1 g. of S-benzyl-L-cysteinyl-D-valine (II), m.p. 204–209°, transition at 185–195° (micro-block); $[\alpha]^{23}D$ +23.5° (*c* 1.63 in 2.5 *N* hydrochloric acid).

Anal. Calcd. for $C_{15}H_{22}N_2O_3S$: C, 58.04; H, 7.15; N, 9.03. Found: C, 58.31; H, 7.10; N, 8.79.

N-Phenylacetyl-S-benzyl-L-cysteinyl-D-valine Triethylamine Salt.—A solution of 3.6 g. of S-benzyl-L-cysteinyl-D-valine in 11.5 ml. of 1.01 *N* sodium hydroxide was cooled until it was partially frozen and 12.7 ml. of 1.01 *N* sodium hydroxide was added. With stirring, 1.7 ml. of phenylacetyl chloride was added to the partially frozen solution. The mixture was stirred at 0° for 30 minutes and an additional 30 minutes with no external cooling. The clear solution was acidified with dilute hydrochloric acid to *p*H 1 and was extracted twice with ether. After the ether extract was dried over sodium sulfate, 2 ml. of triethylamine was added to the clear ether solution. A crystalline product formed that was recrystallized from a mixture of acetone and ether to give 4.3 g. of the triethylamine salt of N-phenylacetyl-S-benzyl-L-cysteinyl-D-valine, m.p. 111–121°, which was used without further purification in the preparation of the dipeptide (IV).

A sample was also prepared by dissolving crude N-phenylacetyl-S-benzyl-L-cysteinyl-D-valine in acetone, adding triethylamine (20% excess), and then adding ether until crystallization started. The solution was cooled and the crystalline product was removed, washed with acetone–ether, and with ether, and dried to give N-phenylacetyl-S-benzyl-L-cysteinyl-D-valine triethylamine salt, m.p. 127–130°; $[\alpha]^{23}D$ −15.1° (*c* 1.52 in chloroform).

Anal. Calcd. for $C_{29}H_{43}N_3O_4S$: C, 65.75; H, 8.18; N, 7.93. Found: C, 65.65; H, 7.88; N, 7.56.

N-Phenylacetyl-L-cysteinyl-D-valine (IV).—Four grams of N-phenylacetyl-S-benzyl-L-cysteinyl-D-valine triethylamine salt was dissolved in 50 ml. of liquid ammonia; 0.9 g. of sodium was added in portions until a permanent blue color formed. To the solution, 5 g. of ammonium sulfate was added and the ammonia was allowed to evaporate. The residue was dissolved in water, the solution was extracted with ether, and the aqueous solution was acidified with 2 *N* sulfuric acid to *p*H 1. The crystalline product that separated was collected on a filter, washed with water, and dried *in vacuo* to give 2.7 g. of N-phenylacetyl-L-cysteinyl-D-valine (IV), m.p. 178–188°, softening at 173° (micro-block). After five recrystallizations from water–methanol the product melted at 174–193°, $[\alpha]^{23}D$ −45.3° (*c* 0.852 in 0.5 *N* ammonium hydroxide).

Anal. Calcd. for $C_{18}H_{22}N_2O_4S$: C, 56.78; H, 6.55; N, 8.28. Found: C, 56.99; H, 6.68; N, 8.08.

RAHWAY, NEW JERSEY

[CONTRIBUTION FROM THE NATIONAL CANCER INSTITUTE, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

Analogs of the Carcinogen 2-Acetylaminofluorene: The Isomeric 4-Acetylaminofluorene[1]

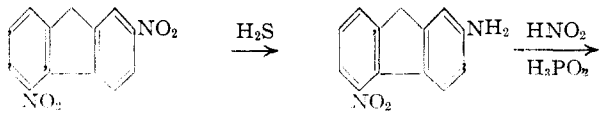
BY JOHN H. WEISBURGER, ELIZABETH K. WEISBURGER[2] AND HAROLD P. MORRIS

RECEIVED JANUARY 9, 1952

A direct synthesis of 4-acetylaminofluorene, an isomer of the carcinogen 2-acetylaminofluorene, is described. The ultraviolet absorption spectra of both compounds in relation to their structures are discussed. Preliminary results indicate that the 4-isomer is not an active carcinogen.

Since the discovery of the carcinogenic effect of 2-acetylaminofluorene[3] a number of related compounds have been prepared and tested for the purpose of studying the effect of chemical structure on biological activity.[4–9]

Of the possible acetylaminofluorenes the 4-isomer has so far been unknown. It is the purpose of this paper to describe a convenient synthesis of this compound achieved according to the reaction scheme



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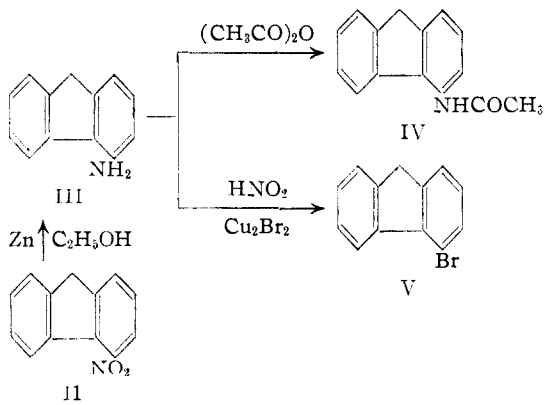

The dinitration of fluorene and separation of 2,7- and 2,5-dinitrofluorene was carried out according to Courtot.[10]

Monoreduction of 2,5-dinitrofluorene with hydrogen sulfide in ammoniacal ethanol gave 2-amino-5-nitrofluorene as a red gummy material, which did not crystallize satisfactorily from a variety of solvents. The addition of dilute sulfuric acid to a hot acetic acid solution of the product, however, resulted in the deposition of the crystalline acid sulfate salt. After this treatment the free base obtained from the salt crystallized readily.

(1) Presented at the Meeting of the XIIth International Congress of Pure and Applied Chemistry, New York, September, 1951.

(2) Public Health Service Research Fellow of the National Cancer Institute, 1949–1951.

(3) R. H. Wilson, F. DeEds and A. J. Cox, Jr., *Cancer Research*, **1**, 595 (1941).

(4) C. Hoch-Logeti, *Brit. J. Cancer*, **1**, 391 (1947).

(5) E. C. Miller, J. A. Miller, R. B. Sandin and R. K. Brown, *Cancer Research*, **9**, 504 (1949).

(6) H. P. Morris, C. S. Dubnik and J. M. Johnson, *J. Natl. Cancer Inst.*, **10**, 1201 (1950).

(7) H. P. Morris and C. S. Dubnik, *Cancer Research*, **10**, 233 (1950).

(8) E. K. Weisburger, THIS JOURNAL, **72**, 1758 (1950).

(9) E. K. Weisburger, J. H. Weisburger and F. E. Ray, *J. Org. Chem.*, **16**, 1697 (1951).

(10) Ch. Courtot and J. Moreaux, *Compt. rend.*, **217**, 453 (1943).

Monoreduction with three moles of stannous chloride per mole of dinitrofluorene indicated that the 2-nitro group was also attacked by this reducing agent. In contrast it was shown[11] in the dinitronaphthalene series that the alkaline sulfides reduced the less positive (α) nitro group while the acidic stannous chloride acted on the more positive (β) nitro group. This points to the important activation of substituents at the extended para positions, 2 and 7, in fluorene which is also borne out in the absorption spectra discussed below.

Hypophosphorous acid removed the diazotized amino group in approximately 36 hours to give 4-nitrofluorene. The crude product was most conveniently purified by chromatography on alumina. Reduction to the amine and acetylation of the latter led to the desired 4-acetylaminofluorene.

A comparison of the ultraviolet absorption spectra of 2- and 4-acetylaminofluorene, shown in Fig. 1, reveals a certain similarity of the spectrum of 4-acetylaminofluorene to that of fluorene,[12] or 4-methylfluorene.[13] Some of the fine structure of the fluorene spectrum has disappeared, and the relative intensities at the maxima or minima have changed slightly. This would indicate a small amount of resonance coupling of the substituent grouping with the fluorene nucleus. On the other hand the spectrum of 2-acetylaminofluorene appears to be considerably different from that of the 4-isomer or fluorene itself. While the three principal maxima still suggest the remnants of the main peaks of fluorene, there is a considerable loss of the fine structure, together with a displacement to longer wave lengths and increased intensities. This points to an appreciable coupling of the side chain with the remainder of the molecule. The similarity of the spectra of 4-acetylaminofluorene and fluorene might indicate that there are steric effects preventing coplanarity of the 4-acetylamino side-chain with the fluorene nucleus, owing to interference with the hydrogen on the 5-carbon atom. On the other hand some of the difference between the 2- and 4-substituted compounds may be ascribed to the fact that the 2-position of fluorene is at the extreme end of the preferred horizontal polarization. This would be appreciably enhanced by the substituent. The 4-position is more centrally located; a substituent would affect mostly the minor vertical polarization of fluorene.[14]

A Sandmeyer reaction on 4-aminofluorene gave a rather poor yield of 4-bromofluorene, m.p. 112°. While the low yield may have been entirely due to the experimental procedure, it is also conceivable that steric effects hinder somewhat the entrance of bulky substituents at the 4-position. The melting point of the 4-bromo derivative does not agree

(11) H. H. Hodgson, *J. Soc. Dyers and Colourists*, **59**, 246 (1943).

(12) R. N. Jones, THIS JOURNAL, **67**, 2021, 2127 (1945).

(13) M. Orchin and E. O. Woolfolk, *ibid.*, **67**, 122 (1945).

(14) This view is supported also by a comparison of the spectra of 1- and 2-substituted fluorenes. One of the referees to this paper suggested that: "1-Hydroxyfluorene has a spectrum related to the 2-isomer (R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, curves 320 and 321) in the same way that the 4-acetylamino spectrum is related to that of the 2-isomer. Extended excitation forms cannot be written for either the 1- or 4-isomer and in the former there is little probability of steric hindrance."

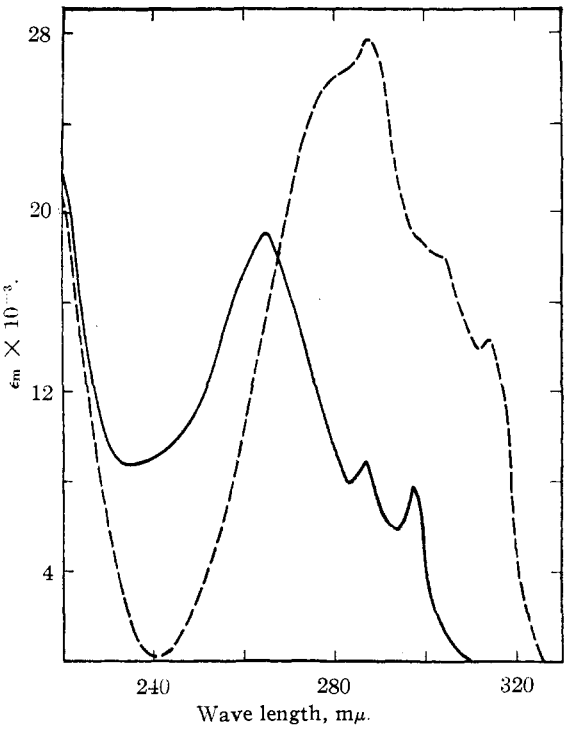

Fig. 1.—Absorption spectra of 4-acetylaminofluorene — and 2-acetylaminofluorene - - - - -.

with that (165°) reported by Miller and Bachman.[15] These authors claimed to have obtained this compound by mercuration of fluorene followed by replacement of the acetoxymercuri group with bromine.

At the end of 13 months of feeding 4-acetylaminofluorene to rats at a level of 0.25% in the diet no gross tumors were observed. Most of the rats were still alive and healthy. The rats in a control group ingesting 2-acetylaminofluorene under comparable conditions had developed tumors; many of these animals had multiple lesions. Details of the biological testing will be reported elsewhere.

Experimental

2-Amino-5-nitrofluorene (I). A. By Hydrogen Sulfide Reduction.—Hydrogen sulfide was passed through a refluxing suspension of 68 g. of 2,5-dinitrofluorene[16] in 1750 ml. of 95% ethanol containing 250 ml. of concentrated ammonium hydroxide. After one and two hours 50-ml. portions of ammonium hydroxide were added.[17] At the end of four hours the mixture was diluted to a volume of 4 liters with ice and cold water. Sodium chloride (50 g.) was added to promote the coagulation of the precipitate. After standing overnight the orange-red solid was filtered off and extracted three times with a total of 6 liters of boiling water

(15) H. F. Miller and G. B. Bachman, THIS JOURNAL, **57**, 2447 (1935).

(16) 2,5-Dinitrofluorene seemed to undergo slight decomposition on storage, as indicated by a decrease in the melting point from 205 to 195° after standing five years at room temperature. Recrystallization from acetic acid and benzene failed to raise the melting point to its original value, while monoreduction of this low-melting compound to the desired aminonitrofluorene gave a very poor yield (similar difficulties were encountered with stored 2,7-dinitrofluorene). The contaminant was not identified, although it could be removed by passing a dilute benzene solution of the 2,5-dinitrofluorene through a column of activated alumina. The red and blue bands on the column were eluted with ethanol and acetic acid; these fractions were not investigated.

(17) F. E. Cislak and C. S. Hamilton, THIS JOURNAL, **53**, 746 (1931).

containing 80 ml. of concentrated hydrochloric acid. The solution was boiled for five minutes with Norit, filtered by suction, cooled and made basic with ammonium hydroxide. The gummy red material weighed 43 g., m.p. 80–100°. The crude product was dissolved by refluxing in 860 ml. of acetic acid. A mixture of 17 ml. of concentrated sulfuric acid and 97 ml. of water was added. Upon cooling 37.2 g. (47%) of the acid sulfate salt of the amine crystallized. A further 7.5 g. (9.5% or a total yield of 56.5%) of material was obtained from the filtrate on standing a few days. A portion (6.6 g.) recrystallized again from 150 ml. of acetic acid, 20 ml. of water and 1 ml. of sulfuric acid yielded 5.7 g. of yellow needles, decomposing around 290°.

Anal. Calcd. for $C_{13}H_{10}O_2N_2 \cdot H_2SO_4$: C, 48.14; H, 3.73; N, 8.64. Found: C, 47.79; H, 4.25; N, 8.23.

One gram of the sulfate gave 0.7 g. of the free amine, m.p. 120–135°, upon suspension in ammonium hydroxide. After crystallization from 15 ml. of benzene 0.3 g. of large red needles, m.p. 162–163°, was obtained.

Anal. Calcd. for $C_{13}H_{10}O_2N_2$: C, 69.01; H, 4.46; N, 12.39. Found: C, 69.17; H, 4.98; N, 12.37.

B. By Stannous Chloride Reduction.—Hydrogen chloride gas was bubbled through a refluxing suspension of 7 g. of stannous chloride in 15.6 ml. of glacial acetic acid until solution occurred. The solution was then cooled in an ice-bath and saturated with hydrogen chloride.

Two and six-tenths grams of 2,5-dinitrofluorene was dissolved in 70 ml. of boiling glacial acetic acid. The solution was cooled rapidly giving a slush of small crystals; this was cooled in an ice-bath and saturated with hydrogen chloride gas. The stannous chloride solution obtained above was added dropwise over a period of 90 minutes to the mechanically stirred dinitrofluorene suspension which was cooled in an ice-bath. Stirring was continued for 150 minutes; the mixture was then allowed to stand at room temperature for three days. A white solid was filtered off and the filtrate reduced to dryness *in vacuo* in order to remove the excess free hydrogen chloride. The resulting solids were combined, suspended in 250 ml. of 10% sodium hydroxide solution and stirred for one hour. After filtration the red product obtained was extracted twice with 200 ml. of boiling 0.2 *N* hydrochloric acid.

The tan-yellow, acid-insoluble material weighed 0.9 g. and melted at 185–188°. One recrystallization from benzene followed by three crystallizations from glacial acetic acid gave 0.3 g. of yellow needles, m.p. 206–208°, mixed m.p. with 2,5-dinitrofluorene, 205–207°. Hence this portion was unchanged starting material.

The ice-cold acid solution was made basic with 25 ml. of 25% sodium hydroxide solution giving a red precipitate. After filtration 1.5 g. of crude 2-amino-5-nitrofluorene, m.p. 135–150°, was obtained. Two recrystallizations of the acid sulfate salt from acetic acid, as described above, conversion to the free base followed by crystallization from benzene yielded 0.5 g. of red needles, m.p. 160–162°, mixed m.p. with material obtained by hydrogen sulfide reduction, 160–162°. After acetylation the acetyl derivative melted at 280–282°, mixed m.p. with the 2-acetylamino-5-nitrofluorene described below, 280–282°.

2-Acetylamino-5-nitrofluorene.—Acetic anhydride (0.6 ml.) was added to a refluxing solution of 0.7 g. of I in 30 ml. of benzene. The red solution turned yellow and shortly thereafter yellow needles formed. Upon cooling 0.5 g. of 2-acetylamino-5-nitrofluorene, m.p. 282°, was obtained. Crystallization from 60 ml. of acetic acid produced 0.4 g. of lemon yellow needles, m.p. 284–285°.

Anal. Calcd. for $C_{13}H_{12}O_3N_2$: C, 67.15; H, 4.51; N, 10.44. Found: C, 66.82; H, 4.79; N, 10.15.

4-Nitrofluorene (II).—In a 2-l. flask 37.2 g. (0.11 mole) of 2-amino-5-nitrofluorene sulfate was dissolved in 750 ml. of acetic acid, 77 ml. of water and 27 ml. of concentrated sulfuric acid by refluxing for 30 minutes. The solution was cooled rapidly to 5° in an ice-bath giving a slush. This dissolved upon the addition over a period of five minutes, with mechanical stirring, of 10.2 g. of sodium nitrite in 23 ml. of water. The solution was stirred for another 90 minutes. Precooled 50% hypophosphorous acid (214 ml.) was added rapidly and the flask (kept at 0–5°) was connected to a system permitting the measurement of the volume of gas evolved. Stirring was maintained by means of a magnetic stirrer. A few minutes after the addition of hypophosphorous acid the clear solution became cloudy.

In 3¼, 9½, 18½, 22¼, 28½, 32 and 42 hours 620, 1300, 1800, 2020, 2240, 2310 and 2510 ml., respectively, of gas were collected. The theoretical volume of nitrogen would be 2580 ml. The data agreed approximately with a first-order reaction scheme.

After 32 and 42 hours, 500 and 400 ml., respectively, of cold water were added. Filtration and air-drying yielded a precipitate weighing 33.7 g. This solid was extracted successively with 500, 120 and 130 ml. of boiling benzene. The white residue (11.0 g.), which did not melt and remained white on calcination, was probably of an inorganic nature and was not investigated further.

The brown benzene solution was chromatographed on a column of Merck and Co., Inc., alumina 7.5 cm. long and 3.5 cm. in diameter. Brown, tan, gray-green and orange-red bands were found, in descending order. The eluate was orange-yellow. After the solution had been added, the column was washed with 200 ml. of benzene. The combined eluates were taken to dryness giving an orange-yellow solid weighing 21.8 g. (90%) and melting at 68–74°; a portion (0.4 g.) crystallized from 4 ml. of methanol gave 130 mg. of lemon-yellow needles, m.p. 75–76°.

Anal. Calcd. for $C_{13}H_9O_2N$: C, 73.92; H, 4.30; N, 6.63. Found: C, 73.57; H, 4.65; N, 6.86.

4-Nitrofluorenone.—Two grams of chromic anhydride dissolved in 20 ml. of a 1:1 mixture of water and glacial acetic acid was dropped into a refluxing solution of 1.0 g. of II in 25 ml. of glacial acetic acid over a period of ten minutes. After refluxing for one hour the solution was added to 100 ml. of ice-cold 3 *N* sulfuric acid. The resulting precipitate was filtered, washed with 1 *N* sulfuric acid followed by water. The air-dried solid weighing 1.0 g. was dissolved in 20 ml. of benzene and the solution allowed to percolate through a column of alumina 7 cm. long and 1 cm. in diameter. The column was washed with 20 ml. of solvent. The yellow eluate was taken to dryness and recrystallized twice from 95% ethanol yielding 0.3 g. of long orange needles of 4-nitrofluorenone, m.p. 172.5–173°, in agreement with published data.[18,19]

4-Aminofluorene (III).—A mixture of 7.0 g. of II, 1.8 g. of calcium chloride, 20 g. of zinc dust, 20 ml. of water and 100 ml. of ethanol was refluxed until colorless (approximately 45 minutes). Norit (0.5 g.) was added and refluxing continued for another hour. The solids were filtered off by suction through a warm buchner funnel. The colorless solution was reheated to the boiling point and 5 ml. of concentrated hydrochloric acid was added. On cooling to 5° the amine hydrochloride (5 g.), m.p. 290° (dec.), crystallized out. The free amine (4 g. or 67%), m.p. 113–115°, was obtained on treatment with concentrated ammonium hydroxide. A sample (0.7 g.) recrystallized successively from 150 and 80 ml. of ligroin gave 0.3 g. of long white needles, m.p. 115–116°.

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.05; H, 6.02; N, 7.61.

From the alcoholic mother liquor 1.5 g. (25%, or a total yield of 92%) of light tan amine, m.p. 92–98°, was recovered by addition of 500 ml. of ice-water and ammonium hydroxide. This product was suitable to prepare the acetyl derivative, described below, but required more recrystallizations at that stage.

4-Acetylaminofluorene (IV).—A solution of 1.75 ml. of acetic anhydride in 10.5 ml. of dry benzene was dropped into a refluxing solution of 2.9 g. of III in 40 ml. of benzene. Crystals appeared after boiling for one-half hour. Upon cooling 3.1 g. of fluffy white needles, m.p. 194–195°, was obtained. Recrystallization by solution in 150 ml. of benzene (refluxing one hour) and treatment with Norit, gave 2.7 g. (75%) of material, m.p. 199–200°.

Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.28. Found: C, 80.81; H, 5.90; N, 6.19.

The ultraviolet absorption spectra of 4-acetylaminofluorene and that of the 2-isomer in alcohol were determined in a Beckman DU spectrophotometer.

4-Bromofluorene (V).—A hot solution of 1.05 g. of 4-aminofluorene hydrobromide in 30 ml. of glacial acetic acid and 2 ml. of 48% hydrobromic acid was cooled rapidly to 5° yielding a slush of the salt. With mechanical stirring a solution of 280 mg. of sodium nitrite in 3 ml. of water was

(18) Ch. Courtot, *Ann. chim.*, [10] **14**, 5 (1930).

(19) J. Schmidt, *Ber.*, **38**, 3737 (1905).

added in several portions, whereupon a clear solution formed. Stirring was continued for 90 minutes at 5°.

In the meantime 0.5 g. of sodium sulfite was added to a mixture of 2.0 g. of hydrated copper sulfate, 4.0 g. of sodium bromide, and 1.5 ml. of 1 *N* sulfuric acid in 10 ml. of water yielding a precipitate of cuprous bromide which was washed repeatedly with water by decantation in a centrifuge tube. This salt, dissolved in 10 ml. of 48% hydrobromic acid, was added to the diazonium solution. The dark mixture was allowed to stand for four hours while coming to room temperature. It was then refluxed for 15 minutes and poured onto cracked ice giving a white precipitate and a brown gum. The mixture was extracted twice with benzene. The benzene solution was washed with water until the washings were neutral, extracted three times with a total of 50 ml. of 1 *N* potassium hydroxide, and washed again until neutral. Only a small amount of material precipitated upon acidification of the aqueous alkaline solution.

The benzene layer was dried over calcium chloride and percolated through an alumina column (1 cm. diameter, 8 cm. high). The column was washed with 20 ml. of benzene and the combined eluates taken to dryness. Methanol (6 ml.) was added to the residue and the mixture was refluxed for five minutes giving a light yellow solution and a mobile brown gum. The solution was decanted through a filter. Crystallization occurred overnight at −10° to give 140 mg. of a mixture of white crystals, m.p. 100–103°, and a tan gum (re-extraction of the brown gum obtained above produced no further crystalline material). Three successive recrystallizations from 3, 2 and 0.7 ml. of methanol eliminated the gum and yielded 20 mg. of 4-bromofluorene, m.p. 112°.

Anal. Calcd. for $C_{13}H_9Br$: Br, 32.60. Found: Br, 32.80.

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

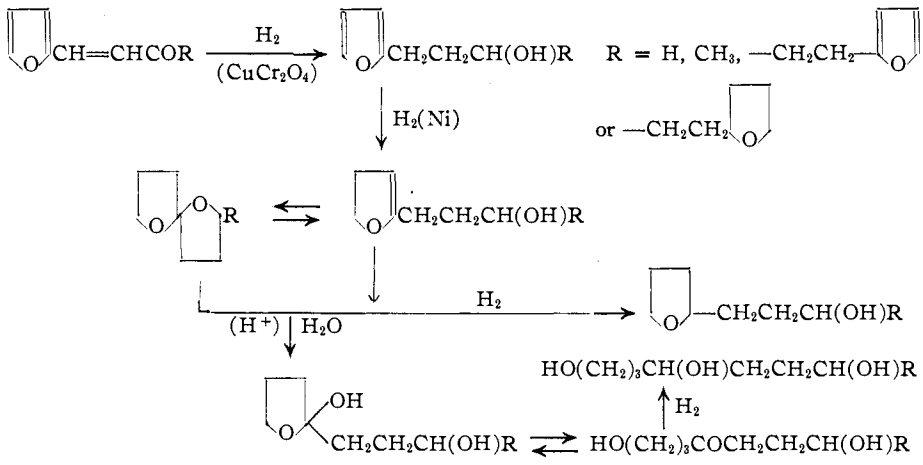
Polyhydroxyalkanes from Furfural Condensation Products

BY CHARLES R. RUSSELL, KLIEM ALEXANDER, W. O. ERICKSON, L. S. HAFNER AND L. E. SCHNIEPP

RECEIVED FEBRUARY 29, 1952

The reaction products from the copper chromite-catalyzed hydrogenation of the condensation products of furfural with acetaldehyde and with acetone are converted to polyols by further hydrogenation in the presence of water and a small amount of formic acid. The preparation of 1,4,7-heptanetriol, 1,4,7-octanetriol, 1-tetrahydrofuryl-3,6,9-nonanetriol and 1,4,7,10,13-tridecanepentaol is described.

The hydrolytic cleavage of furan rings under hydrogenating conditions has been shown to be a useful way of preparing 1,4-dihydroxy-substituted compounds. Leuck, Pokorny and Peters[2] used the method to prepare di- and trihydroxypentanes from furfural and furfuryl alcohol. Methylfuran has been similarly converted to 1,4-pentanediol.[3] The method is apparently applicable to any furan having an alkyl or hydroxyalkyl substituent in the 2-position. The course of the reaction is most readily explained in terms of the mechanism proposed by Topchiev[4] for the formation of acetopropanol from methylfuran. Confirmatory evidence for this mechanism, which involves the initial formation of a 4,5-dihydrofuran, has been presented by Swadesh, Smith and Dunlop.[5]



Previous work[6] on the hydrogenation of furfural condensation products made available several γ-(2-furyl)-alkanols which should yield 1,4,7-triols under the conditions of the hydrolytic-hydrogenation reaction. Three of these, 1-furylpropanol-3,1-furylbutanol-3 and 1,5-difurylpentanol-3 were selected, on the basis of ready availability of the raw materials for their preparation, for a study of conditions leading to optimum yields of cleavage products.

In addition to the purified furylalkanols, pure spirononanes[7] and the crude reaction mixtures, obtained by copper chromite-catalyzed hydrogenation of furylacrolein and the mono- and difurfuralacetones, were investigated as source materials for the preparation of triols. It was found that the 1,6-dioxaspiro[4.4]nonanes gave higher yields of triols than the corresponding furyl-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) G. J. Leuck, J. Pokorny and F. N. Peters, Jr., U. S. Patent 2,097,493 (1937).

(3) L. E. Schniepp, H. H. Geller and R. W. Von Korff, THIS JOURNAL, **69**, 672 (1947).

(4) K. S. Topchiev, *Compt. rend. acad. sci.* (*U.R.S.S.*), **19**, 497 (1938) [*C. A.*, **32**, 8411 (1938)].

(5) S. Swadesh, S. Smith and A. P. Dunlop, *J. Org. Chem.*, **16**, 476 (1951).

(6) K. Alexander, G. H. Smith, L. S. Hafner and L. E. Schniepp, THIS JOURNAL, **72**, 5506 (1950).

(7) K. Alexander, L. S. Hafner and L. E. Schniepp, *ibid.*, **73**, 2725 (1951).