was separated as white crystals upon concentration of the filtrate. The yield of sodium salt was 42 g. (77%).

The *p*-toluidine salt of 2-bromo-4-methylbenzenesulfonic acid after recrystallization from water melted at 216–218°.

Anal. Calcd. for $C_{14}H_{16}O_3BrNS$: S, 8.95. Found: S, 8.76.

Potassium Salt of 2-Iodo-4-methylbenzenesulfonic Acid.—The 2-iodo compound was prepared by diazotization of the 2-amino compound and subsequent reaction with potassium iodide solution. A 94% yield of crude potassium salt was obtained by concentration of the reaction mixture.

The *p*-toluidine salt melted at 227.5–230° after recrystallization from water.

Anal. Calcd. for $C_{14}H_{16}O_3INS$: S, 7.90. Found: S, 8.00.

2-Bromo-4-methylbenzenesulfonyl Chloride.—An intimate mixture of 5 g. (0.0183 mole) of powdered sodium 2-bromo-4-methylbenzenesulfonate and 15 g. (0.072 mole) of finely divided phosphorus pentachloride was heated for 1 hour at 160°. The initial reaction began at about 130–140°. The melt was poured onto ice and a crude sulfonyl chloride (82% yield) melting at 56–62° was recovered. A sample recrystallized from petroleum ether melted at 64–65°.

Anal. Calcd. for $C_7H_6O_2BrClS$: S, 11.9. Found: S, 12.1.

The methyl and ethyl esters of the 2-bromo-4-methylbenzenesulfonic acid melted at 62–63° and 70–71°, respectively.

Anal. Calcd. for $C_8H_9O_3BrS$: S, 12.1. Found: S, 12.0. Calcd. for $C_9H_{11}O_3BrS$: S, 11.45. Found: S, 11.80.

2-Iodo-4-methylbenzenesulfonyl Chloride.—This material was prepared in the same manner as the 2-bromo compound. A crude yield of 83% was obtained, and after recrystallization from petroleum ether the pure sulfonyl chloride melted at 66–67°.

Anal. Calcd. for $C_7H_6O_2ClIS$: S, 10.10. Found: S, 9.85.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

An "Isoaromatic" Product from 2-Methyl-3-benzofurylmethylmagnesium Chloride

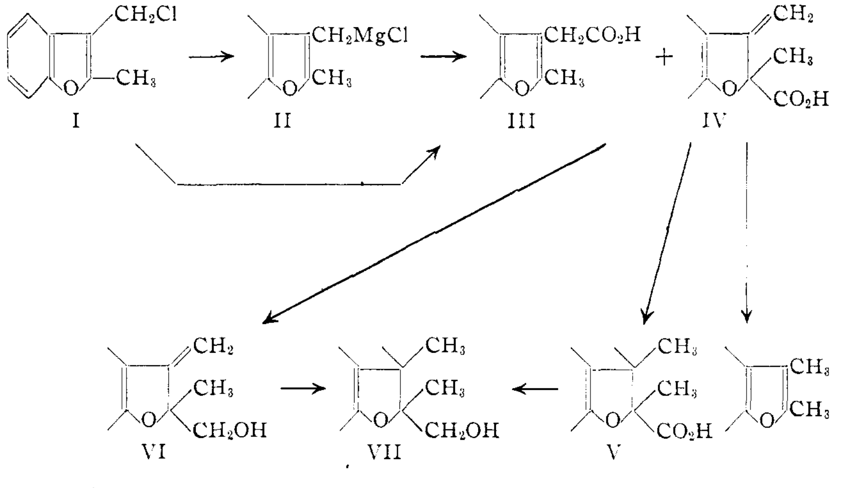
BY RUSSELL GAERTNER[1]

RECEIVED JUNE 2, 1952

A Grignard reagent has been prepared from 3-(chloromethyl)-2-methylbenzofuran and allowed to react with carbon dioxide and ethyl chlorocarbonate. A trace of the normal product was isolated only with carbon dioxide. In both reactions, the major product, after hydrolysis, was the "isoaromatic" 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid, the result of a novel "abnormal" reaction. This β,γ-unsaturated acid decarboxylated at its melting point (110°) to give 2,3-dimethylbenzofuran, a reaction analogous to the similar behavior of β-keto acids.

Two previous attempts to obtain "isoaromatic"[2] products in abnormal reactions of heteroarylmethyl Grignard reagents have been reported. The first, involving 3-methyl-2-thianaphthenylmethylmagnesium chloride, resulted mainly in cleavage of the C_2–S bond,[3] while the second, using 2-bromo-3-(bromomethyl)-thianaphthene, gave only polymers.[4] Since benzofuran is less aromatic than thianaphthene its arylmethyl Grignard reagents should react abnormally even more readily; to avoid cleavage of the furan moiety,[5] a 3-chloromethyl derivative was indicated.

3-Chloromethyl-2-methylbenzofuran (I) was obtained by chloromethylation of 2-methylbenzofuran. It was converted normally in the cyclic reactor and the reagent II was obtained in yields of about 80%. The presence of a coupling product, probably 1,2-bis-(2-methyl-3-benzofuryl)-ethane, was demonstrated by isolation of the picrate. Small amounts of 2,3-dimethylbenzofuran were also present in all reactions, resulting from unavoidable hydrolysis of the reagent.



When the reagent II was carbonated, only a trace of the normal product, 2-methyl-3-benzofurylacetic acid (III), could be isolated; III was also prepared for comparison from I *via* the nitrile. The main product of carbonation, and the sole acid product isolated from the reaction of I with ethyl chlorocarbonate followed by alkaline hydrolysis, was 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid IV. The structure of this compound has not been unequivocally established but any other appears to be inconceivable in view of the mode of its formation and its reactions.

The acid, IV, or its ethyl ester, absorbed very nearly one mole of hydrogen over platinum oxide,

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[2] "Isoaromatic" is used to refer to a structure with adjacent quaternary and doubly bonded carbon atoms in an otherwise aromatic nucleus. Application of this usage here presupposes agreement that benzofuran is "aromatic," although it must be granted that this nucleus undergoes many reactions typical of arylethylenes.

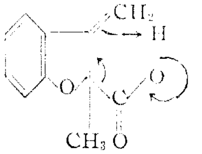
[3] R. Gaertner, THIS JOURNAL, **74**, 2991 (1952).

[4] R. Gaertner, *ibid.*, **74**, 4950 (1952).

[5] R. Gaertner, *ibid.*, **73**, 4400 (1951).

giving 2,3-dimethyl-2,3-dihydro-2-benzofuroic acid (V). IV was also reduced by lithium aluminum hydride to the alcohol VI, which was hydrogenated to VII, the alcohol also obtained by reduction of the ester of V with lithium aluminum hydride.

Both the unsaturated acid IV and the corresponding alcohol VI were significantly unstable to heat. IV melted with decomposition at 110–111°, evolving a gas. The product was 2,3-dimethylbenzofuran, obtained in 83% yield by boiling a solution of the acid in pyridine. To the author's knowledge no other β,γ-unsaturated acid can be decarboxylated under such mild conditions; the reaction is analogous to the behavior of β-keto acids, since in both cases a cyclic intermediate, depicted for IV, is probably involved.[6]



Presumably the promoting factor in this example is the simultaneous restoration of the aromatic benzofuran nucleus. Further attempts to prove these structures by oxidation of the double bond or cleavage of the ether linkage were fruitless.

Experimental[7]

3-(Chloromethyl)-2-methylbenzofuran.—In the best run[8] 7.5 g. of 2-methylbenzofuran was added dropwise to a rapidly stirred solution below 30° of 4.5 g. of trioxane in 100 ml. of concentrated hydrochloric acid. After being stirred for 90 minutes, the mixture was extracted with ligroin (30–60°). 3-(Chloromethyl)-2-methylbenzofuran (7.1 g., 69%) was a colorless mobile liquid, b.p. 85–86° (0.2 mm.), $n^{20}\text{D}$ 1.5779. It slowly decomposed to a black resin.

Anal. Calcd. for $C_{10}H_9ClO$: C, 66.49; H, 5.02. Found: C, 66.25; H, 4.91.

2-Methyl-3-benzofurylmethylmagnesium Chloride.—Using the cyclic reactor[9] the highest yield was 81.7%. With a freshly amalgamated column of magnesium turnings, yields of 80% were obtained consistently.

Reactions. Carbonation.—From a solution (85 ml.) containing 0.0269 mole of reagent was obtained a mixture of acids which was recrystallized from hexane. A total of 2.11 g. (30%) of the less soluble compound separated as colorless prisms, m.p. 110–112° (with evolution of a gas). Recrystallization from hexane–acetone with a minimum of heating did not improve the melting point and was attended by decomposition; 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid decomposed too readily to obtain a pure sample.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 70.00, 70.12; H, 5.79, 5.85.

The liquid remaining after decomposition had the odor of 2,3-dimethylbenzofuran.

From the mother liquors, by first heating to 150° to destroy a trace of the above compound, then recrystallizing from hexane and subliming twice was obtained 0.10 g. of 2-methyl-3-benzofurylacetic acid, m.p. 95–97°.

From the neutral material was isolated 1.66 g. (b.p. 98–105°) of 2,3-dimethylbenzofuran.

Ethyl Chlorocarbonate.—From 10.8 g. of chloride, by hydrolysis of the crude ester, was obtained 5.52 g. (49%) of 2-methyl-3-methylene-2,3-dihydro-2-benzofuroic acid (m.p. 110–112°), but no trace of 2-methyl-3-benzofurylacetic acid. The neutral material yielded 0.6 g. of 2,3-dimethylbenzofuran. The non-volatile neutral gum did not crystallize and was dissolved in ethanol saturated with picric acid; 1.48 g. of 1,2-bis-(2-methyl-3-benzofuryl)-ethane dipicrate separated as yellow needles which were recrystallized from ethanol–acetone, m.p. 150–150.6°.

Anal. Calcd. for $C_{32}H_{24}N_6O_{16}$: C, 51.34; H, 3.23. Found: C, 51.64; H, 3.44.

If the crude mixture obtained in the reaction with ethyl chlorocarbonate, after hydrolysis of the excess reactant, was distilled, 26.7 g. of the chloride gave 13.6 g. (42%) of ethyl 2-methyl-3-methylene-2,3-dihydro-2-benzofuroate, b.p. 90–96° (0.3 mm.). All fractions rapidly developed a red to purple color in air; redistilled twice, the middle fraction no longer became colored, but it was still impure; b.p. 91–92° (0.3 mm.), $n^{20}\text{D}$ 1.5445.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 72.53; H, 6.69.

Combined small samples of 2,3-dimethylbenzofuran[10] were redistilled; b.p. 101–102° (19 mm.), $n^{20}\text{D}$ 1.5537.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.68; H, 6.98.

The picrate separated from ethanol in canary yellow needles, m.p. 91–93°.

Anal. Calcd. for $C_{16}H_{13}N_3O_8$: Cl, 51.20; H, 3.49. Found: C, 51.32; H, 3.57.

2-Methyl-3-benzofurylacetonitrile.—A mixture of 5.0 g. of the chloride, 10 g. of powdered potassium cyanide and 30 ml. of a 5% potassium iodide solution in acetone was stirred and heated under reflux for 12 hours. The nitrile (3.56 g., 75%) distilled principally at 115–118° (0.3 mm.), $n^{20}\text{D}$ 1.5643. It was not pure but could not be purified by distillation.

Anal. Calcd. for $C_{11}H_9NO$: C, 77.17; H, 5.30. Found: C, 76.46, 76.37; H, 5.53, 5.36.

2-Methyl-3-benzofurylacetic Acid.—A solution of 3.1 g. of the nitrile was heated under reflux for 18 hours with excess alcoholic potassium hydroxide. A total of 2.44 g. (71%) of felted colorless needles separated from hexane; m.p. 96.6–97.6°. Sublimation at 90° (0.1 mm.) did not improve the melting point.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.38; H, 5.16.

Reactions of 2-Methyl-3-methylene-2,3-dihydro-2-benzofuroic Acid.—A solution of 1.50 g. of the acid in 5 ml. of pyridine was heated under reflux for 4 hours. After aspiration of the solvent, 0.96 g. (83%) of 2,3-dimethylbenzofuran distilled at 95–105° (24 mm.), $n^{20}\text{D}$ 1.5556. The picrate was prepared, m.p. 91–93°.

A solution of 0.70 g. of the acid in ethanol slowly absorbed 105% of the theoretical volume of hydrogen over two successive portions of platinum oxide. Similarly the redistilled ester (4.93 g.) took up 97% of the hydrogen required for one double bond. A total of 4.74 g. (95%) of ethyl 2,3-dimethyl-2,3-dihydro-2-benzofuroate was isolated; b.p. 81–83° (0.2 mm.). The 82° cut was analyzed; $n^{20}\text{D}$ 1.5098.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.82; H, 7.47.

The saturated ester was hydrolyzed with alcoholic potassium hydroxide. 2,3-Dimethyl-2,3-dihydro-2-benzofuroic acid (quantitative yield) distilled at 112–114° (0.3 mm.), solidified and melted at 80–90°. Recrystallization with loss from hexane gave colorless flat needles, m.p. 98–99°. They were sublimed at 90° (0.1 mm.) for analysis.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.92; H, 6.37.

Attempts to oxidize the unsaturated ester or acid with

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(6) See, concerning the evidence for such intermediates in the decarboxylation of β-keto acids, F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).

(7) Melting points, but not boiling points, are corrected. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois. The obvious mixture melting points were performed without noticeable depressions.

(8) The pure 2-methylbenzofuran used in this run was obtained by ring-closure of *o*-allenylphenol and its derivatives.[5] In larger preparations (25–50 g. of starting material), the less pure[5] compound obtained by the method of R. Adams and R. E. Rindfusz, THIS JOURNAL, **41**, 648 (1919), gave 45% and lower yields. Hydrogen chloride was evolved during heating prior to distillation of the product, leaving a tarry residue; although the chloride from these runs decomposed more rapidly in storage, it was otherwise equivalent to that described above.

(9) See, for procedures, R. Gaertner, *ibid.*, **73**, 3934 (1951).

(10) R. Vladesco, *Bull. soc. chim. France*, [3] **6**, 807 (1891), prepared this compound by cyclization of 3-phenoxybutanone but gave few characterizing data.

potassium permanganate, or performic acid followed with lead tetraacetate, resulted only in the recovery of small amounts of the starting materials. Attempts to cleave the ether linkage of the saturated acid with hydrobromic acid gave inconclusive results.

The unsaturated acid (6.90 g.) was reduced with lithium aluminum hydride in ether. A total of 4.98 g. (78%) of colorless crystals separated from hexane; m.p. 65.5–67.5°. Further recrystallization and sublimation at 50° (0.3 mm.) gave pure 2-methyl-3-methylene-2,3-dihydro-2-benzofurylcarbinol, m.p. 67.6–68.8°. Overheating caused decomposition.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.78; H, 6.94.

A solution of 4.20 g. of the alcohol in ethanol absorbed 103% of the theoretical amount of hydrogen over platinum oxide. The product (3.76 g., 89%), 2,3-dimethyl-2,3-dihydro-2-benzofurylcarbinol, also obtained (82% yield) by reducing the saturated ethyl ester with lithium aluminum hydride in ether, was a viscous colorless liquid, b.p. 81–89° (0.5 mm.). The 84–85° cut was analyzed; n^{20}D 1.5383. The best of three samples, it was still impure.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92. Found: C, 73.54; H, 8.11.

An attempt to convert the alcohol to the bromide with phosphorus tribromide gave only a trace of recovered alcohol; similar results were observed upon treatment with thionyl chloride, alone or with an equivalent of pyridine.

EUGENE, OREGON

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

1,4-Dimethoxy-5-methyl-6-tetralone and 1,4-Dimethoxy-5,5-dimethyl-6-tetralone

BY T. R. LEWIS, WILLIAM B. DICKINSON AND S. ARCHER

RECEIVED JUNE 7, 1952

The adduct obtained from benzoquinone and 2-ethoxybutadiene upon aromatization and methylation furnished 6-ethoxy-1,4-dimethoxy-5,8-dihydronaphthalene (VI) which isomerized on recrystallization from ethanol in the presence of Darco to yield the conjugated 7,8-dihydro derivative, VIII. In the methoxy series the adduct yields V. This 5,8-dihydronaphthalene gave a ketal, X, when recrystallized from methanol in the presence of Darco. The true 7,8-dihydro compound, VII, was obtained by refluxing the ketal in acidified methanol. Hydrolysis of all the above aromatic ethers gave 1,4-dimethoxy-6-tetralone. Alkylation of this compound with methyl iodide and sodium sand gives a mixture of three compounds: the tetralol, XIII, the dimethyltetralone, XI, and the monomethyltetralone, XII.

Grob and Wicki[1] condensed 2-methoxybutadiene with benzoquinone in petroleum ether and obtained in 58% yield the adduct, III, which they aromatized and methylated in alkaline medium. The resulting dimethyl ether was isolated in 65% yield and melted at 80–82°. It was originally assigned structure V, but in a later paper[2] it was pointed out that the ultraviolet absorption spectrum exhibited two maxima, one of which was due to conjugation of the double bond with the benzene ring. On this basis the substance was assigned structure VII.

When 2-ethoxybutadiene[3] (II) was condensed with benzoquinone in ethanol the desired adduct (IV) was obtained in 85% yield.[4] Grob's procedure for converting the adduct to the dimethyl ether proved to be unsatisfactory in our hands. By suitable modification of his procedure we prepared VI in 79% yield. On hydrolysis this compound furnished the tetralone IX.[5] It showed a maximum at 284 mμ in the ultraviolet. Absorption at this wave length was attributed to the presence of the substituted benzene ring since the tetralone, IX, absorbed at 289 mμ (see Table I).

When a sample of VI was recrystallized from ethanol with the aid of a small amount of Darco, the melting point of the recovered material dropped markedly. The compound that was isolated was isomeric with VI, hydrolyzed to the tetralone, IX, and in contrast to VI, showed two peaks in the ultraviolet, one at 274 mμ and the other at 312 mμ. The conjugated structure, VIII, is compatible with these properties.

In view of these results it was thought advisable to reinvestigate the methoxy series. Methoxybutadiene (I)[6] and benzoquinone were refluxed in methanol for three hours to furnish the adduct, III, in 52% yield. It was converted to an aromatic ether, m.p. 80–81°, by the procedure used in the ethoxy series. The tetralone, IX, was obtained on hydrolysis and the ultraviolet absorption spectrum revealed only one maximum at 284 mμ (Table I). This is the same wave length at which the 5,8-dihydro isomer in the ethoxy series (VI) absorbed. Accordingly, the ether was assigned structure V in contrast to Grob's later claim.[2]

When a dry methanol solution of V was refluxed in the presence of Darco a new substance was formed, the analysis of which agreed well with structure X. In harmony with this formulation were the facts that the compound hydrolyzed to yield IX and showed a maximum only at 286 mμ (Table I). This ketal was probably formed by the addition of a molecule of methanol across the double bond of V.

In an attempt to prepare an authentic specimen of X the tetralone, IX, was treated with methyl orthoformate. The reaction mixture was resolved into two components by means of chromatography on alumina. The minor product proved to be the desired ketal X. The substance present in major amounts was an isomer of V. The tetralone, IX, was formed on hydrolysis of this isomer and the ultraviolet absorption spectrum revealed two maxima, one at 274 mμ and the other at 312 mμ. Thus this new ether must be the conjugated compound, VII. It was prepared from X by simply refluxing a methanol solution containing a small amount of hydrogen chloride for a few hours.

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(1) C. A. Grob and H. Wicki, *Helv. Chim. Acta*, **31**, 1706 (1948).

(2) C. A. Grob, N. Jundt and H. Wicki, *ibid.*, **32**, 2127 (1949).

(3) H. L. Holmes and K. M. Mann, THIS JOURNAL, **69**, 2001 (1947).

(4) This compound was first prepared by Dr. R. L. Clarke of this Laboratory; purification and analyses will be reported by him.

(5) C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948).

(6) Reference 1 gives the pertinent literature on the preparation of this diene.