for the *n*-butyl and isobutyl compounds are of intermediate magnitude, as are their dissociation constants. Coming to the most stable derivatives, the *n*-propyl and isopropyl, the derived bases are stronger than any of the members of the series, with the exception of the ethyl compound. However, the methyl, ethyl, and *n*-amyl compounds show no such correlation.

Acknowledgment.—The authors wish to thank Mr. Robert E. Powers for aid in the preparation of the manuscript.

Summary

1. Seven previously unreported thioimidobenzoate hydrochlorides in a series of eleven compounds have been prepared by the general method of Pinner.

2. The thermal behavior of the series has been investigated. It has been shown that they pyrolyze according to the Pinner reaction giving the corresponding thioamide and alkyl halide, although minor quantities of benzonitrile, mercaptan, and hydrogen chloride are also produced. They are considerably more stable than the analogous oxygen compounds.

3. Characteristic "mean temperatures of pyrolysis" are reported for this series and for a variety of ordinary imido ester salts.

4. Alkyl thioimidobenzoate salts react normally with water giving thiolesters and ammonium chloride, although the abnormal reaction yielding benzonitrile, mercaptan, and hydrogen chloride occurs to some extent. The hydrolytic stability of these substances is also greater than that of the corresponding oxygen derivatives.

5. The data suggest a linear relationship between the logarithms of the velocity constants for hydrolysis and the "mean temperatures of pyrolysis" of the *n*-alkyl thioimidobenzoate hydrochlorides.

6. The phenyl derivative behaves abnormally when subjected to the action of heat and water.

7. The dissociation constants of the thioimido esters have been determined, and in their strengths as bases these substances are found to be comparable with the ordinary imido esters. The general relationship of high velocity constant and low dissociation constant, reported previously for the oxygen compounds, does not exist for the sulfur derivatives, although some of the data are in harmony with this view.

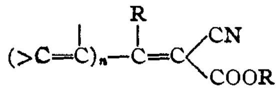
TROY, NEW YORK RECEIVED FEBRUARY 12, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Polyenes. III. The Absorption Spectra of Some Alkylidene Derivatives of Cyanoacetic Acid and its Esters[1]

BY LAWRENCE J. ANDREWS, STANLEY J. CRISTOL, SEYMOUR L. LINDENBAUM AND WILLIAM G. YOUNG

Recent experiments performed in this Laboratory have been directed toward the preparation of conjugated polyenes through the condensation of cyanoacetic acid and its esters or their alkylidene derivatives with unsaturated aldehydes and ketones. In searching for a simple method of detecting variations in the positions of the unsaturated linkages from those anticipated from the method of synthesis, a detailed study of the absorption spectra of compounds of the type



$$(>\overset{|}{C}{=}\overset{|}{C})_n{-}\overset{\overset{R}{|}}{C}{=}C\begin{cases}CN\\COOR\end{cases}\qquad R = H,\ CH_3 \text{ or } C_2H_5$$

has been undertaken. The present investigation has been concerned with compounds in which *n* in the above formula equals 0, 1 or 2. This study has been pursued mainly to determine the effects on spectra of increasing the number of ethylenic linkages in conjugation with the cyano and carboxyl groups. Attention has also been given to the effects of introducing side chain methyl substituents onto the olefinic linkages, and a comparison of the spectra of the carboxylic acids with those of their esters has been made.

The compounds chosen to represent the case $n = 0$ in the above formula were methyl isopropylidenecyanoacetate, ethyl 1-methylpropylidenecyanoacetate, α-cyanocrotonic acid and its methyl ester, the preparations of which have all been described previously.[2] The compounds of the group $n = 1$, citrylidenecyanoacetic acid, α-cyanosorbic acid and α-cyano-δ-methylsorbic acid were prepared, respectively, by the condensation of citral, crotonaldehyde and β-methylcrotonaldehyde with cyanoacetic acid. The methyl esters of the two substituted sorbic acids were prepared by the silver salt–methyl iodide method. As representatives of the group $n = 2$, β-ionylidenecyanoacetic acid and its methyl ester[3] were used. The α isomers of these compounds[3] were considered in the $n = 1$ series.

The ultraviolet absorption spectra of these compounds in 95% ethanol solution were measured on the Beckman Spectrophotometer. The values of the maximum molecular extinction coefficient, ε, and the corresponding wave lengths of maximum absorption are listed in Table I. The absorption curves are given in Fig. 1.

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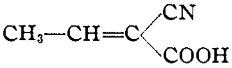
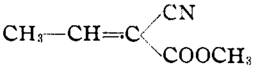
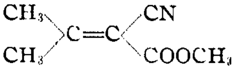
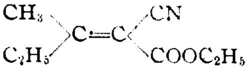
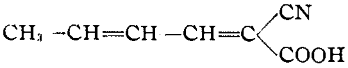
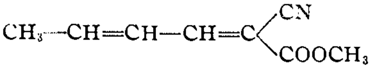
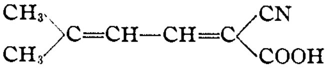
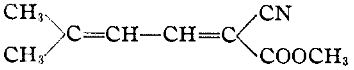
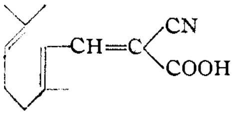
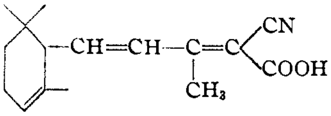
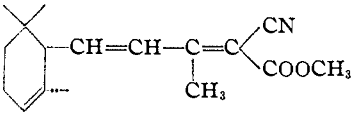
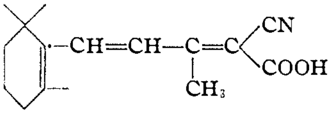
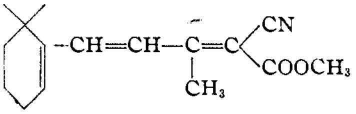
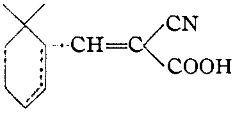
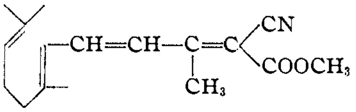
[1] This work was made possible by a research grant from Sharp and Dohme, Inc.

[2] (a) Cope, THIS JOURNAL, 63, 3452 (1941); (b) Young, Andrews, Lindenbaum and Cristol, *ibid.*, 66, 810 (1944).

[3] Young, Andrews and Cristol, *ibid.*, 66, 520 (1944).

TABLE I

THE ABSORPTION SPECTRA OF SOME ALKYLIDENE DERIVATIVES OF CYANOACETIC ACID[a]

	Compound	Formula	$\lambda_{max.}$, mμ	$\epsilon_{max.}$
1	Cyanocrotonic acid	 $CH_3{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOH}$	215	9700
2	Methyl cyanocrotonate	 $CH_3{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOCH_3}$	220	8400
3	Methyl isopropylidenecyanoacetate	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOCH_3}$	230	11100
4	Ethyl 1-methylpropylidenecyanoacetate	 $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}C{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOC_2H_5}$	232	12200
5	α-Cyanosorbic acid	 $CH_3{-}CH{=}CH{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOH}$	276	21700
6	Methyl α-cyanosorbate	 $CH_3{-}CH{=}CH{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOCH_3}$	282	22300
7	α-Cyano-δ-methylsorbic acid	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{=}CH{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOH}$	295	20900
8	Methyl α-cyano-δ-methylsorbate	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C{=}CH{-}CH{=}C{<}\genfrac{}{}{0pt}{}{CN}{COOCH_3}$	302	22700
9	Citrylidenecyanoacetic acid		300	21900
10	α-Ionylidenecyanoacetic acid		286	14300
11	Methyl α-ionylidenecyanoacetate		293 355	16100 6850
12	β-Ionylidenecyanoacetic acid		331 275	12500 8700
13	Methyl β-ionylidenecyanoacetate		353 286	11900 10300
14	α- and β-cyclocitrylidenecyanoacetic acid		307 223	4350 5500
15	Methyl pseudoionylidenecyanoacetate		353	17300

[a] The solvent was 95% ethanol.

The compounds belonging to the class $n = 0$ showed absorption maxima in the range 215–232 mμ with values of $\epsilon_{max.}$ ranging from 9700–12200. Those belonging to the $n = 1$ series which were not contaminated with members of the $n = 0$ and $n = 2$ series showed maxima in the range 276–302 mμ with corresponding ε values of 20900–22300. In line with the general observation that an increase in the number of conjugated double bonds in a polyene chain shifts the absorption maximum toward the visible, the members of the $n = 2$ series showed maxima at about 350 mμ.

It has been noted previously[4] that there seems to exist a linear relationship between the number

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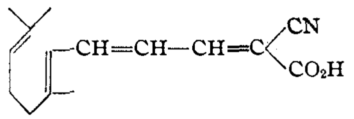
[4] (a) Smakula, *Angew. Chem.*, **47**, 657 (1934); (b) Hausser, Kuhn and Seitz, *Z. physik. Chem.*, **B29**, 391 (1935).

of double bonds in a conjugated system and the intensity of maximum absorption. With this assumption in mind one should predict that for a member of the $n = 2$ class of compounds considered in this work the maximum extinction coefficient should lie in the range 32000–35000. In agreement with this prediction is the report of Heilbron and co-workers[5] that citrylidene-α-cyanocrotonic acid



has an $\epsilon_{\max.}$ of 34100 ($\lambda_{\max.}$ 348 mμ) in ethanol. The extinction coefficients of β-ionylidenecyanoacetic acid and its methyl ester in the 330–350 mμ range were considerably lower than 34100. However, these compounds also showed absorption maxima in the range of compounds of the class $n = 1$, owing to the fact that they were prepared from samples of β-ionone which contained some α-ionone.[3] Similarly the $n = 1$ maxima in the spectra of α-ionylidenecyanoacetic acid and its methyl ester, which were prepared from α-ionone contaminated with its β isomer,[3] were lowered owing to the presence of the $n = 2$ type isomer.

It is interesting to compare the wave length of maximum absorption of the acids with those of their corresponding esters. In general the esters displayed maximum absorption 5–7 mμ farther toward the visible than did the acids from which they were derived (compounds 1 and 2, 5 and 6, 7 and 8, 10 and 11 of Table I). The difference between the positions of the maxima of β-ionylidenecyanoacetic acid (12) and its methyl ester (13) was considerably larger (22 mμ). It may be, however, that the positions of the true maxima of these compounds are disguised because of the fact that they contain an impurity of the corresponding α or β isomer. No consistent differences between the extinction coefficients of the acids and their esters were observable.

It is further interesting to note the effects of replacing a hydrogen attached to one of the conjugated olefinic linkages with a methyl or ethyl group. When the group is substituted on the carbon beta to the carboxyl group, a shift of 10–12 mμ toward the visible takes place (*cf.* 2 and 3, 2 and 4, 5 and 10, 6 and 11 in Table I). When the methyl substitution takes place on the carbon delta to the carboxyl group, the shift amounts to about 20 mμ (*cf.* 5 and 7, 6 and 8, 5 and 9). These shifts may be the result of increased polarization of the molecule through the added hyperconjugation offered by the new alkyl group as suggested by Mulliken and co-workers.[6]

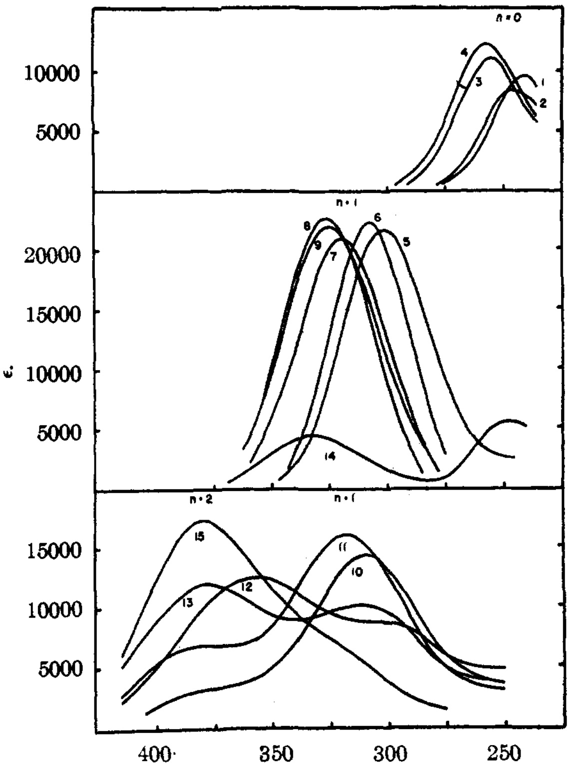
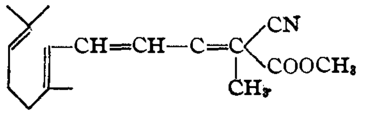


Fig. 1.

The Use of the Absorption Spectra in the Determination of Structure.—The data presented above have been found quite useful in the study of the structures of other polyene derivatives of cyanoacetic acid which have been prepared in this Laboratory. For example, the product from the base catalyzed condensation of cyanoacetic acid with β-cyclocitral[7] showed absorption maxima at both 307 mμ (ε 4350) and 223 mμ (ε 5500) [see Table I and Fig. 1] indicating that the material was very likely a mixture of α- and β-cyclocitrylidenecyanoacetic acids. It is probable that the β-cyclocitral used was contaminated with some of the α-isomer since the aldehyde had been recovered from its semicarbazone by a method which was later shown to cause rearrangement in the ionone series.[8]

The absorption data were also used in considering the structure of the product obtained by the condensation of citral with methyl isopropylidenecyanoacetate. The high boiling oil obtained by distillation of the crude product gave the proper combustion analysis for methyl pseudoionylidenecyanoacetate



The absorption maximum of this material was

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(5) Batty, Burowoy, Heilbron, Jones and Lowe, *J. Chem. Soc.*, 755 (1937).

(6) (a) Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941); (b) Mulliken and Rieke, *ibid.*, **63**, 1770 (1941).

(7) Prepared from citral by the method of Tiemann, *Ber.*, **33**, 3719 (1900).

(8) Young, Cristol, Andrews and Lindenbaum, THIS JOURNAL, **66**, 855 (1944).

found to lie in the expected range (353 mμ) (see Table I and Fig. 1). The maximum extinction coefficient, however, had about one-half the magnitude predicted for a compound of the $n = 2$ series. This decrease in extinction coefficient may be due to the presence of *cis-trans* isomers[9] or to the presence of an isomer of the compound of the above formula in which the conjugation of the double bonds with the cyano and carbomethoxy groups is broken.

Experimental Part

α-Cyanosorbic Acid.—This was prepared by a modification of the procedure of Hamann[10] as follows: Forty-five grams (0.53 mole) of cyanoacetic acid was dissolved in 21 ml. of water, and sufficient 18 *N* sodium hydroxide solution was added to make the mixture basic to nitrazine paper. The mixture was cooled to 2°, and 37 g. (0.53 mole) of freshly distilled crotonaldehyde was added over a ten-minute period with vigorous stirring. A few drops of sodium hydroxide solution were added until the mixture was again basic. The temperature rose quickly to 35°, and a yellow salt precipitated. Sixty ml. of ice water was added, and the mixture was cooled to 10° and stirred for one and one-half hours. Water was added to dissolve the yellow salt, and the solution was acidified with 2 *N* sulfuric acid. The light yellow precipitate was recrystallized from water. The yield of dry α-cyanosorbic acid was 37.6 g. (51.5%), m. p. 163–5° (with decarboxylation). Haerdtl[11] reports m. p. 163°.

α-Cyano-δ-methylsorbic Acid.—β-Methylcrotonaldehyde diethylacetal was prepared according to the method of McElvain and co-workers.[12] The acetal was hydrolyzed to β-methylcrotonaldehyde (b. p. 60–65° (60 mm.)) in an aqueous solution of tartaric acid.[13]

Four and one-half grams (0.053 mole) of cyanoacetic acid was allowed to react with 4.45 g. (0.053 mole) of freshly distilled β-methylcrotonaldehyde in sodium hydroxide solution in a manner similar to that described for the preparation of α-cyanosorbic acid. When the reaction was complete (two hours), the basic solution was acidified with dilute sulfuric acid and the resulting brick-red precipitate weighed 6.25 g.; yield, 78%. Two grams of this material was recrystallized twice from water using decolorizing carbon. The dried product, a brilliant orange crystalline material, weighed 1.22 g. The properties of α-cyano-δ-methylsorbic acid were as follows: m. p. 168–171°. *Anal.* Calcd. for $C_8H_9O_2N$: C, 63.57; H, 6.00; neut. eq., 151.2. Found: C, 63.66; H, 6.05; neut. eq., 148.4.

Methyl α-Cyanosorbate and Methyl α-Cyano-δ-methylsorbate.—These esters were prepared conveniently by refluxing and stirring the water-insoluble silver salts of the corresponding acids for several hours in ether which contained an excess of methyl iodide. When the reaction was complete, the ether solution was filtered from the silver residues which were washed with ether and the washings were added to the filtrate. The esters crystallized after evaporation of the solvent.

From 37.6 g. (0.272 mole) of α-cyanosorbic acid was obtained 30.1 g. of crude, light orange crystalline ester (yield 73%). After two recrystallizations from aqueous methanol using decolorizing carbon and two recrystallizations from ligroin, white needles were obtained. The properties of methyl α-cyanosorbate were as follows: m. p. 54–59°. *Anal.* Calcd. for $C_8H_9O_2N$: C, 63.57; H, 6.00. Found: C, 63.52; H, 6.04.

From 3.02 g. (0.020 mole) of α-cyano-δ-methylsorbic acid was obtained 2.80 g. of crude canary-yellow crystalline ester (yield 84.5%). After two recrystallizations from ligroin, yellow crystals of methyl α-cyano-δ-methylsorbate having the following properties were obtained: m. p. 70.5–75.5°. *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71. Found: C, 65.10; H, 6.81.

Citrylidenecyanoacetic Acid.—This material was prepared by the base catalyzed condensation of 152 g. (1.0 mole) of citral (Dodge and Olcott Co.) with 100 g. (1.18 mole) of cyanoacetic acid according to the directions of Tiemann.[7] It was found necessary to use an excess of cyanoacetic acid in order to obtain a crystalline product. The solid from two such runs after two recrystallizations from a mixture of benzene and ligroin weighed 82.8 g. and had a m. p. 119.5–122.5° (Tiemann[7] gives m. p. 122°).

Conversion of Citrylidenecyanoacetic Acid to β-Cyclocitral.—Recrystallized citrylidenecyanoacetic acid (103 g., 0.47 mole) was cyclized and cleaved by the method of Tiemann.[7] The crude cyclocitral was dissolved in ether, extracted with dilute sodium hydroxide and dried over sodium sulfate. After removal of the ether, the cyclocitral was distilled under nitrogen at reduced pressure. The fraction boiling 88–123° (12 mm.) weighed 21.3 g. (0.14 mole); 30% yield. The crude aldehyde was converted to the semicarbazone according to Tiemann[7] in a 50% yield; m. p. 148–158°. This material was crystallized from glacial acetic acid and then from methanol to give 7.0 g. of m. p. 166–168°; $\lambda_{max.}$ 273 mμ (ϵ 24500) in 95% ethanol. Burowoy[14] reports $\lambda_{max.}$ 272 mμ (ϵ 23800) for β-cyclocitral semicarbazone of m. p. 167°. The semicarbazone was decomposed by steam distillation in the presence of phthalic anhydride.[7] From 5.6 g. (0.027 mole) of the semicarbazone was obtained 2.5 g. (0.016 mole) of β-cyclocitral (b. p. 89–97° (9 mm.) $n^{17}D$ 1.4965, $\lambda_{max.}$ 249 mμ (ϵ 7700) in 95% ethanol) Burowoy[14] reports $\lambda_{max.}$ 245 mμ (ϵ 8300) in ethanol for β-cyclocitral. The over-all yield from citrylidenecyanoacetic acid was 3–10%.

The use of 85% phosphoric acid as a cyclizing agent in place of sulfuric acid and water gave β-cyclocitral as reported by Strain[15] but in a much lower yield. Strain,[16] using a method similar to that of Tiemann,[7] reports that the yield varies widely with experimental conditions, obtaining over-all yields of 5–16% starting with crude, noncrystalline citrylidenecyanoacetic acid.

Cyclocitrylidenecyanoacetic Acid.—A mixture of 2.47 g. (0.0162 mole) of β-cyclocitral and a solution of 1.85 g. (0.0218 mole) of cyanoacetic acid in 15 ml. of 4 *N* sodium hydroxide was shaken overnight, by which time the β-cyclocitral had dissolved completely. The solution was acidified with dilute hydrochloric acid. The oil which formed was extracted in ether, and the acid was extracted from the ether solution with 3 *N* sodium hydroxide. This basic solution was washed with ether and acidified with 3 *N* hydrochloric acid. The oil formed was extracted in ether, and the solution was dried over sodium sulfate. The ether was removed leaving a viscous light yellow liquid which crystallized to form yellowish-white needles after standing for two days under vacuum. The crude product weighed 2.60 g. (yield 73%). After one recrystallization from aqueous acetic acid and two recrystallizations from ligroin, white crystals having the following properties were obtained: m. p. 111–113.5° (with softening below this range). *Anal.* Calcd. for $C_{13}H_{17}O_2N$: C, 71.20; H, 7.82; neut. eq., 219.3. Found: C, 71.19; H, 8.01; neut. eq., 217.2. The spectrum of this material indicated that it was a mixture of α- and β-cyclocitrylideneacetic acids.

Methyl Pseudo-ionylidenecyanoacetate.—The method used is a modification of that described[17] for the condensation of benzaldehyde and methyl isopropylidenecyanoacetate. A mixture of 9.12 g. (0.060 mole) of citral and 8.34 g. (0.060 mole) of methyl isopropylidenecyanoacetate

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(9) Heilbron, Johnson, Jones and Spinks, *J. Chem. Soc.*, 727 (1942).

(10) Hamann, U. S. Patent, 2093519, Sept. 21, 1937; *Chem. Abst.*, **31**, 7883 (1937).

(11) Haerdtl, *Monatsh.*, **26**, 1394 (1905).

(12) McElvain, Clarke and Jones, THIS JOURNAL, **64**, 1966 (1942).

(13) Fischer, Ertel and Lowenberg, *Ber.*, **64**, 33 (1931).

(14) Burowoy, *J. Chem. Soc.*, 20 (1941).

(15) Strain, *J. Biol. Chem.*, **102**, 137 (1933).

(16) Strain, private communication.

(17) Wittig and Hartmann, *Ber.*, **72B**, 1387 (1939).

was treated with 0.2 g. of piperidinium acetate and six drops of piperidine. The solution darkened immediately, and water droplets appeared. Every hour for six hours the water was removed under vacuum and fresh piperidine was added. The mixture was then heated for two days at 45°. The dark red mixture was dissolved in 100 ml. of ether, and the solution was washed with water, 1 *N* sulfuric acid and 2% aqueous sodium carbonate, and was dried over sodium sulfate. After removing the ether the residue was distilled under reduced pressure. The fractions from the two such runs which distilled 170–185° (2.5 mm.) were combined (7.4 g.) and redistilled. A fraction (2.7 g.) distilling from 170–180° (2.5 mm.) was collected as methyl pseudo-ionylidenecyanoacetate. It had the following properties: n^{24}D 1.5760. *Anal.* Calcd. for $C_{17}H_{23}O_2N$: C, 74.69; H, 8.48. Found: C, 74.61; H, 8.56.

The authors are indebted to Mr. Bruce Day and Mr. Robert Sprague for the combustion analyses.

Summary

The absorption spectra of a number of polyene derivatives of cyanoacetic acid and its esters have been measured and compared. Particular attention has been paid to the effects on the spectra of increasing the number of double bonds in conjugation with the cyano and carboxyl groups. The effects of methyl substitution on the olefinic linkages have been noted; and the spectra of some of the acids have been compared with those of the corresponding esters. The application of such data to the study of the structure of alkylidenecyanoacetic acids has been illustrated.

LOS ANGELES, CALIFORNIA RECEIVED JANUARY 20, 1945

[CONTRIBUTION FROM THE UNITED STATES PUBLIC HEALTH SERVICE VENEREAL DISEASE RESEARCH AND POSTGRADUATE TRAINING CENTER, JOHNS HOPKINS HOSPITAL]

Aminoarsenosobenzoic Acids[1]

BY G. O. DOAK, H. G. STEINMAN AND HARRY EAGLE

The failure of the carboxyl group to inhibit the treponemicidal activity of 4-arsenosoanthranilic acid has been discussed previously.[2] In order to study this effect further we have attempted the preparation of the remaining nine isomeric aminoarsenosobenzoic acids.

We have previously reported[3] unsatisfactory results with Maschmann's procedure[4] for the preparation of 2-arsono-4-nitrobenzoic acid. Similar difficulties have since been encountered in this Laboratory with the permanganate oxidation of 2-nitro-*p*-toluenearsonic acid and 4- and 6-nitro-*o*-toluenearsonic acids. Maschmann's procedure left these compounds nearly unchanged; in order to complete the reaction it was found necessary to reflux with permanganate solution for as long as a week. Accordingly, we have prepared all the desired arsononitrobenzoic acids, except 3-arsono-5-nitro- and 2-arsono-3-nitrobenzoic acids, from the corresponding amines by the Bart reaction as used by Karrer[5] for the preparation of 2-arsono-5-nitrobenzoic acid. When the amine was particularly difficult to diazotize, *e. g.*, 3-amino-4-nitrobenzoic acid, the best results were obtained by precipitating the acid from alkaline solution in a finely divided state just prior to diazotization. The majority of the arsononitrobenzoic acids were surprisingly soluble in water and the solutions from the Bart reactions had to be concentrated to small volumes before the acids could be precipitated. 3-Arsono-5-nitro, 3-arsono-2-nitro- and 2-arsono-3-nitrobenzenearsonic acids precipitated as acid salts even from solutions strongly acid to congo red. A similar effect has been noted with 4-arsono-2-nitrobenzenearsonic acid.[6] The free acids were obtained by recrystallization from hydrochloric acid. Even under these conditions, however, the 3-arsono-2-nitrobenzoic acid precipitated as an acid salt. The melting points of 4-arsono-3-nitro- and 2-arsono-4-nitrobenzoic acids prepared by this procedure, and also of the corresponding amino compounds, differed considerably from those reported by Maschmann. In view of the slowness of the permanganate oxidation, we believe that the compounds he reported were mixed with unoxidized material.

The preparation of the 3-arsono-5-nitro- and 2-arsono-3-nitrobenzoic acids offered unexpected difficulties. The Bart reaction applied to the 3-amino-5-nitrobenzoic acid, and several modifications including the Scheller reaction, failed to give any trace of an arsonic acid. The Bart reaction also failed with 3-nitro-anthranilic acid. We were unable to nitrate *m*-arsonobenzoic acid even under the most drastic conditions. Accordingly, it was necessary to prepare both 3-arsono-5-nitro- and 2-arsono-3-nitrobenzoic acids by oxidation of the corresponding nitrotoluenearsonic acids.

5-Arsonoanthranilic acid was prepared by the method of Cohen, King and Strangeways.[6] The other aminoarsonobenzoic acids were obtained by reduction of the arsononitrobenzoic acids. With compounds containing a nitro group ortho to the arsonic acid group, the method of Jacobs, Heidelberger and Rolf[7] was used, as it had previously been noted that the reduction of such compounds with Raney nickel was unsatisfactory.[8] The other arsononitrobenzoic acids were reduced with

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[1] Paper IX in the series entitled "The Preparation of Phenylarsenoxides;" previous paper, THIS JOURNAL, **66**, 197 (1944).

[2] Eagle, Hogan, Doak and Steinman, *J. Pharmacol.*, **74**, 210 (1942).

[3] Doak, Steinman and Eagle, THIS JOURNAL, **66**, 194 (1944).

[4] Maschmann, *Ber.*, **57**, 1759 (1924).

[5] Karrer, *ibid.*, **48**, 1058 (1915).

[6] Cohen, King and Strangeways, *J. Chem. Soc.*, 3236 (1931).

[7] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1580 (1918).

[8] Doak, Steinman and Eagle, *ibid.*, **63**, 99 (1941).