$>C(CH_3)_2$	8.63	6

[a] See ref. 16.

The proton n.m.r. spectra of the three hydrolysis products XVII, XXb, and XXc are summarized in Table III.

All three hydrolysis products are probably best represented as equilibrium mixtures of the conformers A and B shown at the top of Table III. Examination of a model of the system shows that carbons 1, 2, 4, 5, and 6 are fixed in a plane and that carbon 3 can flip above and below this plane easily. The observed proton n.m.r. spectra of compounds XVII, XXb, and XXc are in each case an average of the resonances of the two conformers A and B. In compound XVII where both substituents on carbon 2 are cyano groups (Y = CN) the hydrogens on carbon 4 are interconverted by the change from conformer A to conformer B. In addition, each conformer has one axial (H_a) and one equatorial (H_e) proton. Since A and B are in rapid equilibrium, however, only one unsplit resonance is observed and appears at an average position between H_a and H_e.

In the case of XXb and XXc where Y is an ester function and carbon 2 is thus unsymmetrically substituted, the spectra are more complex. Inspection of the hydrogens at carbon 4 shows that H_e and H_a of conformer A are not equivalent to H_e and H_a of conformer B. For example, in conformer A the axial hydrogen, H_a, extends below the ring on a line parallel to the ester group Y whereas the axial hydrogen, H_a, in conformer B is on a bond parallel to the bond of a cyano group. Conformer A should have resonances for the two hydrogens at carbon 4 consisting of a quartet arising from the chemical shift between H_e and H_a and their spin-spin coupling. Conformer B should show a similar but different set of four lines. Because of rapid equilibrium between A and B, the observed quartet is an average of the quartet from conformer A and that from conformer B. Examination of models shows that the methyl groups on carbon 3 are poorly oriented for coupling with the 4-hydrogens and for interaction with the groups on carbon 4. Nevertheless the methyl resonances appear as double peaks in compounds XXb and XXc. The doublet observed for the geminal 3-methyl groups can be explained by their non-equivalency in conformers A and B by an argument analogous to that used to explain the splitting of the hydrogens on carbon 4.

Isopropylidenemalononitrile Dimer (IV).—Reaction of malononitrile with excess acetone in the presence of base[1,2] or dimerization of isopropylidenemalononitrile (prepared by the method of Prout)[19] according to Cope and Hoyle[3] gave identical products (IV). The infrared spectrum of IV showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.92, 3.01, 3.11, 3.34 (w), 4.43 (w), 4.51, 6.02, 6.15 (w), and 6.32 μ. However, when three equivalents of malononitrile were allowed to react with two equivalents of acetone, the cyclohexene IXa was formed as described below.

1-Amino-2,6,6-tricyano-3,5,5-trimethyl-3-(dicyanomethyl)-cyclohexene (IXa). A. From Acetone and Malononitrile.—To a solution of 12 g. of sodium hydroxide in 1350 ml. of ethanol was added a mixture of 450 g. (6.82 moles) of malononitrile and 264 g. (4.55 moles) of acetone. The mixture was stirred until its temperature had risen to 50°. It was cooled in an ice bath for 1 hr. and then stirred without cooling for 20 hr. The solid that precipitated was collected and washed on the filter with alcohol until the washings were colorless. The yield of pale yellow, microcrystalline IXa was 506 g. (80%). This material did not melt below 300° but evolved a gas at 163°. In a similar preparation, a sample was submitted for analysis after crystallization from acetonitrile with treatment with Darco.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.90 (sh), 2.96, 3.02, 3.06, 4.46, 4.52, 6.03, 6.18, and 6.33 μ.

Anal. Calcd. for $C_{15}H_{14}N_6$: C, 64.7; H, 5.07; N, 30.2; mol. wt., 278. Found: C, 65.0; H, 5.17; N, 29.8; mol. wt. (cryoscopic in dimethylsulfoxide), 252.

B. From Isopropylidenemalononitrile Dimer and Malononitrile.—A mixture of 10.6 g. of isopropylidenemalononitrile dimer, 3.3 g. of malononitrile, 200 ml. of ethanol and 0.5 g. of sodium hydroxide was stirred at room temperature for 18 hr. The solid that had formed was collected and washed with ethanol

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[14] All melting points are corrected.

[15] All proton n.m.r. spectra were measured on a Variān A-60 nuclear magnetic resonance spectrometer.

[16] Intensities were determined by electronic integration; τ values were obtained using 0.05 *M* tetramethylsilane as an internal standard.

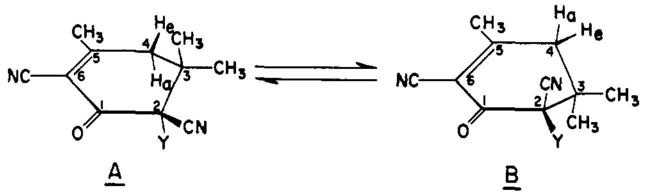
[17] In 1 *M* solution in deuterioacetone the methyl resonance of isopropylidenemalononitrile occurs at 7.64 τ.

[18] The proton n.m.r. spectra were determined at room temperature in 0.5 *M* solution in deuteriochloroform containing 0.05 *M* tetramethylsilane as an internal reference.

[19] F. S. Prout, E. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).

TABLE III

N.M.R. SPECTRA OF HYDROLYSIS PRODUCTS[a]



Compound	Chemical shift; τ, p.p.m.			R
	5-CH_3	4-H	3-CH_3	
XVII Y = CN	7.52	7.12	8.60	
XXb Y = —CO_2CH_3	7.59	AB quartet 7.01, 7.45 J = 26.3 c.p.s.	8.69 partly resolved doublet Δ = 1 c.p.s.	6.11
XXc Y = —$CO_2C_2H_5$	7.58	AB quartet 7.01, 7.45 J = 26.3 c.p.s.	8.67, 8.71 doublet Δ = 2.1 c.p.s.	CH_3-triplet 8.67, J = 7.5 c.p.s.; CH_2- quadruplet 5.65, J = 7.5 c.p.s.

[a] See Ref. 18.

to give 3.1 g. (22%) of IXa having an infrared spectrum identical to that of the material prepared by method A.

1-Amino-2,6,6-tricyano-3,5,5-trimethyl-3-methoxycyclohexene (IXb).—A mixture of 10.6 g. of isopropylidenemalononitrile dimer, 0.5 g. of sodium methoxide, and 200 ml. of methanol was stirred at room temperature for 16 hr. The solid that had precipitated was collected and washed with methanol to give 9.6 g. (79%) of IXb, m.p. 217–219° with gas evolution at 147°. A sample, m.p. 210–212°, with gas evolution at 140°, was prepared for analysis by crystallization from acetonitrile.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.90, 3.00, 3.18, 3.36, 4.43 (w), 4.54, 5.97, and 6.19 μ.

Anal. Calcd. for $C_{13}H_{16}N_4O$: C, 63.9; H, 6.60; N, 22.9; mol. wt., 244. Found: C, 64.2; H, 6.73; N,2 2.9; mol. wt. (ebullioscopic in acetone), 258.

1-Amino-2,6,6-tricyano-3,5,5-trimethyl-3-ethoxycyclohexene (IXc).—A mixture of 1 g. of sodium hydroxide, 200 ml. of ethanol, and 21.2 g. of isopropylidenemalononitrile dimer was stirred at room temperature for 3 days. The solid IXc that precipitated was collected and washed with ethanol. After crystallization from acetonitrile it weighed 10.9 g. (42%) and melted at 240–242° with gas evolution at 147–152°. In another experiment a sample having the same decomposition temperature and melting point was prepared for analysis by crystallization from acetonitrile.

Infrared bands were observed for IXc at $\lambda_{\max}^{\mathrm{KBr}}$ 2.92, 3.02, 3.20, 4.44, 4.57, 6.01, and 6.23 μ.

Anal. Calcd. for $C_{14}H_{18}N_4O$: C, 65.1; H, 7.02; N, 21.7; mol. wt., 258. Found: C, 65.4; H, 7.22; N, 21.3; mol. wt. (ebullioscopic in acetone), 248.

1,3-Diamino-2,6,6-tricyano-3,5,5-trimethylcyclohexene (IXd).—A mixture of 2.12 g. of isopropylidenemalononitrile dimer, 10 ml. of concentrated aqueous ammonia, and 10 ml. of ethanol was stirred at room temperature for 20 hr. The solid that precipitated was collected and washed with ethanol to give 1.3 g. (57%) of IXd as a microcrystalline powder not melting below 300°. A sample was prepared for analysis by recrystallization from acetonitrile.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.91, 2.98, 3.09, 4.42, 4.56, 5.93, 6.07, and 6.18 μ.

Anal. Calcd. for $C_{12}H_{15}N_5$: C, 62.8; H, 6.59; N, 30.6. Found: C, 63.0; H, 6.49; N, 30.7.

2-Amino-1,1,3,5,5-pentacyano-4-methylpentadiene-1,3 (Xa).—A suspension of 50.0 g. of 1-amino-2,6,6-tricyano-3,5,5-trimethyl-3-(dicyanomethyl)cyclohexene (IXa) in 250 ml. of decahydronaphthalene was heated to reflux (190°) over the course of 20 min. Vigorous gas evolution took place at 160°. This gas was collected in a trap at −80° and was shown to be isobutylene (93% yield) by comparison of its infrared spectrum with that of an authentic sample. The hot suspension was filtered and the solid that was collected was washed with 300 ml. of benzene. The diene, Xa, was obtained as a pale yellow powder that weighed 39.6 g. (96%), m.p. >300°. It was insoluble in the usual organic solvents but was soluble in dimethylformamide and aqueous base. The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 3.00, 3.10, 4.53, 6.00, 6.26, and 6.57 μ.

The piperidine salt of Xa was found to be more suitable for purification for analysis and was prepared by reaction of Xa with an equivalent of piperidine in water. It crystallized from water as a hydrate that was freed of water of crystallization by drying at 80°/0.01 mm., m.p. 169–171.6°.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.92 (sh), 3.00, 3.10, 4.55, 4.64, 6.09, 6.38, and 6.52 μ.

Anal. Calcd. for $C_{16}H_{16}N_7$: C, 62.5; H, 5.58; N, 31.9. Found: C, 62.3; H, 5.89; N, 32.0.

2-Amino-1,1,3-tricyano-4-methoxy-1,3-pentadiene (Xb).—A suspension of 6.1 g. of 1-amino-2,6,6-tricyano-3,5,5-trimethyl-3-methoxycyclohexene in 100 ml. of decahydronaphthalene was heated to reflux. At 164° vigorous evolution of isobutylene took place (identified by the infrared spectrum). After the mixture came to the reflux temperature, it was allowed to cool to room temperature. The solid that crystallized was collected and washed with petroleum ether to give 4.7 g. (100%) of Xb, m.p. 209–211°. A sample prepared for analysis by crystallization from acetonitrile melted at 210–211.6°.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.92, 2.98, 3.08, 4.49, 4.60 (w), 6.05, 6.35, and 6.80 μ.

Anal. Calcd. for $C_9H_8N_4O$: C, 57.5; H, 4.28; N, 29.8. Found: C, 57.2; H, 4.41; N, 30.2.

2-Amino-1,1,3-tricyano-4-ethoxy-1,3-pentadiene (Xc).—A mixture of 1.0 g. of 1-amino-2,6,6-tricyano-3,5,5-trimethyl-3-ethoxycyclohexene and 10 ml. of decahydronaphthalene was heated to reflux. A gas, identified as isobutylene by infrared analysis, was evolved during the heating period. The mixture was allowed to cool to room temperature. The Xc that crystallized was collected and washed with petroleum ether. It weighed 0.70 g. (97%), m.p. 240–242°. An analytical sample, m.p. 241–242°, was prepared by two crystallizations from acetonitrile.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.93, 3.00, 3.08, 4.50, 4.60 (w), 6.05, and 6.37 μ.

Anal. Calcd. for $C_{10}H_{10}N_4O$: C, 59.4; H, 4.98; N, 27.7; mol. wt., 202. Found: C, 59.5; H, 5.02; N, 27.8; mol. wt. (ebullioscopic in ethylene chloride), 208.

2,4-Diamino-1,1,3-tricyano-1,3-pentadiene (Xd).—A suspension of 35.0 g. of 1,3-diamino-2,6,6-tricyano-3,5,5-trimethylcyclohexene in 150 ml. of decahydronaphthalene was heated to reflux. Isobutylene was evolved vigorously when the temperature of the mixture reached 155–158°. The mixture was heated at reflux for 0.5 hr. and then was allowed to cool to room temperature. The pale yellow solid was collected and washed with benzene, then ether, to give 26.0 g. (99%) of Xd, m.p. >300°. A sample was prepared for analysis by crystallization from acetonitrile.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{KBr}}$ 2.86, 2.98, 3.07, 3.17, 4.50, 4.60 (w), 5.98, 6.07, 6.34, and 6.69 μ.

Anal. Calcd. for $C_8H_7N_5$: C, 55.5; H, 4.08; N, 40.6. Found: C, 55.5; H, 4.02; N, 40.7.

2,6,6-Tricyano-3,5,5-trimethyl-2-cyclohexen-1-one (XVII).—Hydrolysis of IV as described by Coenen[13] give XVII, m.p. 126–127°, in 72% yield. The two following experiments were modeled after this preparation.

The infrared spectrum showed λ_{max}^{KBr} 4.47 (CN), 5.84 (C=O), and 6.19 (C=C) μ.

Methyl 1,3-Dicyano-4,6,6-trimethyl-2-oxo-3-cyclohexene-1-carboxylate (XXb).—A mixture of 12.2 g. of IXb, 200 ml. of ethanol, 200 ml. of water and 10.5 ml. of concentrated hydrochloric acid was stirred at room temperature for 25.5 hr. The white solid was collected and washed with water to give 11.1 g. (90%) of XXb, m.p. 142.8–143.4°. The melting point was not raised when a sample was prepared for analysis by crystallization from an ethanol-water mixture.

The infrared spectrum showed λ_{max}^{KBr} 4.42 (w) (sat. CN), 4.45 (conj. CN), 5.74 (ester C=O), 5.89 (conj. ketone C=O), 6.17 (C=C) μ.

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 62.9; H, 5.69; N, 11.3. Found: C, 62.9; H, 5.71; N, 11.4.

Ethyl 1,3-Dicyano-4,6,6-trimethyl-2-oxo-3-cyclohexene-1-carboxylate (XXc).—A mixture of 5.16 g. of IXc, 80 ml. of methanol, 80 ml. of water and 4.2 ml. of concentrated hydrochloric acid was stirred at room temperature for 25 hr. The white solid that precipitated was collected, washed with water, and dried to give 4.85 g. (93%) of XXc, m.p. 108.2–109.1°. A sample prepared for analysis by crystallization from benzene-cyclohexene melted at 108.4°.

The infrared spectrum showed λ_{max}^{KBr} 4.45 (w) (sat. CN), 4.47 (conj. CN), 5.78 (ester C=O), 5.90 (conj. ketone C=O), 6.17 (C=C) μ.

Anal. Calcd. for $C_{14}H_{16}N_2O_3$: C, 64.7; H, 6.20; N, 10.8. Found: C, 64.5; H, 6.20; N, 10.8.

1-Amino-2-cyanocyclohexene (XI).—A mixture of 30 g. of pimelonitrile, 400 ml. of toluene and 11 g. of sodium hydride dispersion (53% in oil) was heated under reflux for 17 hr. To the hot mixture was added successively 20 ml. of ethanol, 100 ml. of water and 15 ml. of acetic acid. The toluene layer was collected, washed with 150 ml. of water and filtered. The filtrate was reduced to a volume of 300 ml. by distillation and diluted while hot with 500 ml. of petroleum ether (b.p. 30–60°). The cooled solution was diluted to 1500 ml. with petroleum ether and refrigerated. The solid that crystallized was collected to give 20 g. of XI, m.p. 96.5–99.0°.[7] A small sample prepared for spectral measurement by two crystallizations from methanol-water mixture melted at 98–99°.

The infrared spectrum showed λ_{max}^{KBr} 2.89, 2.92, 3.07, 4.57, 6.07, and 6.19 μ.

The Chemistry of Xylylenes. XVIII. The Gas Phase Synthesis of α,α'-Bistrichloromethyl-*p*-xylene *via* Coaxial Pyrolysis of *p*-Xylene and Chloroform

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Contribution No. 234 from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company,[1]

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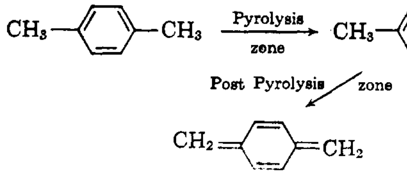
Fast flowing streams of *p*-xylene and chloroform were pyrolyzed in separate concentric tubes. The resulting pyrolyzates were allowed to mix at a predetermined point downstream where coupling of the chlorocarbon and hydrocarbon radicals occurred to produce a mixture of products. The composition of reactive species in the respective gas streams changed with distance away from the point of generation *via* pyrolysis. Hence, the product distribution changed accordingly with the blend point. Thus, *p*-methylbenzyl chloride and β,β-dichloro-*p*-methylstyrene were isolated as major products when the two streams were made to blend within the pyrolysis zone, whereas *p*-methylbenzyl chloride and α,α'-bistrichloro-methyl-*p*-xylene were isolated as major products when the pyrolyzates were allowed to blend five inches beyond the pyrolysis zone.

An earlier investigation of the fast flow pyrolysis of *p*-xylene at low pressure has shown that thermal rupture of the C—H bond occurs in the pyrolysis zone to give *p*-methylbenzyl radicals that are dehydrogenated catalytically to give *p*-xylylene as the pyrolyzate travels away from the furnace.[2,3]



(1)

It was also demonstrated that *p*-methylbenzyl radicals and *p*-xylylene can be used selectively as reactive intermediates for gas phase synthesis of mono- and difunctional derivatives of *p*-xylene. The technique involves quenching the fast flowing pyrolyzate with a second stream of reactive intermediates at an appropriate blend point. The proportion of mono- to difunctional derivatives obtained is a function of the corresponding ratio of *p*-methylbenzyl radicals to *p*-xylylene present at the point of mixing.

Similarly, fast flow pyrolysis of carbon tetrachloride at low pressure generates a stream of $CCl_3\cdot$ and Cl· that subsequently undergo coupling reactions to give CCl_3CCl_3 and chlorine as the gas stream travels away from the pyrolysis zone.[2] When *p*-xylene and carbon tetrachloride were pyrolyzed in two separate concentric tubes and the resulting pyrolyzates allowed to blend at a predetermined point downstream, as shown in Fig. 1 of ref. 3, the products isolated were dependent upon the relative concentration of reactive species in the respective gas streams at the point of mixing. The approximate flow patterns for the hydrocarbon and chlorocarbon streams emanating from a common pyrolysis zone are shown in Fig. 1A and 1B. Thus, *p*-methylbenzyl chloride and β,β-dichloro-*p*-methylstyrene were isolated as the two major products of interaction (equations 2 and 3) when the two streams were allowed to blend at the exit point of the pyrolysis zone,[2] whereas *p*-xylylene dichloride was the major product of interaction (reaction 4) when the two fast flowing pyrolyzates were allowed to blend far downstream.[3]

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(1) This work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Company with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Company in March, 1957.

(2) L. A. Errede and J. P. Cassidy, Paper XVI, *J. Phys. Chem.*, **67**, 69 (1963).

(3) L. A. Errede and J. P. Cassidy, Paper XVII, *ibid.*, **67**, 73 (1963).