solution was cooled in an ice-bath, treated with a mixture of 20 ml. of pyridine and 25 g. of allyl alcohol, and allowed to stand overnight. The resulting solution was washed with 500 ml. of water, 100 ml. of dilute (7:100) hydrochloric acid, 10 ml. of 10% sodium bicarbonate solution, and finally with 200 ml. of water. The organic layer was dried over magnesium sulfate; the solvents were removed; and the residue was distilled at 3 mm. The fractions distilling between 170 and 180° at 3 mm. weighed 10.5 g. (50.7%), $n^{30}\text{D}$ 1.6000 to 1.6022. A center fraction was redistilled for analysis, b. p. 174° at 2 mm., $n^{30}\text{D}$ 1.6012.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.84; H, 5.92.

A direct esterification of 20.0 g. of 9-fluorenecarboxylic acid by heating it under reflux overnight with 200 ml. of allyl alcohol and 1.0 g. of *p*-toluenesulfonic acid produced 12.2 g. (51.2%) of allyl 9-fluorenecarboxylate.

9-Allyl-9-fluorenecarboxylic Acid.—A mixture containing 2.24 g. (0.009 mole) of allyl 9-fluorenecarboxylate, 25 ml. of anhydrous toluene, and 0.92 g. (0.04 mole) of lithium amide was heated under reflux for three hours. The mixture was cooled, and 5 ml. of ethanol was added to destroy the excess lithium amide. The resulting solution was washed into a separatory funnel with alternate portions of water and ether. The organic layer was extracted with three 10-ml. portions of 10% sodium hydroxide. The combined aqueous solutions were extracted with ether. Acidification of the alkaline solution with concentrated hydrochloric acid precipitated 2.18 g. (97.5%) of 9-allyl-9-fluorenecarboxylic acid, m. p. 129.5–131°. The acid, after crystallization from petroleum ether (b. p. 60–70°), melted at 131.5–132.5°. A mixture with an authentic sample of 9-allyl-9-fluorenecarboxylic acid prepared according to the method of Wislicenus and Mocker[7] showed no depression of melting point.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.85; H, 5.62.

Allyldiphenylacetic Acid.—A mixture of 5 g. of allyl diphenylacetate, 1.89 g. of lithium amide, and 40 ml. of anhydrous toluene was treated as described above. From this reaction, 3.6 g. (72%) of allyldiphenylacetic acid, m. p. 138–140°, was obtained. A mixture with an authentic sample of allyldiphenylacetic acid showed no depression of melting point.

Acknowledgment.—This research was supported by a grant from General Mills, Inc.

Summary

Allyl 9-fluorenecarboxylate and allyl diphenylacetate have been rearranged with lithium amide to 9-allyl-9-fluorenecarboxylic acid and allyldiphenylacetic acid, respectively.

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(7) W. Wislicenus and W. Mocker, *Ber.*, **46**, 2772 (1913).

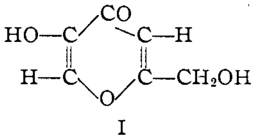
MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 21, 1949

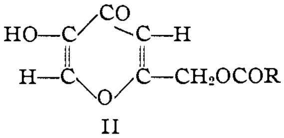
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Derivatives of Kojic Acid

BY CHARLES D. HURD AND REX J. SIMS[1]

Kojic acid (I) is prepared by the action of *A. flavus* on dextrose. A recent note[2] on the behavior of kojic acid toward hot acetic anhydride in the presence of zinc chloride overlapped some work we had done. In view of this, and especially in view of the different results obtained, we are reporting some of our findings.


I


II

Woods reported isolation of a ketone of m. p. 106°, with analytical data supporting a formula given as $C_{10}H_{13}O_7$. No structure was suggested. When this material was hydrolyzed with boiling water for fifteen hours, another ketone, $C_8H_{11}O_6$, of m. p. 55° was reported to be formed.

It is known that kojic acid, $C_6H_6O_4$, undergoes acetylation at 100° with acetic anhydride in the presence of sodium acetate to form the simple diacetate,[3] $C_{10}H_{10}O_6$, m. p. 103°. We have confirmed this observation; but we obtained the same substance (m. p. and mixed m. p. 103°) by acetylating according to Woods' procedure with acetic anhydride and zinc chloride at 135–140°. It did not give a 2,4-dinitrophenylhydrazone. Furthermore, this material hydrolyzed to kojic acid, m. p. 148–150°, on refluxing in water for eighteen hours. Since these results differ from those of Woods, we have no opinion regarding the identity of his reported materials. It should be pointed out, however, that his two formulas both possess the unreasonable feature of an odd number of electrons.

We have found that the diacetate changes to the monoacetate (II) if heated with aluminum chloride at 110°. In other words, the Fries rearrangement does not occur. The same monoacetate, m. p. 133°, is formed by heating a mixture of kojic acid, acetyl chloride and aluminum chloride.

Kojic acid gives rise to the monocaproic ester (II) if treated with caproic acid and zinc chloride at 130°. There was no evidence for a Nencki condensation with a caproyl group substituting next to the phenolic hydroxyl.

Allyl kojate (III) was readily prepared by interaction of sodium kojate and allyl bromide. The allyl group migrated to the adjacent position on heating at 180–200°, thus showing resemblance to III to allyl aryl ethers. 6-Allylkojic acid (IV) was obtained in 54% yield. It was found that IV could be obtained quantitatively from III if warmed with alcoholic hydrogen chloride at

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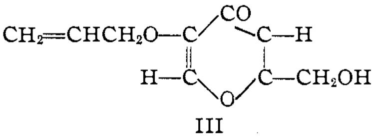
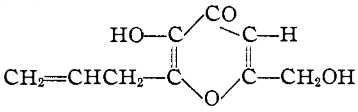
(1) Corn Products Refining Company Fellow, 1947–1948.

(2) L. L. Woods, THIS JOURNAL, **70**, 2608 (1948).

(3) Yubata, *J. Chem. Soc. Japan*, **37**, 1185, 1234 (1916); *C. A.*, **17**, 1475 (1923).



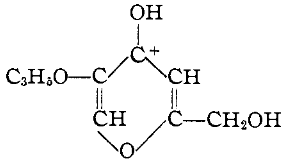
III



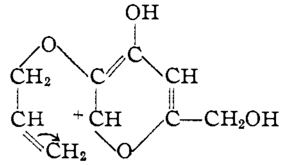
IV

60°. For this remarkable behavior to occur it seems evident that the pyrone system must supplement the ether system, since no such rearrangement occurs with allyl phenyl ether and alcoholic hydrogen chloride at 60°.

To explain this behavior, one may assume that the thermal rearrangement of III follows the general mechanism suggested by Hurd and Pollack[4] involving incipient ionization at the allyl-oxygen bond, thus changing the original skeleton of $CH_2{=}CH{-}CH_2{-}\ddot{\underset{..}{O}}{-}CR{=}CHR$ into $\overset{+}{C}H_2{-}\underset{..}{\overset{-}{C}}H{-}\overset{+}{C}H_2\ :\overset{-..}{\underset{..}{O}}{-}\overset{+}{C}R{-}\underset{..}{\overset{-}{C}}HR$ which rearranges. Essentially, an ionization pattern is set up so that the terminal carbons will bear opposite charges. One may expand this skeleton as it appears in allyl kojate to include the carbonyl group, $CH_2{=}CH{-}CH_2{-}O{-}\underset{\substack{|\\ {-}C{=}O}}{C}{=}CHR$. Then, if the proton of hydrochloric acid adds to the carbonyl oxygen, which is reasonable in a pyrone system, this would produce IIIa and it would induce the sequence of ionization effects resulting in rearrangement $III \xrightarrow{H^+} IIIa \longleftrightarrow IIIb \longrightarrow IV + H^+$.



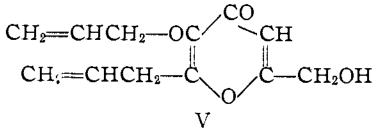
IIIa



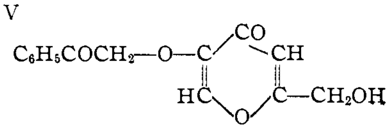
IIIb

Reaction of either III or IV with acetic anhydride and sodium acetate yielded the diacetate of IV, a light yellow crystalline product. Allylation of IV produced allyl 6-alkylkojate, V.

We have also prepared phenacyl kojate, m. p. 145°, by reaction of phenacyl bromide or chloride with sodium kojate.



V



VI

The analysis was satisfactory for structure VI, as was the molecular weight determination and the absence of phenolic reactions. Also, its acetyl derivative, m. p. 116°, was unambiguous. This would be conventional information except for the fact that Woods[5] has reported on this topic and with different results.

The substance obtained by Woods, following reaction of an aqueous alcoholic solution of phenacyl bromide and sodium kojate, melted at 158°. Analysis supported $C_{14}H_{12}O_6$ (C, 60.9; H, 4.35) but no structure was suggested. Acetylation (Ac_2O, NaOAc) yielded material melting at 129–130°, and the formula given was $C_{16}H_{14}O_7$ (C, 60.4; H, 4.43). Since we never obtained compounds from kojic acid with these physical properties, we cannot speak about them with confidence, but we suggest that the 130°- and 158°-compounds may be α- and β-bromobiphenacyl, respectively. These two isomeric compounds (C, 60.6; H, 4.14) were prepared by Paal and Demerer[6] by the action of aqueous–alcoholic sodium hydroxide solution on phenacyl bromide. The melting points reported were 161° for the β-isomer which was formed in largest quantity, and 129° for the α-. We have confirmed these observations.

An unexpected observation was made in the reaction of phenacyl bromide and sodium kojate when anhydrous methanol was the solvent. A crystalline compound was obtained, m. p. 197–197.5°, which contained both sodium and bromine. Analysis was satisfactory for this complex: $(C_6H_5COCH_2O{-}C_5H_2O_2{-}CH_2OH)_2{\cdot}NaBr$. The corresponding chloride, m. p. 158–158.5°, was prepared similarly from phenacyl chloride. Both compounds lost the elements of sodium halide and changed to VI on washing with water.

Experimental

Acetylation with Acetic Anhydride (a) with Sodium Acetate.—Yubata's directions were followed, giving the crystalline diacetate. The light tan crystals melted at 100–102°. After crystallization from methanol, with decolorization by Norit, white crystals were obtained, m. p. 102–103°. This diacetate is soluble to the extent of 36 g. in 100 g. of water at 60°.

(b) With Zinc Chloride.—Woods' directions[2] were followed. A mixture of 5 g. of kojic acid (m. p. 151–152°), 31.3 g. of acetic anhydride, and 2.5 g. of freshly fused zinc chloride was heated under reflux over a water-bath at 98° for ninety minutes. There was intense darkening but no observable vigorous reaction. Then the mixture was gradually heated to 145° and was maintained at 135–145° for ninety minutes. Considerable charring took place. Then the volatile material was distilled off at 20 mm. and the residue was treated with 50 ml. of boiling water and set aside to cool. A black tar separated which later crystallized. The crystals were separated, and the filtrate extracted with three 25-ml. portions of benzene. The combined extracts were added to the crystals and the mixture was heated to effect solution. Attempts at decolorization with Norit A were not successful. The benzene solution was washed once with water, dried, and evaporated leaving 5.7 g. of yellow-tan

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[4] Hurd and Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[5] Woods, THIS JOURNAL, **68**, 2116 (1946).

[6] Paal and Demerer, *Ber.*, **29**, 2093 (1896).

crystalline residue, m. p. 84-90°. It was recrystallized from 26 ml. of boiling water, using Norit, giving 4.4 g. of lighter tan-colored solid, m. p. 99-101°, and filtrate A. Crystallization of this solid from methanol (Norit) produced white crystals, m. p. (and mixed m. p.) 102-103°.

Anal. Calcd. for $C_{10}H_{10}O_8$: C, 53.10; H, 4.42. Found: C, 52.84; H, 4.46.

Concentration of filtrate A gave 0.8 g. of solid, m. p. 90-92° and a filtrate which only gave tar on evaporation. Crystallization of the 0.8 g. of solid from water purified this to 0.6 g. of crystals of m. p. 100-102°, and a filtrate giving 0.1 g. of solid, m. p. 88-92° on evaporating. The physical and chemical properties of the 0.6 g. of product were satisfactory for the diacetate.

A solution of 0.5 g. of the above product, m. p. 100-102°, in 25 ml. of hot water was refluxed for eighteen hours. Then the water was evaporated, and the residue was crystallized from methanol; m. p. 148-150°. It gave a deep coloration with ferric chloride and gave no depression on mixed melting with kojic acid.

The products from (a) and (b) behaved identically toward 2,4-dinitrophenylhydrazine in giving no hydrazone. To a warm, homogeneous solution of 0.5 g. of the hydrazine, 1 ml. of concentrated hydrochloric acid, and 15 ml. of methanol was added 0.5 g. of the product of m. p. 102-103°. The solution was heated for five minutes on a steam-bath, cooled and finally concentrated. A total of 0.5 g. of 2,4-dinitrophenylhydrazine hydrochloride, m. p. about 196°, was recovered. Finally all the methanol was evaporated leaving a dark oil which was completely water soluble. The water was evaporated but the residue would not crystallize from any solvent.

O-Caproylkojic Acid (II, R = C_5H_{11}).—A mixture of 12.2 g. of pure caproic acid and 5.2 g. of fused zinc chloride was heated to 130°. To it was added portionwise 5 g. of kojic acid with stirring during thirty minutes. Heating (130°) and stirring were continued for an additional two hours. The residue was separated from excess zinc chloride by washing with water, and was then extracted into 200 ml. of ether. The combined ether extracts were dried, the ether removed, and excess caproic acid distilled off using an aspirator pump. The residue was redissolved in ether, neutralized with sodium bicarbonate solution, dried, and concentrated to yield 4.9 g. (60.5%) of a white crystalline solid, m. p. 66-67°. After two recrystallizations from ether, it melted at 66.5-67°. It gave a deep red, nearly opaque, coloration with ferric chloride in dilute hydrochloric acid. Hydrolysis by acid or alkali regenerated the caproic acid.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.80; H, 6.68. Found: C, 59.33; H, 6.72.

O-Acetylkojic Acid (II, R = CH_3).—(a) A mixture of 2 g. of kojic acid and 2.2 g. of anhydrous[7] aluminum chloride was heated to 120° for five minutes. When cool, there was added cautiously 8 ml. of acetyl chloride. The mixture was heated under reflux for thirty minutes after which the excess of acetyl chloride was distilled off. The cooled residue was treated with ice and concentrated hydrochloric acid and filtered. The yield was 1.5 g. (58%) of white, crystalline solid which, after recrystallization from ethanol, melted at 133-133.5°. It gave a red color test with ferric chloride.

Anal. Calcd. for $C_8H_8O_5$: C, 52.20; H, 4.35. Found: C, 52.14; H, 4.28.

(b).—A mixture of 3.7 g. of the diacetate of kojic acid[3] and 4.5 g. of aluminum chloride was heated to 110°. A vigorous evolution of fumes resulted, and heating was continued at this temperature for ten minutes. Working up as in (a) gave rise to 2.6 g. (86.3%) of the monoacetate. Acetylation by heating with acetic anhydride and sodium acetate regenerated the diacetate.

Methyl O-Acetylkojate.—To 0.5 g. of O-acetylkojic acid in 15 ml. of dry methanol was added 1.4 g. of dry silver oxide and 1.9 g. of methyl iodide. The mixture was refluxed for fifteen minutes, then the same amounts of the reagents added again and the refluxing continued for another fifteen minutes. After filtration, the residue of silver iodide was washed well with methanol and the combined filtrates evaporated to give 0.6 g. of crystalline residue. This was recrystallized thrice from ether using Norit A to form white crystals of m. p. 120-122°.

Anal. Calcd. for $C_9H_{10}O_5$: C, 54.60; H, 5.08. Found: C, 54.67; H, 5.19.

Allyl Kojate (III).—To a suspension of 10 g. of kojic acid in 100 ml. of dry methanol was added a solution formed by dissolving 1.61 g. of sodium in 40 ml. of dry methanol. This mixture was then refluxed with 8.5 g. of allyl bromide until it tested neutral to litmus (about two hours). It was then concentrated on a steam-bath, cooled, and the salt was separated. Further concentration left an oil which only partially crystallized on standing for several days. The material was distilled at 160° (1 mm.) to remove a vile smelling oil which was not investigated further. The residue, which solidified on cooling, was recrystallized from acetone, m. p. 125-125.5°. The white crystalline product gave no color test with ferric chloride. The yield was 5.9 g. or 46%.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.40; H, 5.53. Found: C, 59.59; H, 5.76.

6-Allylkojic Acid (IV).—(a) In preparing this compound, it was not necessary to isolate and purify the allyl kojate. The yields were just as good if the intermediate oil was pyrolyzed without isolation of crystalline III. In either case the material obtained from 10 g. of kojic acid was heated between 180-200° at 1 mm. for fifteen minutes. The residue was then fractionally crystallized from absolute ethanol. There was obtained 3.4 g. of m. p. 160-160.5° and 3.5 g. of m. p. 186-187°. Further recrystallization of the higher melting material resulted in a sudden drop to 160° with no m. p. depression when mixed with the lower melting form. The total yield was 6.9 g. or 54% theoretical.

(b).—A solution of 0.45 g. of crystalline III in 15 ml. of absolute ethanol was maintained at 60° while bubbling in dry hydrogen chloride for one hour. The ethanol was then evaporated and the residue was recrystallized from methanol giving 0.4 g. of m. p. 160-161° which gave no depression on mixed melting with the product in (a).

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.40; H, 5.53. Found: C, 59.66; H, 5.71.

2-Acetoxymethyl-5-acetoxy-6-allyl-1,4-pyrone.—The method involved refluxing either III or IV for about thirty minutes with an excess of acetic anhydride in the presence of sodium acetate. The product was isolated by pouring on ice and filtering. Recrystallization from 95% ethanol using Norit A gave light yellow plates, m. p. 112.5-113°. From 4 g. of III there was obtained 2.9 g. of product or 79%. From 1 g. of IV there was obtained 1.2 g., or 82%.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.70; H, 5.27. Found: C, 58.61; H, 5.34.

Behavior of Phenyl Allyl Ether toward Hydrochloric Acid.—A solution of 30 g. of phenyl allyl ether (b. p. 90° (26 mm.)) in 50 ml. of absolute ethanol was heated to 70° and kept there while bubbling in dry hydrogen chloride for one hour. After processing, the residue was distilled giving 29 g. of material, b. p. 90° (26 mm.) which was not soluble in dilute alkali.

Allyl 6-Allylkojate (V).—To a solution of 1 g. of IV in 20 ml. of dry methanol was added a solution of 0.13 g. of sodium in 10 ml. of dry methanol. This was refluxed with 1 ml. of allyl bromide for one hour, concentrated, filtered from the sodium bromide, and crystallized from absolute ethanol. There was obtained 0.4 g. of unchanged IV and 0.6 g. of product, m. p. 92-95°. Further recrystallization from ether raised the m. p. to 96-97° (white needles).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 65.00; H, 6.30. Found: C, 65.47; H, 6.47.

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[7] Contact with atmospheric moisture must be avoided or the yield will be considerably reduced.

Phenacyl Kojate (VI).—Kojic acid, 2.12 g., was dissolved in 25 ml. of warm 95% ethanol. To this was added a solution of 0.6 g. of sodium hydroxide pellets in 2.5 ml. of water, and then 2.98 g. of phenacyl bromide. The solution was shaken by hand in a stoppered flask for fifteen minutes, then refluxed for thirty minutes. On chilling and concentrating, there was obtained 3.6 g. of material which was recrystallized thrice from absolute ethanol, m. p. 144.5–145°. The product (2.8 g. or 72%) appeared as white needles, giving no color test with ferric chloride. Drying in the oven at 110° resulted in partial decomposition, but a sample desiccated over sulfuric acid *in vacuo* for several hours showed no change in melting point.

Anal. Calcd. for $C_{14}H_{12}O_6$: C, 64.63; H, 4.65; mol. wt., 260. Found: C, 64.43; H, 4.84; mol. wt.,[8] 257.

Substitution of an equivalent amount of phenacyl chloride for the bromide in this reaction gave a 62% yield of the same product.

2-Acetoxymethyl-5-phenacyloxy-1,4-pyrone.—A mixture of 1.3 g. of VI, 6.5 ml. of acetic anhydride and 0.5 g. of dry sodium acetate was heated for two hours at 100°. After processing, the solid residue was recrystallized from methanol, giving 0.8 g. of white plates, m. p. 116–116.5° (53% theoretical). It was dried *in vacuo* over sulfuric acid with no change.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.53; H, 4.67; mol. wt., 302. Found: C, 63.40; H, 4.87; mol. wt.,[8] 299.

bis-(Phenacyl Kojate) Sodium Halide.—(a) To a solution of 2.0 g. of kojic acid in 20 ml. of dry methanol was added an equivalent amount of sodium methoxide in 10 ml. of dry methanol. This was refluxed for one hour with 2.81 g. of phenacyl bromide. Chilling and concentrating gave 2.67 g. of m. p. 197–197.5°. Recrystallization from 25 ml. of methanol gave no change. Qualitative tests showed the presence of sodium and active halogen. Washing with water resulted in a sharp drop in melting point to 145–146°. Mixed melting with VI then gave no depression.

Anal. Calcd. for $C_{28}H_{24}BrNaO_{10}$: C, 53.90; H, 3.86; Na, 3.70; Br, 12.84. Found: C, 53.35; H, 3.94; Na, 3.58; Br, 13.20.

(b).—When an equivalent amount of phenacyl chloride was substituted for the bromide, an eight-hour reflux period gave 2.45 g. of white needles, m. p. 158–158.5°. Qualitative tests showed the presence of sodium and active halogen, and washing with water left a residue identical with VI.

Anal. Calcd. for $C_{28}H_{24}ClNaO_{10}$: C, 58.10; H, 4.15; Na, 3.96; Cl, 6.14. Found: C, 56.10; H, 4.20; Na, 3.88; Cl, 6.15.

Phenylhydrazone, m. p. 140.5–141.5° (dec.), yield 85%, contains sodium and halogen, which was inert toward aqueous or alcoholic silver nitrate solutions. It was recrystallized from methanol.

Anal. Calcd. for $C_{40}H_{36}ClN_4NaO_8$: N, 7.39. Found: N, 7.52.

2,4-Dinitrophenylhydrazone, m. p. 235° (dec.), yield 91%, contains sodium and inactive halogen. It was recrystallized from ethanol.

Anal. Calcd. for $C_{40}H_{32}ClN_8NaO_{16}$: N, 11.93. Found: N, 11.48.

Acknowledgments.—The kojic acid was supplied by Dr. A. L. Elder of Corn Products Refining Company. Microanalyses for carbon and hydrogen were performed by Mrs. J. Gibbs and by Miss M. Hines. Those for nitrogen were done by Miss V. Hobbs.

Summary

Acetyl, caproyl, allyl and phenacyl derivatives of kojic acid are discussed.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 21, 1949

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[8] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Preparation of Pregnane-17α,21-diol-3,11,20-trione Acetate

BY L. H. SARETT

It was shown recently that pregnane-17α,21-diol-3,11,20-trione acetate (IV), a chemical precursor of Kendall's Compound E, could be prepared from pregnane-3α,21-diol-11,20-dione 21-acetate *via* the 20-cyanohydrin, the 3-keto-20-cyanohydrin, the 3-keto unsaturated nitrile and the 3-keto-20-cyano-17,20-osmate as successive intermediates.[1] Since the dehydration step went quite poorly because of the adverse influence of the 3-keto group, a revised scheme has now been tried. As starting material Δ^{17}-20-cyanopregnene-3α,21-diol-11-one (I), which may be prepared from pregnane-3α,21-dione diacetate in excellent yield, was used. Partial acetylation gave the 21-monoacetate (II) and the latter with osmium tetroxide afforded the osmate ester (III). It has been found that the osmate bridge in this molecule is sufficiently stable toward chromic acid in acetic acid to permit oxidation of the C-3 hydroxyl group.[2] Neutralization of the acetic acid with potassium bicarbonate followed by hydrolysis of the 3-keto osmate yielded IV. It has been found that by the addition of a suitable volume of benzene to the aqueous sulfite hydrolysis solution, the saponification of the C-21 acetoxy group could be largely suppressed. The combined contributions to the efficiency of the process resulted in an over-all yield of IV from pregnane 3α,21-diol-11,20-dione acetate which is somewhat more than twice the previous value.

Experimental

Δ^{17}-20-Cyanopregnene-3α,21-diol-11-one 21-Acetate (II).—A solution of 754 mg. of Δ^{17}-20-cyanopregnene-3α,21-diol-11-one (I) in 2.75 cc. of pyridine containing 255 mg. of acetic anhydride (1.0 molecular equivalent) was left at room temperature overnight. The solution was then diluted with ether, washed successively with dilute hydrochloric acid, dilute potassium carbonate and water, then concentrated to dryness. Several crystallizations of the residue from dilute alcohol and finally from ben-

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[1] Sarett, THIS JOURNAL, **70**, 1454 (1948).

[2] However this stability seems to rest upon the presence of the negative cyano group at C-20 since the 17,20-osmate of pregnane-3α,17α,20α-triol-11-one was converted by chromic acid and subsequent sulfite hydrolysis into a mixture from which no dioldione could be isolated.