Kiliani's dichromate mixture. After the final addition the mixture was refluxed for two hours, then poured into water to give 1.9 g. of material. Recrystallization from alcohol yielded yellow needles; m. p. 247–248°.

*Anal.* Calcd. for $C_{14}H_8N_2O_4$: C, 62.68; H, 2.98; N, 10.44. Found: C, 62.60; H, 3.16; N, 10.54.

## Summary

1. An improvement in the yield of 3-nitro-2-acetaminobiphenyl was accomplished.

2. The synthesis of 4-nitro-6-methylphenanthridine is described. This compound was used to prepare 4-amino-6-methylphenanthridine by reduction, 4-nitrophenanthridone by oxidation and phenanthridine-6-carboxylic acid by condensation with formaldehyde followed by oxidation.

3. 4-Amino-6-methylphenanthridine was converted to 4-acetamino-6-methylphenanthridine, 4-(β-diethylaminoethylamino)-6-methylphenanthridine, and 4-chloro-6-methylphenanthridine.

LINCOLN 8, NEBRASKA RECEIVED FEBRUARY 18, 1949

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

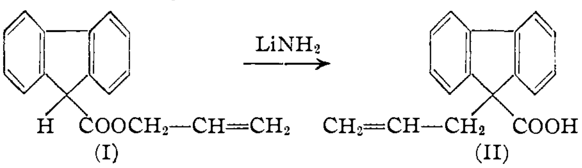
# The Rearrangement of Allyl 9-Fluorenecarboxylate

BY RICHARD T. ARNOLD, WILLIAM E. PARHAM AND R. M. DODSON

The rearrangement of allyl, *n*-crotyl, and isocrotyl diphenylacetates to the respective α-substituted diphenylacetic acids by means of mesitylmagnesium bromide or sodium hydride has recently been reported.[1] This reaction has now been extended to allyl 9-fluorenecarboxylate.

9-Fluorenecarboxylic acid was prepared from benzilic acid and aluminum chloride by a modification of the method previously described.[2] This modified procedure avoided the intractable emulsions obtained by the published directions and resulted in a better yield and a purer product. An attempt to prepare 9-fluorenecarboxylic acid by the catalytic dehydration of benzilic acid with *p*-toluenesulfonic acid in boiling xylene resulted in the formation of benzilide (the lactide of benzilic acid).

9-Fluorenecarboxylic acid was esterified both by treatment of its acid chloride with allyl alcohol and pyridine and by direct reaction with excess allyl alcohol in the presence of *p*-toluenesulfonic acid. When allyl 9-fluorenecarboxylate (I) was heated under reflux with lithium amide[3] in toluene, a practically quantitative yield of 9-allyl-9-fluorenecarboxylic acid (II) resulted.



(I) (II)

In a similar manner, allyl diphenylacetate was rearranged to allyldiphenylacetic acid by the use of lithium amide.

Preliminary experiments have indicated that, on treatment of benzyl 9-fluorenecarboxylate with lithium amide in toluene, a mixture of acids is obtained. Results from the rearrangement of the benzyl esters will be reported at a later date.

## Experimental[4]

**9-Fluorenecarboxylic Acid.**—A solution of 22.8 g. (0.10 mole) of benzilic acid in 350 ml. of dry, thiophene-free benzene was cooled in ice and the crystalline mass which resulted was treated with 40.0 g. (0.30 mole) of anhydrous aluminum chloride. The mixture was thoroughly shaken, then heated under reflux for three hours. Large quantities of hydrogen chloride were evolved. The resulting dark-red solution was cooled and was cautiously decomposed by the addition of small pieces of ice. The mixture was diluted with 200 ml. of water and 100 ml. of concentrated hydrochloric acid and the benzene was distilled from the reaction. The product was separated by filtration; all the lumps were crushed; then the product was extracted by boiling with 200 ml. of 10% sodium carbonate solution. This extraction was repeated on the undissolved residue with 100 ml. of 10% sodium carbonate solution. The basic filtrates were strongly acidified with concentrated hydrochloric acid, and the resulting suspension was digested on the steam-bath for one-half hour. By filtration 21.0 g. (quantitative yield) of 9-fluorenecarboxylic acid, m. p. 200–225°, was obtained. To purify the product, the dry acid was suspended in 100 ml. of benzene; the mixture was warmed on the steam-bath; the product was recovered by filtration and washed on the filter with 25 ml. of benzene and finally with petroleum ether (b. p. 28–38°). In this way 17.3 g. (82.5%) of 9-fluorenecarboxylic acid, m. p. 226–229°, was obtained. The melting points[2,5] reported for this compound range from 222 to 232°.

**Benzilide.**—A solution of 10.0 g. of benzilic acid and 2.0 g. of *p*-toluenesulfonic acid in 150 ml. of dry xylene was heated under reflux for two hours and the water which formed was separated by an azeotropic separator. Extraction of the xylene solution with aqueous sodium hydroxide produced only traces of acidic material. The xylene solution was diluted with petroleum ether (b. p. 28–38°). The resulting solution was cooled, and the product was separated by filtration. In this manner, 5.90 g. (64%) of benzilide, m. p. 195–196°, was obtained. The compound is reported to melt at 196°.[6]

*Anal.* Calcd. for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79. Found: C, 80.07; H, 4.90.

**Allyl 9-Fluorenecarboxylate.**—A mixture of 17.3 g. of 9-fluorenecarboxylic acid and 50 g. of purified thionyl chloride was heated under reflux for 45 minutes. The excess thionyl chloride was removed *in vacuo*. The residue was dissolved in 75 ml. of dry carbon tetrachloride. The

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(1) R. T. Arnold and S. Searles, Jr., THIS JOURNAL, **71**, 1150 (1949).

(2) D. Vorländer and A. Pritzsche, *Ber.*, **46**, 1793 (1913).

(3) Obtained from the Metalloy Corporation, Rand Tower. Minneapolis, Minnesota.

(4) Microanalyses by Jay Buckley and William Hunter. The melting points were taken on a Fisher-Johns melting point apparatus.

(5) R. Burtner and J. W. Cusic, THIS JOURNAL, **65**, 262 (1943); W. Schlenk and E. Bergmann, *Ann.*, **463**, 98 (1928).

(6) A. Einhorn and C. Mettler, *Ber.*, **35**, 3639 (1902).

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%), $n^{30}D$ 1.6000 to 1.6022. A center fraction was redistilled for analysis, b. p. 174° at 2 mm., $n^{30}D$ 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

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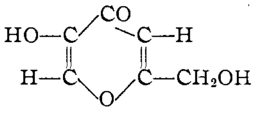
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# 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.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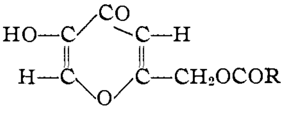
II

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).