Polyacetylenes of *Clitocybe candida*.—Shake cultures of *C. candida* were grown in cornsteep medium[19b] in the dark at 25°, either in 2-l. flasks containing 520 ml. of culture medium, or in 1-l. flasks containing 260 ml. of culture medium. Production of polyacetylenes was followed spectrophotometrically. The concentration of polyacetylenes slowly increased for about 4 weeks and showed little change thereafter. The mycelium was removed by filtration through cheesecloth and the culture liquid was extracted successively with 1400-, 700, and 700-ml. portions of ethyl acetate. The combined extracts were dried over anhydrous sodium sulfate and concentrated to a volume of about 25 ml. The remainder of the ethyl acetate was removed over 20 ml. of water. To this was added 40 ml. of methanol and the resulting solution was distributed between Skellysolve B and a 2:1 methanol–water solution for 50 transfers, using the first two tubes for the initial sample. Spectrophotometric analysis showed the presence of an enetriyne in tubes 0–9 with peak concentration in tube 3 and a second enetriyne in tubes 35–48 with peak concentration in tube 43.

***trans*-2-Decene-4,6,8-triyn-1-ol (1).**—Tubes 2–9 from the countercurrent distribution were combined, the lower layer was separated and concentrated to a volume of about 170 ml., and the resulting aqueous solution was extracted first with the top layer from tubes 2–9, then with two 100-ml. portions of fresh Skellysolve B. The combined Skellysolve extracts were concentrated to a volume of 15 ml. and the mixture was distributed between Skellysolve B and 1:2 methanol–water solution for 60 transfers. Spectrophotometric analysis showed the polyacetylene in tubes 25–40 with maximum concentration in tube 32. The total amount (estimated spectrophotometrically) was about 25 mg. Tubes 25–40 were combined. The lower layer was separated and concentrated to about half its initial volume, then extracted with two 100-ml. portions of benzene. The extract was concentrated to a small volume, combined with the top layer from the countercurrent distribution, and concentrated to about 0.5 ml. Thin layer chromatography (developer Skellysolve B–ethyl acetate, 1:1 v./v.) indicated that the concentrate was a mixture of about seven or eight components. The polyacetylene was separated by preparative t.l.c. in which the developed chromatogram was divided into seven portions using a previously run chromatogram as a guide and extracting each portion with methanol. The extracts with polyacetylene ultraviolet spectra were combined (R_f approximately 0.52 for a Skellysolve B–ethyl acetate 1:1 developer) and evaporated to dryness, giving a semicrystalline residue. After several recrystallizations from benzene–Skellysolve B and finally from methanol–water a few milligrams of crystalline product was obtained, identical with **1** isolated from *C. truncicola* in melting point, ultraviolet and infrared spectra, and t.l.c. behavior.

In the preparative thin layer chromatogram an extract was obtained of a compound with higher R_f (0.71) that had an ultraviolet spectrum with peaks at 252, 265, and 283 mμ, typical of an enediyne. However, there was too little material for identification.

***trans*-1-Methoxy-2-decene-4,6,8-triyne (5).**—Tubes 38–48 from the countercurrent distribution of the initial extract of the culture liquid of *C. candida* were combined, the layers were separated, and the lower layer was concentrated, then extracted with two 75-ml. portions of Skellysolve B. The combined upper layer and Skellysolve B extracts were concentrated to a volume of about 5 ml. and the mixture was distributed between Skellysolve B and a 9:1 methanol–water solution for 60 transfers. The polyacetylene appeared in tubes 23–32, with highest concentration in tube 28. These tubes were combined, the lower layer was separated, and most of the methanol was removed. The aqueous concentrate was extracted with Skellysolve B four times. The extracts were combined with the original top layer, dried over anhydrous sodium sulfate, and concentrated. A thin layer chromatogram of the concentrate using Skellysolve B–ethyl acetate (4:1 v./v.) as developer showed two spots, of which the upper (R_f 0.60) was the polyacetylene. Preparative t.l.c. followed by methanol extraction of the appropriate regions of the chromatogram gave a solution from which a small amount of semisolid material was obtained. This was crystallized from Skellysolve B. The amount of sample available was insufficient for elemental analysis. The compound sintered at 34° and melted at 40–40.5°: λ_{max}^{MeOH} 229 mμ (log ε 4.88), 240 (5.09), 257 (3.62), 271 (3.93), 288 (4.20), 307 (4.29), and 328 (4.14); ν_{max} 2900 (C—H), 2220, 2190 (C≡C), 1448 (OCH_3), and 944 cm.$^{-1}$ (*trans*-CH=CH). The n.m.r. spectrum (in carbon tetrachloride) showed peaks[15,25] at τ 3.5–3.8 (a region of weak peaks obscured by background, α-vinyl H), 4.2 (broad peak, β-vinyl H), 6.05, 6.07, 6.14, and 6.17 (CH_2), 6.71 (O—CH_3), and 8.04 (C≡C—CH_3). Mass spectrum[13] showed a molecular ion with *m/e* 158.

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The Benzohydroxamate Anion

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The benzohydroxamate anion exists in aqueous solution in forms $RCONHO^-$ (A) and $RC(=O)N\bar{O}H \longleftrightarrow RC(-\bar{O})=NOH$ (B) in approximately equal concentration. The possible existence of a third form, $RC(-OH=NO^-$ (C), cannot be disproved; however, if it does exist, its maximum concentration would be not more than 10^{-3} to 10^{-4} times that of the other species.

The hydroxamate anion is a particularly effective nucleophile for attack on the phosphorus atom in phosphoric and phosphonic anhydrides and halides.[1,2] In aqueous solution, the monoanion can potentially exist in three forms in equilibrium with two protonated forms as indicated in Scheme I. From the analysis of ultraviolet absorption spectra Plapinger[3] concluded that in aqueous solution the anion exists in at least two, and possibly all, of the three forms, and that one of the forms is certainly A. In addition, the spectral evidence pointed to the existence of M as the predominant protonated form. Infrared spectra of hydroxamic acids in solvents of graded polarity (but not including water) give strong support to this conclusion.[4–7]

In early reports of the reaction between hydroxamate anions and phosphonofluoridates[2,8,9] it was suggested

(1) B. E. Hackley, Jr., R. Plapinger, M. Stolberg, and T. Wagner-Jauregg, *J. Am. Chem. Soc.*, **77**, 3651 (1955).

(2) R. Swidler and G. M. Steinberg, *ibid.*, **78**, 3594 (1956).

(3) R. E. Plapinger, *J. Org. Chem.*, **24**, 802 (1959).

(4) E. M. Usova and E. M. Voroshia, *Proc. Acad. Sci. USSR, Chem. Sect.*, **113**, 425 (1957).

(5) D. Hadzi and D. Prevorsek, *Spectrochim. Acta*, **10**, 38 (1957).

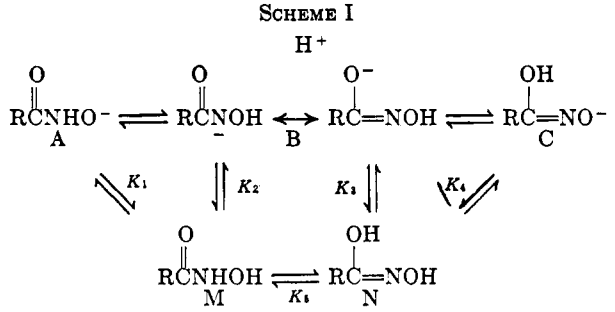
(6) From infrared spectra, Exner[7] has recently concluded that in dioxane and chloroform solutions and in the crystalline state the benzohydroxamate anion exists in form B.

(7) O. Exner, *Collection Czech. Chem. Commun.*, **28**, 1656 (1964); **29**, 1337 (1964).

(8) T. Wagner-Jauregg, *Arzneimittel-Forsch.*, **6**, 194 (1956).

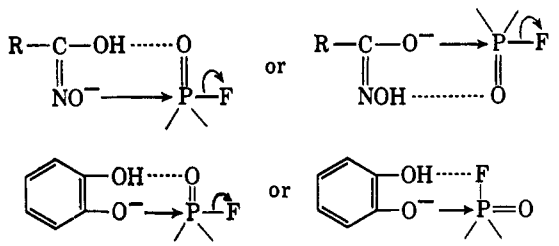
(9) M. A. Stolberg and W. A. Mosher, *J. Am. Chem. Soc.*, **79**, 2618 (1957).

SCHEME I



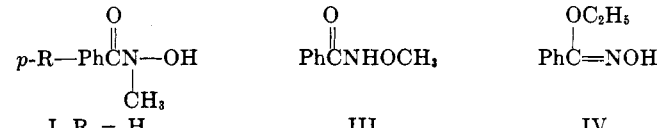
that the very high reaction rates might be due to participation of hydrogen bonding in the transition state, *per* Scheme II. This suggestion was supported by the enhanced reaction rate of the monoanion of catechol where such participation was established,[10-12] over that of the phenolate ion.

SCHEME II



However, the high reaction rates of hypohalites[13] and oximate anions,[14,15] wherein such an assisted attack cannot occur, diminished the force of such argument. A later report by Green and co-workers[16] that N-hydroxyphthalimide, an N-acylhydroxamic acid which cannot "enolize," has the same order of reactivity as the conventional hydroxamic acids eliminated entirely the *need* for invoking a hydrogen-bonded reaction pathway.

Although the need for a cyclic transition state in the reaction of a conventional hydroxamate ion has been eliminated, definitive information on the species involved in the reaction was lacking and the structures present in aqueous solution were incompletely defined. To gain such information, a comparison was made of selected physical and chemical properties of several substituted hydroxamic and one hydroximic acid with those of the corresponding unsubstituted compound, benzohydroxamic acid. Those studied include N-methylbenzohydroxamic acid (I), *p*-methoxy-N-methylbenzohydroxamic acid (II), O-methylbenzohydroxamate (III), and ethylbenzohydroximic acid (IV).



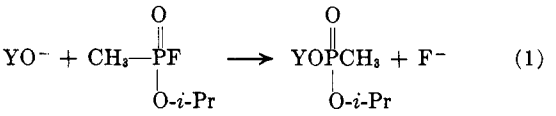
I, R = H
II, R = OCH_3

III

IV

Experimental

Compounds I–IV were kindly provided by Dr. R. E. Plapinger. Their preparation has been described.[3] Procedures for the determination of pK_a and reaction kinetics are identical with those previously reported: pK_a from pH at half neutralization,[2,17] kinetics in unbuffered solution by titration with alkali to maintain constant pH with a Beckman Autotitrator,[2] kinetics in bicarbonate–carbon dioxide buffer determined manometrically in a Warburg apparatus.[18] In each case, the hydroxamate ion was present in large excess, so that the liberation of acid or CO_2 followed a good first-order kinetic relationship. The stoichiometry of acid production in the reaction of isopropyl methylphosphonofluoridate (GB) and compounds I, II, and IV is consistent with the formation of phosphonylated products according to reaction 1. Stoichiometry requires the formation of



(1)

somewhat less than 1 mole of acid: 1 mole per mole of F^- produced, less the mole percentage of hydroxamic acid present as the anion at reaction pH.[2] Depending upon their constitution, phosphonylated hydroxamic acids display a wide range in stability. In neutral aqueous solution phosphonylated unsubstituted hydroxamic acids undergo "instantaneous" Lossen rearrangement.[2] Under identical conditions, N-hydroxyphenylcarbamate (PhOCONHOH) yields products of a sufficiently high degree of stability to warrant its recommendation as a reagent for their identification.[19] Although no examination was made of the products of the present reaction, they would appear to be quite stable. At the completion of reaction, the pH remained constant. There was no evidence of a further acid-producing reaction such as would be expected if phosphonate ion were expelled.

In all prior reaction studies of phosphonofluoridates with hydroxamic acids and oximes, under the conditions employed here, *i.e.*, near neutral aqueous solution, the reactions were always observed to be first order each in the nucleophilic anion and the phosphorus compound, with no significant contribution from the protonated form of the reagent, YOH.[2,14-16] A similar presumption was made in this work. Second-order rate constants were calculated, therefore, from the first-order rate data using the relationship, $k_1 = k_2[A]$, where k_1 and k_2, are, respectively, the first- and second-order rate constants and [A] the initial concentration of the hydroxamate anion.

Results and Discussion

Table I gives the pK_a values and rate constants for the reactions between GB and benzohydroxamic acid and the other four substituted hydroxamic acids. Compounds I and II[20] react rapidly with GB. Compound IV reacts, albeit slowly, but compound III gives no reaction at all. Thus, only those compounds which yield anions by protonic dissociation at the N terminal oxygen atom react with GB. It may be concluded, therefore, that the reactive form of the benzohydroxa-

(10) B. J. Jandorf, T. Wagner-Jauregg, J. J. O'Neill, and M. A. Stolberg, *J. Am. Chem. Soc.* **73**, 5202 (1951).

(11) J. Epstein, D. H. Rosenblatt, and M. M. Demek, *ibid.*, **78**, 341 (1956).

(12) For the reaction of catecholate ion with GB in aqueous solution at 25°, k = 589 l. mole^{-1} min.$^{-1}$ (ref. 11); for phenate in 0.1 *M* KCl at the same temperature, k = 34.3 l. mole^{-1} min.$^{-1}$ for reaction with GB [J. Epstein, R. E. Plapinger, H. C. Michel, J. R. Cable, R. A. Stephani, R. J. Hester, C. Billington, Jr., and G. A. List, *ibid.*, **86**, 3075 (1964)].

(13) J. Epstein, V. Bauer, M. Saxe, and M. M. Demek, *ibid.*, **78**, 4068 (1956).

(14) B. E. Hackley, Jr., Ph.D. Dissertation, University of Delaware, 1956.

(15) A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956).

(16) A. L. Green, G. L. Sainsbury, B. Saville, and M. Stansfield, *ibid.*, 1583 (1958).

(17) Determination of the pK_a of compound IV was made by Dr. H. Michel. It was calculated from the pH at 10% neutralization in 0.1 *N* KCl, corrected for water "blank."

(18) T. Wagner-Jauregg and B. E. Hackley, Jr., *J. Am. Chem. Soc.*, **75**, 2125 (1953).

(19) G. M. Steinberg and J. Bolger, *J. Org. Chem.*, **21**, 660 (1956).

(20) The N-methylhydroxamic acids produced no acid on standing for several hours at pH 7.6 and were thus adequately stable for reaction study using constant pH titration methods. The stability of compound II was confirmed by a colorimetric determination as the complex with ferric ion [S. Hestrin, *J. Biol. Chem.*, **180**, 249 (1949)]. There was no observed change in concentration during a 3-hr. period at room temperature at pH within the range 7–11.

mate ion is limited to either A or C. Compound IV acts as a typical oxime. Its pK_a of 11.6 compares reasonably with that of the benzaldoximes: α, 10.7 and β, 11.3.[21] It has been shown that a reaction rate–pK_a relationship of the Brønsted type exists for the reaction of a large number of oximate anions with GB.[14] Extrapolation of the range of this data to a pK_a of 11.6 gives a calculated $t_{1/2}$ for an oxime of this acid strength of 50–60 min. Because of the errors inherent in the extrapolation and also of the difficulty in accurate determination of the pK_a of compound IV, we do not assign significance to the difference between this value and the observed 111 min. half-time (Table I).

TABLE I

KINETICS OF THE REACTION OF GB WITH SUBSTITUTED HYDROXAMIC ACIDS IN DILUTE AQUEOUS SOLUTION AT 30° AND pH 7.6

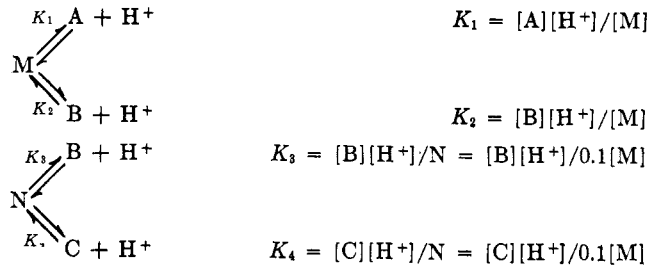
Compd.	pK_a	k,[a] M^{-1} sec.$^{-1}$	$t_{1/2}$,[b] min.	k,[c] M^{-1} sec.$^{-1}$
I, N-methylbenzohydroxamic acid	8.59	3.6	6.5	1.7
II, *p*-methoxy-N-methylbenzohydroxamic acid	8.80	5.75	...	...
III, O-methylbenzohydroxamate	8.88	N.R.[d]	N.R.[d]	...
IV, ethylbenzohydroximic acid	11.6	N.R.[d]	111	58.5
V, benzohydroxamic acid	8.80	20.9[e]	...	...

[a] k is the second-order rate constant for the reaction between the anion and GB in aqueous 0.1 N potassium nitrate solution. Concentrations: compound, 6×10^{-4} M; GB, 6×10^{-5} M. [b] $t_{1/2}$ is half-time of reaction with GB in bicarbonate–CO_2 buffer (ref. 18). Concentrations: compound, 1.12×10^{-2} M; GB, 1.12×10^{-3} M. [c] k is the second-order rate constant for reaction in bicarbonate–CO_2 buffer, calculated from the $t_{1/2}$ values. It is noteworthy that for both the oximes and the hydroxamic acids, reaction rates are somewhat lower in bicarbonate–CO_2 than in the unbuffered solution. [d] No reaction that was appreciably more rapid than the hydrolysis reaction of GB with aqueous solvent ($t_{1/2}$ = *ca.* 300 min.) was observed. [e] See ref. 2.

It is noteworthy that the acidic dissociation constants (K_a) of compounds I–III are of the same magnitude as that of benzohydroxamic acid, while the K_a of IV is about 1000 times smaller. If we make the assumption that the K_a values for the acidic dissociation of benzohydroxamic acid to yield species A, B, and C, respectively, are not changed *substantially* by replacement of the bound hydrogen atom by a methyl or ethyl group, we can obtain estimates of their values from the acidic dissociation constants or compounds I, III, and IV. This type of assumption is most strongly justified where the group effects are primarily inductive; however, even in cases where resonance interaction may be involved, the observed differences are generally small.[22–25] On this basis we assign *approximate* values to the acidic dissociation constants in Scheme I: $K_1 = 10^{-8.6}$, $K_2 = 10^{-8.9}$, $K_4 = 10^{-11.6}$. Spectroscopic evidence suggests that the acid exists in form M^{3-}; however, since such evidence is not highly precise, we will arbitrarily assume, for purpose of the following calculations, a *minimum* probable ratio, M:N, of 10, *i.e.*, $K_5 = 0.1$.

Approximate concentration ratios of the three anionic species in Scheme I can be calculated as follows (Scheme III.)

SCHEME III



$K_1 = [A][H^+]/[M]$

$K_2 = [B][H^+]/[M]$

$K_3 = [B][H^+]/N = [B][H^+]/0.1[M]$

$K_4 = [C][H^+]/N = [C][H^+]/0.1[M]$

$[A]:[B]:[C] \sim K_1:K_2 + 0.1K_3:0.1K_4 \sim 10^{-8.6}:10^{-8.9}:10^{-12.6}$

Thus, we conclude that the benzohydroxamate anion consists essentially of two species, forms A and B, in approximately equivalent amounts and that form C, *if it exists at all*, may be present only in extremely low concentration, perhaps four orders lower in concentration than A or B.

From these results we conclude that species A is certainly a reactive form of the benzohydroxamate anion. The approximately sevenfold reduction in rate (when corrected for actual concentration of form A) that one finds on N-methylation is easily accounted for on steric grounds. However, it is not necessarily the only significant reactive form since we are unable to exclude form C as a *possible* contributor. For C to contribute appreciably to the reaction, its reaction rate should be 10^3–10^4 times greater than that of A. The reaction rate ratio of the anions of IV:I = 35. If we multiply this value by 20, the enhancement in reaction rate of catechol anion over phenolate, we obtain a rate factor of 700, which brings it too close to the required range to permit its exclusion.

It is noteworthy that the N-methyl and O-methylbenzohydroxamates, closely related compounds which have similar basicity (Table I) exhibit markedly different nucleophilicities toward phosphorus. Basicity, while important, is only one of several factors which contribute to nucleophilic reactivity. In comparing the two ions it is instructive that in the N-methyl case there is high electron density on the oxygen atom at the point of reaction, which is buttressed by an attached electronegative atom having a pair of unshared electrons. Such compounds display unusually high nucleophilicity, to which Edwards and Pearson have assigned a factor which they call the α effect.[26] In the anion of the O-

(21) O. L. Brady and N. M. Choski, *J. Chem. Soc.*, 946 (1929).

(22) A. Albert and J. N. Phillips, *ibid.*, 1294 (1956).

(23) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Co., New York, N. Y., 1943, p. 96.

(24) H. C. Brown, D. H. McDaniel, and O. Hafliger in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p. 628.

(25) One exception of this generalization is salicylic acid, which is a much stronger acid than its O-methyl ether. This effect has been ascribed to the formation of a strong intramolecular hydrogen bond in the salicylate anion. However, it has been pointed out (G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 52), that such hydrogen bonds are rarely formed unless the resulting ring structure contains six atoms (including the hydrogen atom) and two conjugated double bonds. Thus, in the case of catechol [O. Gawron, H. Duggan, and C. J. Gulecki, *Anal. Chem.*, **24**, 969 (1952)] and α-hydroxyacetic acid (ref. 24), the effect of O-methylation on pK_a is small, *i.e.*, less than 0.45 units. Even in the case of salicylic acid, the change in pK_a on O-methylation (ether) is only 1.2 units.

(26) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

methyl compound, on the other hand, the negative charge is distributed by resonance stabilization. Nucleophiles with dispersed charges, such as carbonate and carboxylates, generally show decreased reactivity.[27]

(27) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

Acknowledgment.—We wish to thank Dr. R. E. Plapinger for his gift of chemical samples, Drs. H. H. Jaffé and W. F. Sager for valuable discussions, and Dr. B. E. Hackley, Jr., for performing the Warburg runs.

The Reactions of Bromomalononitrile with Bases

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Pentacyanopropenide anion and bromomalononitrile anion are the products of the reaction of ammonia with bromomalononitrile and not aminomalononitrile as reported previously. These products are also obtained when potassium hydroxide, triethylamine, or morpholine is used in place of ammonia. The 1,2-dicyano-1,2-dimorpholinoethylene structure previously assigned to a by-product obtained from the reaction of morpholine with bromomalononitrile has been revised to 1,1-dimorpholino-2,2-dicyanoethylene. We believe that tetracyanoethylene is an intermediate in the formation of the pentacyanopropenide ion and of 1,1-dimorpholino-2,2-dicyanoethylene.

Recently, it has been suggested that the synthesis of adenine from hydrogen cyanide and aqueous ammonia proceeds *via* an intermediate, aminomalononitrile, a trimer of HCN.[1] It had been reported independently that aminomalononitrile is formed from bromomalononitrile on treatment with ammonia in methanol at −80°, and that a material similar to hydrogen cyanide polymer is obtained on allowing the solution to warm to room temperature.[2] We decided to investigate this reaction further, with the hope of elucidating the role of aminomalononitrile in the polymerization of HCN.[3]

Addition of ammonia to bromomalononitrile in methanol at −80° caused an immediate yellow coloration of the solution, as originally reported.[2] However, a similar coloration was produced by potassium hydroxide, triethylamine, or morpholine. The solutions all showed similar absorption maxima at 395 and 413 mμ after reaching room temperature. We have succeeded in isolating the pentacyanopropenide anion as its tetraethylammonium and tetramethylammonium salts from each solution. The latter is identical with an authentic sample prepared from tetracyanoethylene, as shown by its melting point, infrared spectrum, and ultraviolet spectrum.[4]

The spectra of all the reaction mixtures include an additional maximum at 235 mμ which does not appear in the spectrum of the pentacyanopropenide anion. We believe it to be due to the bromomalononitrile anion. When bromomalononitrile was added to excess methanolic potassium hydroxide (0.45 *N*) at room temperature and the spectrum was measured immediately, only a trace amount of the yellow propenide anion was observed and the major ultraviolet-absorbing product was the substance with an ultraviolet peak at 235 mμ (ε 15,000 if complete conversion is assumed). On addition of acid this peak disappeared, but could be regenerated by subsequent treatment with alkali. Bromomalononitrile could be recovered unchanged from the acidified solution. We considered the possibility that in alkaline solution the bromomalononitrile decomposed to give positive bromine, *e.g.*, as follows.

$$BrCH(CN)_2 + 2OH^- \longrightarrow {}^-CH(CN)_2 + OBr^- + H_2O$$

However, neither $CH(CN)_2^-$ nor OBr^- absorbs at 235 mμ—the OBr^- ion has an absorption maximum at 330 mμ, which we did not observe.[5]

When ammonia was used as the base a shoulder was present in the ultraviolet spectrum of the reaction mixture which suggested the presence of a fourth band at about 255 mμ in addition to the main bands discussed above. If the reaction mixtures were diluted with excess methanol before being brought to room temperature, this shoulder became a well-resolved peak. Attempts to isolate the compound responsible for the 255-mμ peak were abandoned when a mixture containing at least seven new compounds was obtained.

Since the pentacyanopropenide ion is one of the principal products obtained on treating tetracyanoethylene with alkalies,[4] it seemed at least possible that our reactions were proceeding *via* tetracyanoethylene. Two further observations are consistent with this mechanism.

When tetracyanoethylene is treated with primary or secondary amines, 1,1-diamino-2,2-dicyanoethylenes are produced.[6] The product obtained from the reaction of tetracyanoethylene and morpholine was found to be identical with a derivative obtained previously[2] by treatment of bromomalononitrile with morpholine and formulated as I. Clearly, this substance is in fact II.

When the solution obtained by adding ammonia to bromomalononitrile in methanol at −80° is analyzed for tetracyanoethylene using the color reaction with dimethylaniline,[6] positive results are obtained. The yield is always small, never exceeding 1.5% in our experience. This is quite consistent with a tetracyano-

(1) J. Oro and A. P. Kimball, *Arch. Biochem. Biophys.*, **94**, 217 (1961); **96**, 293 (1962).

(2) W. Ruske and E. Ruske, *Ber.*, **91**, 2496 (1958).

(3) For a discussion of the structure of polymeric HCN see T. Volker, *Angew. Chem.*, **72**, 379 (1960); W. Ruske, M. Becker, H. J. Jahns, *Z. Chem.*, **1**, 271 (1961); J. Vaughan, *J. New Zealand Inst. Chem.*, **22**, 149 1958).

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

(5) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954); L. Farkas and F. S. Klein, *J. Chem. Phys.*, **16**, 886 (1948).

(6) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).