[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Dehalogenation of α,β-Dibromo Acids. III. Acids of the Pyridine and Quinoline Series[1]

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In continuing our study of the dehalogenation of α,β-dibromo acids it was decided to prepare pyridyl- and quinolylacrylic acid dibromides and to study their decompositions with various bases. Einhorn[2] has reported that β-(2-quinolyl)-acrylic acid upon treatment with bromine in acetic acid solution yields a dibromide, m. p. 180–181°, which forms 2-quinolylacetylene upon reaction with aqueous alkali carbonates. No analyses were given for the dibromide or for the acetylene. In attempting to repeat this work we obtained an acid which analyzed correctly for a quinolylacrylic acid dibromide but which melted at 228–230° (corr.) and gave no acetylene with aqueous sodium or potassium carbonates. The bromination of quinolylacrylic acid was studied in great detail using different solvents, different temperatures and varying amounts of bromine. In no case did a dibromo acid melting at 180–181° result.

The dehalogenations of pyridyl- and quinolylacrylic acid dibromides were expected to proceed as shown in the equations

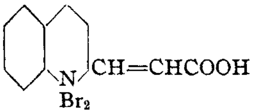
$$\text{RCHBrCHBrCOOH} \xrightarrow{-\text{HBr}} \begin{cases} \text{RCH=CHBr (A)} + \text{CO}_2 \\ \text{RCH=CBrCOOH} \end{cases} \qquad (1)$$

Much to our surprise, however, the dehalogenations proceeded quite differently and the vast majority of the products consisted of the original acrylic acids.

$$\text{RCHBrCHBrCOOH} \xrightarrow{-\text{Br}_2} \text{RCH=CHCOOH}$$

With aqueous potassium hydroxide, sodium carbonate, or pyridine, alcoholic potassium hydroxide or anhydrous pyridine the results were the same. Even when boiled in water or alcohol without the addition of other bases the acrylic acids (hydrobromides) were produced in almost quantitative yields. In so far as we have been able to determine this constitutes the first case on record in which dehalogenation of α,β-dibromo acids with both weak and strong bases has led practically exclusively to olefinic acids.[3]

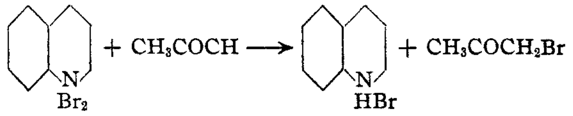
In seeking an explanation of these phenomena, we were struck with the possibility that our acids might contain the bromine atoms bound to the nitrogen atom (Formula A) instead of to the double bond (Formula B)



(A)

(B)

If such were the case the reactions of these substances with bases could be easily explained, since other perbromides of this type readily regenerate the original unbrominated material with bases. In order to decide this point a study of the perbromides of pyridine and quinoline was made and the following points noted. (1) The perbromides[4] are highly colored solids which dissociate on heating to give free bromine. Our acids were all white crystalline solids which were stable up to their melting points (>200°). (2) The perbromides react at room temperatures with



acetone, the lachrymatory properties of the bromoacetone formed constituting a delicate test for their presence. The pyridyl- and quinolylacrylic acid dibromides did not react with acetone even at its boiling point and were in fact conveniently purified by treatment with this solvent. (3) Further bromination of the pyridine and quinoline dibromo acids yielded perbromides which reacted with acetone in the same manner as quinoline and pyridine perbromides. In view of these facts it seems safe to conclude that the compounds in question are accurately represented by formulas of type B.

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[1] First paper in this series, THIS JOURNAL, **55**, 4279 (1933).

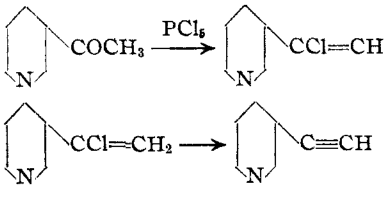
[2] Carlier and Einhorn, *Ber.*, **23**, 2897 (1890).

[3] Although olefinic acids have been previously identified among the products of such dehalogenations the amount has usually been quite small except in a few instances. Pfeiffer [*Ber.*, **43**, 3041 (1910)] reports that the principal product of the reaction of cinnamic acid dibromide with pyridine is cinnamic acid itself, although he actually isolated only about 40% of this material in a pure form. We repeated this work and confirmed the results at least qualitatively. Ingold and Smith [*J. Chem. Soc.*, 2742 (1931)] obtain only crotonic acid from the action of aqueous potassium hydroxide on α-iodo-β-chlorobutyric acid. In both of these cases, however, the yield of olefinic acid is greatly decreased if other bases than those specified are used.

[4] *Cf.* Trowbridge, THIS JOURNAL, **21**, 67 (1899).

The fact that cinnamic acid dibromide with pyridine gave a considerable amount of cinnamic acid led us to look for an analogy between this reaction and the dehalogenation of the pyridine and quinoline acids here studied. In both cases there is present in the reaction mixture a heterocyclic nitrogen atom of the pyridine type. It seemed probable that this basic nitrogen atom was influencing the course of the dehalogenation even in the presence of other bases. In order to determine if this were true in other cases, we turned to the dehalogenation of α,β-dibromobutyric acid. It has already been shown[5] that this acid behaves differently with sodium carbonate and pyridine. With the first reagent only a trace of bromopropene is formed. With the second reagent, however, a 28% yield of bromopropene results. When α,β-dibromobutyric acid (1 mole) was treated with an aqueous solution of a mixture of sodium carbonate (2 moles) and pyridine (2 moles) bromopropene was again obtained in 28% yields just as though pyridine alone were present. This evidence apparently confirms the theory of the directing influence of the pyridine nitrogen. Further work on the role of the base in these dehalogenations is now underway.

Since very few heterocyclic acetylenes are known it was hoped that quinolyl- and pyridylacetylenes could be obtained by the dehalogenation of the bromoolefins that we expected to obtain from the pyridine and quinoline dibromo acids. Since these bromoolefins did not arise, however, this step was impossible. β-Pyridylacetylene was synthesized by the method outlined in the equations



the product is a white crystalline solid which sublimes readily and melts at 38.5°. It gives the characteristic reactions of acetylenes with alcoholic silver nitrate and ammoniacal cuprous chloride and forms a mercury derivative of m. p. 250–252°.

Experimental

All melting points given in this work have been corrected for the emergent thermometer stem.

β-(2-Quinolyl)-acrylic Acid.—The first step in the preparation of this acid according to the method of Einhorn[6] consists in the condensation of quinaldine with chloral. We were able to increase the yields of this condensation product from 60 to 95% and to eliminate the ten to fifteen recrystallizations often necessary for purification by using anhydrous pyridine as a catalyst. A mixture of 100 g. (0.7 mole) of dry quinaldine (Eastman product b. p. (15 mm.) 118–119°), 75–100 g. of dry pyridine and 105 g. (0.78 mole) of chloral was heated on a steam-bath for about two hours. At the end of this time the semi-solid mass was added to 500 cc. of cold water. The oil which first formed soon set to a crystalline solid which was broken up as well as possible and stirred vigorously for about five minutes in order to remove as much of the pyridine as possible. The solid was collected on a filter, washed well with water and dried. Recrystallization from 75% alcohol gave 195 g. (95% yield) of a product melting at 148°.

The hydrolysis of this product with alcoholic potassium hydroxide[7] gave β-(2-quinolyl)-acrylic acid in 75% yields. The product is readily purified by boiling with activated charcoal in dilute aqueous alkali solution. It melts at 194–196°. The hydrochloride melts at 216–218° and the acetate at 203°. The hydrobromide, m. p. 218–220°, was analyzed after recrystallization from alcohol.

Anal. Calcd. for $C_{12}H_{10}O_2NBr$: Br, 28.6. Found: Br, 28.2.

β-(4-Pyridyl)-acrylic Acid.—The condensation of γ-picoline with chloral has been studied most recently by Rabe and Kindler.[8] In this work they report a yield of 8–9%. By means of the following procedure we consistently prepared γ-picoline-chloral, m. p. 166–167°, in yields of 16–18%.

A mixture of 75 g. (0.80 mole) of γ-picoline (b. p. 142.5–144.5°), 118.6 g. (0.80 mole) of chloral and 1 g. of zinc chloride was kept at a temperature of about 34° for twenty-four hours and shaken occasionally. It was then placed on a steam-bath for two hours at the end of which time the reaction product was poured into water. The oil which separated was washed well with water, dissolved in 3 *N* hydrochloric acid and boiled three times with fresh 20 g. portions of animal charcoal. The dark colored liquid obtained from the above treatment was neutralized with sodium carbonate, the precipitate separated and dissolved in about 150 cc. of acetone and again refluxed with animal charcoal for one-quarter of an hour. The mixture was then filtered and the acetone partially evaporated (about one-half). One hundred cubic centimeters of ethyl acetate was added and the whole allowed to crystallize. The product at this point (m. p. 159–163°) was light brown in color and of sufficient purity to warrant its use in the succeeding reactions. However, two to four recrystallizations from ethyl acetate gave a product with a sharp melting point of 166–167°.

β-(4-Pyridyl)-acrylic acid, m. p. 293–295°, resulted in 73% yields from the hydrolysis of γ-picoline-chloral according to the method of Rabe and Kindler. The acetate was prepared by recrystallizing the acrylic acid from glacial acetic acid. It melts at 287–288°.

Bromination of β-(2-Quinolyl)-acrylic Acid.—When equimolecular quantities of the reagents were allowed to

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(5) Farrell and Bachman, THIS JOURNAL, **57**, 1281 (1935).

(6) Einhorn, *Ber.*, **18**, 3465 (1885).

(7) Einhorn and Sherman, *Ann.*, **287**, 27 (1895).

(8) Rabe and Kindler, *Ber.*, **55**, 532 (1922).

react in glacial acetic acid, carbon disulfide, carbon tetrachloride, nitrobenzene or xylene at steam-bath temperatures or without solvent in a desiccator at room temperatures in such a way that only the vapors of the bromine came in contact with the solid acid a product was obtained which, after boiling a few minutes with acetone, melted at 228–230°; yield 92–96%. *Anal.* Calcd. for $C_{12}H_9O_2$: NBr_2: Br, 44.53. Found: Br, 44.39.

In glacial acetic acid or xylene at the boiling point of the solvent substitution occurred and the product was a tarry mass from which none of the dibromo acid could be isolated. With larger mole ratios of bromine and at steam-bath temperatures the product *after treatment with acetone* was again the dibromo acid of m. p. 228–230°. When a bromine ratio of 2:1 was used and the resulting product was not treated with acetone a material which seemed to be the acrylic acid dibromide perbromide was obtained, m. p. 174–176°. Upon standing in the air it gradually lost bromine and after forty-eight hours melted at 179–180° and analyzed for 3.5 atoms of bromine. On treatment with acetone it gave the dibromo acid m. p. 228–230° and bromoacetone. In view of its melting point this dibromide perbromide appears to be the substance reported by Einhorn as the acrylic acid dibromide.

It is probable that a perbromide of β-(2-quinolyl)-acrylic acid is the first product formed in the bromination of this acid. When the reagents were mixed in equimolecular amounts in a solvent at room temperature and the solid product separated within half an hour, it was found to consist of a lower melting substance which reacted with acetone to give bromoacetone and the original acrylic acid hydrobromide. This material on standing for several days in the presence of a solvent or on heating to steam-bath temperatures for fifteen minutes with a solvent was converted into the dibromo acid, m. p. 228–230°.

Bromination of β-(4-Pyridyl)-acrylic Acid.—The bromination of this acid proceeded analogously to the bromination of β-(2-quinolyl)-acrylic acid. The dibromide melted at 258–260° and was obtained in 96% yields. All that was said in regard to the formation of perbromides of the quinoline acid also applies in this case.

Anal. Calcd. for $C_8H_7O_2NBr_2$: Br, 51.77. Found: Br, 51.21.

Dehalogenation Experiments.—The results of the dehalogenation experiments are shown in tabular form. Treatment with strong or weak alkalies at room temperatures or for short periods at higher temperatures gave good recovery of the acrylic acids. Where the yields were low (*e. g.*, experiments 2 and 11), black tarry polymerized materials insoluble in alkali made up a considerable portion of the product. Some evidence of the formation of bromoolefins in small quantities was obtained when the dehalogenation mixtures were steam distilled. From the quinolylacrylic acid dibromide (experiment 3) was obtained a turbid filtrate which gave a picrate, m. p. 125–127°. The corresponding picrate from the pyridylacrylic acid melted at 152–153°. Whether or not these compounds were picrates of the corresponding bromoolefins is difficult to say since they could be isolated in very small amounts only.

Dibromo acid	Base	Moles	Solvent	Temp.	Time	Recovery, %
1 Quinolyl-acrylic	KOH	3	Water	Room	1 hr.	80
2	KOH	6	Alcohol	Reflux	2 hrs.	50
3	Na_2CO_3	1.5	Water	Steam	1 hr.	93
4	C_5H_5N	6	Pyridine	Steam	1.5 hr.	73
5	C_5H_5N	6	Pyridine	Room	7 days	62
6	NaOEt	2.25	Alcohol	Reflux	0.5 hr.	82
7	$NaHCO_3$	3	Water	Room	3 wks.	90
8	.....	..	Alcohol	Reflux	0.5 hr.	90
9	.....	..	Water	Reflux	0.5 hr.	86
10 Pyridyl-acrylic	KOH	6	Alcohol	Reflux	2 hrs.	40
11	Na_2CO_3	3	Water	Reflux	5 min.	88
12	C_5H_5N	3	Pyridine	Steam	5 hrs.	88
13	NaOEt	2.25	Alcohol	Reflux	0.5 hr.	75
14	.....	..	Water	Reflux	0.5 hr.	80

1-Chloro-1-(3-pyridyl)-ethylene.—In a three-necked flask equipped with a thermometer, dropping funnel and mechanical stirrer were placed 72.8 g. (0.35 mole) of phosphorus pentachloride and 50 g. of dry benzene. Forty-two and four-tenths grams (0.35 mole) of β-acetylpyridine was introduced slowly through the dropping funnel and the temperature of the reaction raised to about 60–70°. This temperature was maintained until all the ketone had been added. The thermometer was then replaced by a reflux condenser fitted with a calcium chloride tube and the reactants refluxed with continuous stirring for one and one-half to two hours. After cooling, the contents of the flask were poured onto cracked ice, stirred vigorously for about three-quarters of an hour and then neutralized with sodium carbonate. The benzene layer was separated and the aqueous solution extracted with benzene. The combined benzene extracts were dried over sodium sulfate and distilled under diminished pressure. There was obtained 24 g. (50% theoretical) of 1-chloro-1-(3-pyridyl)-ethylene. The following constants were noted: b. p. 112–114° at 24 mm.: n^{24}_D 1.5549, d^{24}_4 1.179.

Anal. Calcd. for C_7H_6NCl: Cl, 25.45%. Found: Cl, 25.34%.

The hydrochloride was found to melt at 138–140°.

β-Pyridylacetylene.—Twenty grams of freshly distilled 1-chloro-1-(3-pyridyl)-ethylene (0.14 mole) was added to a solution of 25 g. of potassium hydroxide (0.44 mole) in 50 cc. of 95% alcohol. This mixture was refluxed two hours, diluted with 250 cc. of water and steam distilled. Upon addition of the water an oily layer separated. About the first 75 cc. of distillate contained alcohol and some acetylene, after which the distillate assumed a turbid appearance due to the suspension of the moderately soluble acetylenic hydrocarbon in the water. When the distillate again cleared the distillation was stopped. The product was purified by precipitating as silver salt and decomposing with dilute hydrochloric acid. Upon distillation a fraction of b. p. 80–85° (30 mm.) was obtained. This fraction soon solidified and was further purified by sublimation or recrystallization from ligroin. The yield was 6 g., 42%, m. p. 38.5°, b. p. 83–84° (30 mm.).

Anal. Calcd. for C_7H_6N: C, 81.51; H, 4.89. Found: C, 81.36; H, 5.01.

Action of Pyridine on Cinnamic Acid Dibromide.—Pure recrystallized cinnamic acid dibromide, m. p. 100°, 25 g., and anhydrous pyridine, b. p. 113–115°, 54 g., were heated together on the steam-bath for three hours. The product was steam-distilled until the distillate became clear. On acidification of the distillate ω-bromostyrene separated as an oil. It was extracted with ether and distilled; yield 5.4 g. (36.6%), b. p. 219° (19 mm.). The liquid residue from the steam distillation was acidified and the needle-like crystals, 6.8 g., were removed by filtration. All attempts to separate the cinnamic and bromocinnamic acids quantitatively failed; hence the mixture was analyzed for bromine by the method of Carius.

Anal. Calcd. for $C_9H_7O_2Br$: Br, 35.3. Found: Br, 14.2.

Evidently there was sufficient bromine present to account for the bromo acid to the extent of 40.3% of the mixture. Assuming the mixture of acids to contain nothing but cinnamic and bromocinnamic acids, the yields were: cinnamic acid, 4.1 g., 34.1%; bromocinnamic acid, 2.7 g., 14.7%. Pure cinnamic acid and pure α-bromocinnamic acid in small amounts were obtained by fractional crystallization of the analyzed mixture.

Experiments in aqueous solution using pyridine, or sodium carbonate, or mixtures of the two invariably resulted in the formation of ω-bromostyrene in 65–75% yields. The remainder of the product consisted again of a mixture of cinnamic and α-bromocinnamic acids.

Summary

1. Improved methods of preparation of quinaldine and γ-picoline chlorals have been developed.

2. Quinolyl- and pyridylacrylic acid dibromides have been prepared and their dehalogenations studied. Quinolylacrylic acid dibromide was found to have different properties than those previously described for it in the literature.

3. The dehalogenations of the above two dibromo acids with a series of bases led in every case to the formation of the original acrylic acids as the principal products. This constitutes a new type of reaction for the α,β-dibromo acids, differing in degree but not in kind from the dehalogenations of other similar acids.

4. Attention has been called to the similarity between the above-mentioned dehalogenations and the action of anhydrous pyridine upon cinnamic acid dibromide. Apparently the heterocyclic nitrogen atoms in the pyridyl and quinolyl acids influence the course of the dehalogenations even in the presence of other bases.

5. As an example of the heterocyclic acetylenes, β-pyridylacetylene has been prepared and its properties described.

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The Action of Sulfur on Aniline and Similar Amines

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

The desire of securing certain new derivatives of 4,4′-dihydroxydiphenyl sulfide led the authors to study the reaction of sulfur with aromatic amines in the presence of lead oxide, and we now offer an explanation of the mechanism of this reaction.

Hodgson and others[2] have isolated and identified the different products of the reaction between aniline and sulfur, 2,2′-diaminodiphenyl sulfide, 2,2′-diaminodiphenyl disulfide, 2,4′-diaminodiphenyl sulfide, 4,4′-diaminodiphenyl disulfide, and 4,4′-diaminodiphenyl sulfide being among the chief products formed. The presence of lead oxide[2c] promotes the formation of *para*-substituted derivatives, thereby increasing the yield of *p*-thioaniline and at the same time lowering the temperature at which the reaction occurs. The conditions under which this reaction proceeds with the optimum results have been established by Hodgson,[2a] although a considerable amount of dark colored tarry material is obtained and the ultimate yield of the thioaniline is very low. Shukla[3] has found that iodine will lower the reaction temperature as indicated by the evolution of hydrogen sulfide even though his final yield was only 1 g. of thioaniline from 50 g. of aniline.

In determining the extent of this reaction it was found that Merz and Weith[2c] have prepared thioacetanilide by the action of sulfur on acetanilide in the presence of lead oxide. Hodgson[4] obtained thio-*o*-toluidine from *o*-toluidine by the same reaction. The results of these workers led us to examine the reaction with other compounds of a similar nature, namely, benzalaniline,

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[1] A. Homer Smith Research Fellow in Organic Chemistry 1934–1935.

[2] (a) Hodgson, *J. Chem. Soc.*, **125**, 1855 (1924); (b) Hofmann, *Ber.*, **27**, 2807 (1894); (c) Merz and Weith, *ibid.*, **4**, 384 (1871).

[3] Shukla, *J. Indian Inst. Science*, **10A**, pt. 3, 33 (1927).

[4] Hodgson and France, *J. Chem. Soc.*, 296 (1933); 1140 (1934).