[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XV. Ketene Diphenylacetal and Triphenyl Orthoacetate

BY S. M. McELVAIN AND BERNARDO FAJARDO-PINZÓN[1]

As part of the work on the ketene acetals now in progress in this Laboratory, it seemed desirable to prepare ketene diphenylacetal and to compare its chemical properties to those of ketene diethylacetal. Ketene diphenylacetal was the first of this class of compounds to be reported in the literature. Biginelli[2] claimed to have prepared it by the action of an alkaline solution of phenol on methylchloroform and indicated its formation in the following way

$$CH_3CCl_3 + 2C_6H_5OK + KOH \longrightarrow CH_2{=}C(OC_6H_5)_2 + 3KCl + H_2O$$

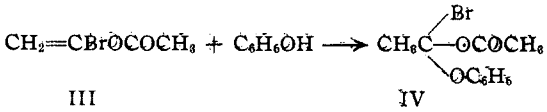
In a later paper on the ketene acetals, Staudinger and Rathsam[3] pictured the formation of Biginelli's compound as passing through the intermediate triphenyl orthoacetate, thus

$$CH_3CCl_3 + 3KOC_6H_5 \longrightarrow CH_3C(OC_6H_5)_3 \longrightarrow CH_2{=}C(OC_6H_5)_2 + C_6H_5OH$$

Biginelli reported ketene diphenylacetal to be a solid melting at 95–96°. At about the same time Heiber[4] described the product of the reaction of methylchloroform with phenol in alkaline solution as triphenyl orthoacetate, m. p. 97–97.5°. This contradiction remained in the literature until Cope[5] presented convincing evidence that neither of these earlier workers had the product he reported, but that both had isolated the diphenyl ether of ethylene glycol; this product had formed from the reaction of sodium phenoxide with ethylene chloride, a contaminant of the methylchloroform that was used. The properties found for ketene diphenylacetal and triphenyl orthoacetate in the work now reported substantiate Cope's conclusions relative to the products described by Biginelli and Heiber.

The main problem in the preparation of ketene diphenylacetal was to obtain its immediate precursor, bromodiphenylacetal (VI). Two approaches to this compound were studied. The first, which was unsuccessful, was an attempt to replace the acetoxy group and the α-bromine of α,β-dibromoethyl acetate (II) by phenoxy groups. This failed because II reacted with sodium phenoxide[6] (one equivalent) in the following manner

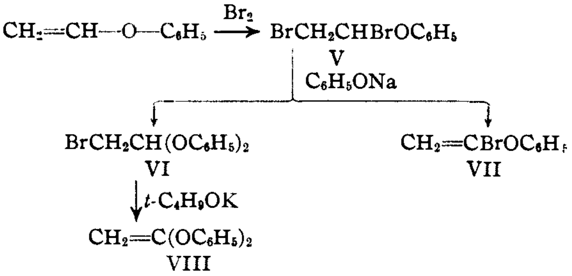
$$\underset{\text{II}}{BrCH_2CHBrOCOCH_3} + NaOC_6H_5 \longrightarrow$$



$$\underset{\text{III}}{CH_2{=}CBrOCOCH_3} + C_6H_5OH \longrightarrow \underset{\text{IV}}{CH_3C(Br)(OC_6H_5){-}OCOCH_3}$$

The phenoxybromoethylacetate (IV) obtained from this reaction is a colorless liquid which fumes copiously on exposure to air, reacts with alcohol to give ethyl acetate and phenyl acetate, and is pyrolyzed into acetyl bromide and phenyl acetate by distillation at ordinary pressure. The validity of the above reaction course was shown by the preparation of III from II through the action of potassium t-butoxide, and the conversion of III to IV by the action of phenol. When II was treated with two equivalents of sodium phenoxide only phenyl acetate was formed.

Bromodiphenylacetal (VI) was prepared from dibromophenetole (V) which was obtained by the bromination of vinyl phenyl ether. The action of sodium phenoxide on V gave VI in 67% yield, together with 18% of the bromovinyl phenyl ether (VII). This latter compound is the result of dehydrobromination of V by the sodium phenoxide. The dehydrobromination of VI by means of potassium t-butoxide produced the desired ketene diphenylacetal (VIII) in 78% yield.



Ketene diphenylacetal is a colorless liquid which boils at 115–116° (1 mm.). It is readily hydrolyzed by water containing a trace of acid to phenol and phenyl acetate. It reacts exothermically with phenol to produce triphenyl orthoacetate (IX), m. p. 61–62°, b. p. 148–153° (0.5 mm.).

$$CH_2{=}C(OC_6H_5)_2 + C_6H_5OH \longrightarrow \underset{\text{IX}}{CH_3C(OC_6H_5)_3}$$

With methyl or ethyl alcohol ketene diphenylacetal remains unchanged even after refluxing for several hours. However, a cold alcoholic solution of the acetal spontaneously becomes quite warm when treated with a drop of hydrochloric acid. The product of this reaction is triphenyl orthoacetate (IX) rather than the mixed orthoester (X). The formation of IX in this reaction

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[1] Institute of International Education Fellow.

[2] Biginelli, *Gazz. chim. ital.*, **21**, 261 (1891).

[3] Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 646 (1922).

[4] Heiber, *Ber.*, **24**, 3678 (1891).

[5] Cope, THIS JOURNAL, **57**, 572 (1935).

[6] The acetate (II) reacts vigorously with phenol to give acetic acid, two equivalents of hydrogen bromide, and a bromine-free, alkali-soluble, solid condensation product which is thought to be 1,1-bis-(p-hydroxyphenyl)-ethylene, $CH_2{=}C(C_6H_4OH)_2$, or its polymer.

may be explained by the following series of reactions

$$\text{VIII} + CH_3OH \longrightarrow \underset{\text{X}}{CH_3C(OCH_3)(OC_6H_5)_2} \xrightarrow{CH_3OH} CH_3C(OCH_3)_2OC_6H_5 + C_6H_5OH$$

$$\text{VIII} + C_6H_5OH \longrightarrow \text{IX}$$

The alcoholysis of one or both of the phenoxy groups of X seems likely since triphenyl orthoacetate (IX) yields 81% of the theoretical quantity of phenol when refluxed with an excess of alcohol containing a trace of acid as catalyst.

The behavior of ketene diphenylacetal toward hydrogen bromide and such reactive organic halides as benzyl bromide is of particular interest. These halides add to ketene diethylacetal to form, presumably, an intermediate which decomposes into the products isolated from the reaction, acetic or a substituted acetic ester and ethyl bromide:[7]

$$CH_2{=}C(OC_2H_5)_2 \begin{cases} \xrightarrow{HBr} CH_3CBr(OC_2H_5)_2 \longrightarrow CH_3COOC_2H_5 + C_2H_5Br \\ \xrightarrow{RBr} RCH_2CBr(OC_2H_5)_2 \longrightarrow RCH_2COOC_2H_5 + C_2H_5Br \end{cases}$$

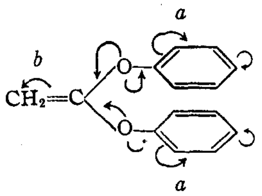
A similar decomposition of the corresponding intermediate addition product (XI) from ketene diphenylacetal (VIII) seemed unlikely because of the strength of the O—C₆H₅ bond. It was found that the addition product from VIII and hydrogen bromide decomposed, when an attempt was made to distil it, into phenol and a brown viscous polymer. This behavior indicates the reaction course

$$\text{VIII} + HBr \longrightarrow \underset{\text{XI}}{CH_3CBr(OC_6H_5)_2} \longrightarrow C_6H_5OH + \underset{\text{VII}}{CH_2{=}CBrOC_6H_5} \longrightarrow \text{polymer}$$

Ketene diphenylacetal (VIII) gave no evidence of reaction with benzyl chloride even after several hours at 150°. However, when this acetal was heated with benzyl bromide the mixture polymerized to a thick red viscous liquid which was not investigated further.

In further contrast to ketene diethylacetal, ketene diphenylacetal shows no tendency to polymerize in the presence of catalytic amounts of cadmium chloride.[8]

A comparison of the properties of ketene diphenylacetal with those of the corresponding diethylacetal shows that the anionoid reactivity of the methylene carbon is greatly diminished in the former compound by the phenyl groups. This would be expected since the oxygens are electronically conjugated in a hetero-enoid system with the aromatic nuclei as well as with the methylene carbon.



To the extent that such polarizations as *a* occur the *b* type, which activates the methylene carbon, are reduced. In ketene diethylacetal the *a* type of polarization is absent so that the entire effect of the oxygens may be concentrated on the methylene carbon through the polarization *b*.

Triphenyl orthoacetate, which boils at 148–153° (0.5 mm.), does not show the facile pyrolysis postulated by Staudinger and Rathsam,[3] even though this decomposition would involve the rupture of one of the relatively weak carbon–oxygen bonds. These bonds, however, may be broken by alcoholysis as evidenced by the fact that 81% of the theoretical amount of phenol is obtained when the phenyl orthoester is refluxed with alcohol containing a trace of acid. The oxygen–phenyl bond shows the expected stability in the orthoacetate structure in view of the fact that the triphenyl orthoester shows no tendency to decompose into diphenyl ether[9]; also the intermediate 1-bromo-1,1-diphenoxyethane (XI) pyrolyzes into phenol instead of phenyl bromide.

Experimental

α,β-Dibromoethyl Acetate.—This compound, prepared by the procedure of Bedoukian,[10] was isolated by fractionation from a modified Claisen flask.

The dibromoester, obtained in 85% yield, boiled at 84–85° (5 mm.); n^{20}_D 1.5052; d^{20}_4 1.9185. The preparation of this ester has been reported in the patent literature.[11]

Anal. Calcd. for $C_4H_6O_2Br_2$: Br, 65.0. Found: Br, 64.8.

Reaction of α,β-Dibromoethyl Acetate with Sodium Phenoxide. α-Bromo-α-phenoxy-ethyl Acetate.—In a 250-ml. 3-neck flask fitted with stirrer, dropping funnel and condenser protected with a calcium chloride tube was placed a solution of 18.8 g. (0.2 mole) of phenol in 100 ml of dioxane. To this solution 4.6 g. (0.2 atom) of metallic sodium was added and the dioxane solution refluxed until the sodium had dissolved completely. The flask then was cooled to room temperature and 49 g. (0.2 mole) of dibromoethyl acetate added slowly while stirring. Precipitation of sodium bromide began at once. After the ester had been added, the reaction mixture was refluxed for an hour to ensure complete reaction. The reaction mixture then was distilled from a modified Claisen flask. After the lower boiling products were removed, 34.2 g. (66%) of α-bromo-α-phenoxy-ethyl acetate, b. p. 58–60° (1 mm.); n^{20}_D 1.5150; d^{20}_4 1.3360, was collected. This ester contained only 27.9% bromine (calcd. 30.8%) probably because of its tendency to decompose into acetyl bromide. It fumes on exposure to air and reacts with ethyl alcohol

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[7] McElvain and Kundiger, THIS JOURNAL, **64**, 254 (1942).

[8] Johnson, Barnes and McElvain, *ibid.*, **62**, 964 (1940).

[9] *Cf.* ref. 3 and McElvain, Anthes and Shapiro, *ibid.*, **64**, 2525 (1942).

[10] Bedoukian, *ibid.*, **66**, 651 (1944).

[11] British Patent 325,115; *Chem. Abst.*, **24**, 3800 (1930).

with sufficient vigor to cause the mixture to boil. Fractionation of the resulting reaction mixture gives 84% of the theoretical amount of ethyl acetate and 62% of the phenyl acetate. When a sample of the bromo-phenoxyethyl acetate was heated at atmospheric pressure it decomposed with the vigorous evolution of acetyl bromide (characterized by conversion to ethyl acetate) into phenyl acetate which was isolated in 75% yield.

α-Bromo-α-phenoxy-ethyl acetate also was prepared from α-bromovinyl acetate in the following manner. A solution of 3.9 g. (0.1 atom) of potassium in 75 g. of *t*-butyl alcohol was distilled from a steam-bath under reduced pressure to remove the *t*-butyl alcohol. The potassium *t*-butoxide was covered with 100 ml. of ether and a stirrer inserted. To the ether suspension of the butoxide was added 24.6 g. (0.1 mole) of the dibromoethyl acetate and the solution refluxed for forty-five minutes. After this time the ether was distilled at atmospheric pressure and the remaining liquid residue at 50–75° (18 mm.).

Refractionation of the latter product gave 10.3 g. (63%) of α-bromovinyl acetate, b. p. 71–73° (18 mm.); $n^{20}\text{D}$ 1.5050; d^{20}_4 1.7178. *Anal.* Calcd. for $C_4H_5O_2Br$: Br, 48.43. Found: Br, 50.05.

A solution of 8.3 g. of the bromovinyl acetate and 4.7 g. of phenol in 20 ml. of dioxane was refluxed for one hour. The solution then was fractionated and the material boiling at 57–59° (1 mm.) collected. It weighed 7.0 g. and showed the same behavior on heating and on treatment with alcohol as described above.

Phenyl Vinyl Ether.—The following modification of the method of Lauer and Spielman[12] was used to prepare this compound. In a 1-liter copper flask was placed 350 g. of potassium hydroxide flakes and 402 g. (2 mole) of β-phenoxyethyl bromide. The copper flask was closed with a cork and shaken vigorously for about five minutes to ensure thorough mixing of the reactants. The flask then was connected to a 35-cm. Vigreux column which carried a thermometer and was attached to a condenser set for distillation. The copper flask was heated in a sand-bath at 160–165° for thirty minutes and then the temperature was raised to 200°. At this point a mixture of phenyl vinyl ether and water distilled from the reaction flask. The temperature of the vapors varied from 120–130° depending on their water content. The temperature of the sand-bath was so controlled that the temperature of the vapors at the top of the column did not exceed 160°. After five hours the distillation was finished. The distillate of phenyl vinyl ether and water was treated with dry calcium chloride and the two layers separated. Distillation of the organic layer gave 161 g. (69%) of phenyl vinyl ether, b. p. 154–155°.

α,β-Dibromophenetole.—In a 1-liter, 3-neck, round-bottomed flask fitted with an efficient stirrer, a 250-ml. dropping funnel and a reflux condenser protected with a calcium chloride tube, was placed 216 g. (1.8 mole) of phenyl vinyl ether and 50 ml. of carbon tetrachloride. The flask was immersed in a Dry Ice–ether mixture and 288 g. (1.8 mole) of bromine dissolved in 60 ml. of carbon tetrachloride was added to the phenyl vinyl ether while stirring. The rate of addition was such that at no time was there an excess of bromine present in the mixture. The end-point was reached when a faint bromine color persisted. This color was destroyed by the addition of 1 ml. of phenyl vinyl ether.

The brominated product was transferred to a 500-ml. Claisen flask and distilled under reduced pressure. The first drops of distillate after the removal of the carbon tetrachloride were deep red in color. Then 450 g. (89%) of the colorless α,β-dibromophenetole was collected. It boiled at 140–145° (18 mm.); $n^{20}\text{D}$ 1.5845; d^{20}_4 1.6321.

Anal. Calcd. for $C_8H_8OBr_2$: Br, 57.9. Found: Br, 56.2.

Bromodiphenylacetal, 1-Bromo-1-phenoxy-ethylene and 1,1,2-Tribromo-1-phenoxyethane.—In a 2-liter 3-neck round-bottom flask fitted with a stirrer, a 250-ml. dropping funnel and condenser protected with a calcium chloride tube was placed 280 g. (1 mole) of α,β-dibromophenetole. The flask was placed in ice-water and a solution of 23 g. (1 atom) of sodium and 94 g. (1 mole) of phenol in 500 ml. of dioxane was added slowly and with stirring. Reaction took place immediately with the precipitation of sodium bromide. The mixture was stirred and refluxed for one hour to ensure complete reaction of the sodium phenoxide. The stirrer then was replaced by a 40-cm. Vigreux column which carried a thermometer and a condenser set for distillation under reduced pressure. The dioxane was distilled off and, after cooling, the contents of the distilling flask was washed with 500 ml. of water and extracted with five 100-ml. portions of ether. The ether solution was dried with calcium chloride and the ether distilled at atmospheric pressure. The remaining liquid was fractionated and fractions boiling at 80–125° (13 mm.) and 140–153° (0.2 mm.) were collected.

The first fraction gave on refractionation 35 g. (12%) of phenol and 53 g. (18%) of **1-bromo-1-phenoxyethylene**, b. p. 120–121° (13 mm.); $n^{20}\text{D}$ 1.5700; d^{20}_4 1.4708. *Anal.* Calcd. for C_8H_8OBr: Br, 39.9. Found: Br, 37.9. The second fraction gave upon refractionation 197 g. (67%) of **bromodiphenylacetal**, b. p. 150–157° (0.2 mm.); $n^{20}\text{D}$ 1.5795; d^{20}_4 1.3940. *Anal.* Calcd. for $C_{14}H_{13}O_2Br$: Br, 27.3. Found: Br, 27.3. If the addition of the reagents in the above procedure was reversed, a much larger amount of the low boiling fraction was obtained with the corresponding decrease in the fraction containing the bromodiphenylacetal. If the original reaction mixture was not distilled under reduced pressure (12 mm.) until all of the dioxane was removed, the extraction of the acetal from the aqueous solution of the salt with ether was incomplete and it was necessary to saturate the aqueous solution with solid calcium chloride in order to obtain a good recovery.

Since the bromine analyses for the bromophenoxyethylene were not very satisfactory, the compound was treated with bromine in the hope of getting a more readily purified product. A solution of 16 g. of 1-bromo-1-phenoxyethylene in 15 ml. of carbon tetrachloride was placed in a 150-ml., 3-neck round-bottomed flask fitted with dropping funnel, a thermometer with the bulb immersed in the liquid, and an air condenser protected with a calcium chloride tube. The flask then was placed in ice-water and 12.8 g. (0.08 mole) of bromine dissolved in 10 ml. of carbon tetrachloride was added from the dropping funnel while the flask was shaken intermittently. Care was taken not to allow the temperature to rise above 10°. After the bromine was added the carbon tetrachloride solution was allowed to come to room temperature and transferred to a 50 ml. modified Claisen flask. After the removal of the carbon tetrachloride under reduced pressure, 23.3 g. (87%) of **1,1,2-tribromo-1-phenoxyethane**, b. p. 173–175° (5 mm.); $n^{20}\text{D}$ 1.6012; d^{20}_4 1.7874, was obtained. *Anal.* Calcd. for $C_8H_7OBr_3$: Br, 66.9. Found: Br, 66.7.

Ketene Diphenylacetal.—In a 1-liter 3-neck round-bottom flask provided with a stirrer, a 250-ml. dropping funnel and a condenser protected with a calcium chloride tube was dissolved 20.2 g. (0.51 atom) of clean potassium in 300 g. of *t*-butyl alcohol. When the potassium had dissolved completely in the boiling alcohol, 150 g. (0.51 mole) of bromodiphenylacetal was added through the dropping funnel. Reaction took place immediately with the precipitation of potassium bromide. The mixture was heated to refluxing for three hours, then cooled and centrifuged. The precipitated salt, after decantation of the alcohol solution, was washed twice with 50-ml. portions of ether. The combined ether–alcohol solution was distilled at atmospheric pressure to remove the solvents after which the ketene diphenylacetal was distilled. A yield of 84.3 g. (78%) of ketene diphenylacetal, b. p. 115–116° (1 mm.); $n^{20}\text{D}$ 1.5583; d^{20}_4 1.1544, was obtained.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.91; H, 5.69.

Triphenyl Orthoacetate.—A 10.6 g. (0.05 mole) sample of ketene diphenylacetal was treated with 4.7 g. (0.05

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[12] Lauer and Spielman, This Journal, **53**, 1533 (1931); **55**, 1573 (1933).

mole) of phenol. The mixture, which became hot, was heated to 70–80° for ten minutes. The reaction mixture was then cooled, and crystallization induced by scratching the wall of the flask with a glass rod. The white, solid triphenyl orthoacetate, after recrystallization from an alcohol–water mixture, weighed 12 g. (78%) and melted at 61–62°. This orthoester could be distilled; it boiled at 148–153° (0.5 mm.). *Anal.* Calcd. for $C_{20}H_{18}O_3$: C, 78.33; H, 6.02. Found: C, 78.22; H, 6.03.

Triphenyl orthoacetate is hydrolyzed by 0.1 *N* hydrochloric acid into phenol and phenylacetate. When 5 g. of the orthoester was refluxed for four hours with 10 ml. of absolute alcohol containing a drop of concentrated hydrochloric acid and the excess of alcohol then removed by distillation, sufficient phenol was extracted from the residue with alkali to yield 12 g. (81%) of tribromophenol, m. p. 94–95°.

Reactions of Ketene Diphenylacetal. (a) With Methyl and Ethyl Alcohol.—A mixture of 11 g. of the acetal and 5 g. of methyl alcohol showed no sign of reaction after standing for several days or even after refluxing for four hours. However, when the mixture was treated with 1 drop of concentrated hydrochloric acid it became quite hot. Fractionation of this reaction mixture under reduced pressure gave 1.2 g. of phenol, b. p. 80–81° (10 mm.), and a fraction that boiled 95–160° (0.1 mm.) and solidified on cooling. Recrystallization of this fraction from an alcohol-water mixture gave 7.4 g. (48%) of triphenyl orthoacetate.

When ethyl alcohol was used in the above experiment instead of methyl alcohol, 0.9 g. (18%) of phenol and 9.4 g. (61%) of triphenyl orthoacetate were obtained.

(b) **Hydrolysis.**—A 5-g. sample of ketene diphenylacetal was heated for two hours with 25 ml. of boiling water that contained one drop of concentrated hydrochloric acid. The resulting liquid mixture, after cooling, was shaken with 50 ml. of a 10% sodium hydroxide solution and extracted twice with 25 ml. of ether. The alkaline portion was acidified with 10% hydrochloric acid and the phenol precipitated as tribromophenol; 2.9 g. (38%) was obtained. Distillation of the ethereal solution gave 1.3 g. (40%) of phenyl acetate, b. p. 196°.

(c) **Reaction with Hydrogen Bromide.**—To a solution of 4 g. of hydrogen bromide in 100 ml. of ether was added 11 g. of ketene diphenylacetal. No appreciable change was observed. The resulting mixture was refluxed for fifteen minutes and then after removal of the ether, the residue was heated under reduced pressure. A distillate of 2.8 g. (58%) of phenol and a viscous, undistillable tar that remained in the flask were obtained.

(d) **Benzyl Halides.**—A mixture of 11 g. of the acetal and 6.5 g. of benzyl chloride was heated at 150° for fifteen hours. No indication of reaction was shown and upon distillation of the mixture the starting materials were recovered. When benzyl bromide was used, following the procedure of McElvain and Kundiger,[7] 8% of the theoretical quantity of hydrogen bromide was evolved and the reaction mixture turned to a red viscous liquid which was not investigated further.

Summary

Ketene diphenylacetal has been prepared by the sequence of reactions: $CH_2{=}CHOC_6H_5 \rightarrow CH_2BrCHBrOC_6H_5 \rightarrow CH_2BrCH(OC_6H_5)_2 \rightarrow CH_2{=}C(OC_6H_5)_2$.

Triphenyl orthoacetate, $CH_3C(OC_6H_5)_3$, has been prepared by the addition of phenol to this ketene acetal.

The properties now found for ketene diphenylacetal and triphenyl orthoacetate indicate that these compounds have not been described previously in the literature, and substantiate the belief that earlier workers who reported these compounds had, in reality, isolated the diphenyl ether of ethylene glycol.

Ketene diphenylacetal shows a much lower anionoid reactivity at the methylene carbon than does ketene diethylacetal.

MADISON, WISCONSIN RECEIVED FEBRUARY 12, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

The Isolation of Kafiroic Acid from Kafir Bran[1]

BY L. L. WOODS[1a] WITH C. W. COLVER

A critical examination of kafir bran has revealed that the material contained a pigmented acid which we have designated as kafiroic acid. The kafir brans used in these experiments were a composite of the usual commercial varieties of kafir and provided by the Department of Chemical Engineering of Kansas State College.

When kafiroic acid was first separated from the bran it was highly contaminated but methods that were devised for purifying the crude substance proved quite effective. Purified kafiroic acid was found to be a high molecular weight compound with a definite rust-brown color, and an approximate empirical formula of $C_{18}H_{30}N_2O_6$. The substance was found to be unstable in the presence of strong oxidizing agents and easily decomposed by the action of alcoholic potassium hydroxide and sulfuric and hydrochloric acids. Degradation with acids and potassium hydroxide gave 5-aminopentanoic acid. The ease with which the 5-aminopentanoic acid was produced indicated that the compound probably contained at least one piperidone structure.[2]

Experimental Part

Isolation of Kafiroic Acid.—Two hundred grams of bran were digested six hours on the hot-plate in 2 liters of 2% sulfuric acid. At the end of the period of digestion the mixture was allowed to cool and then filtered through a linen bag using pressure. The residue was washed without removing it from the bag by allowing a fine stream of water to run through the material for one-half hour. The residue was then placed in 2 liters of 1% sodium hydroxide and digested at the temperature of the boiling solution for four hours. The mixture was allowed to cool overnight and then filtered essentially as before. The filtrate which contained the kafiroic acid as the sodium salt was acidified with concentrated hydrochloric acid, and the acid pre-

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(1) This material is a part of a thesis submitted to the Graduate School of the Kansas State College by Lloyd L. Woods in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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(2) Binz and Räth, *Ann.*, **489**, 107 (1931).