[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Constitution of Carlina-oxide

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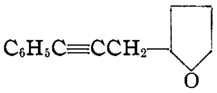
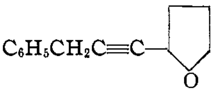
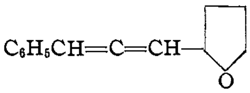
Introduction

Carlina-oxide (an oil obtained from the roots of *Carlina acaulis*) must have one of the three structures.

(A)  (B)  (C) 

Largely on the basis of molecular refractivity, Semmler[1] considered it quite improbable that the compound has an acetylenic linkage.

By a combination of analysis and synthesis it now appears that Carlina-oxide is an acetylenic compound: namely (B), benzyl-2-furylacetylene. We have synthesized (A) (phenyl-2-furfurylacetylene) by the following reaction and have found it to be unlike the natural product.

$$C_6H_5C{\equiv}CMgBr + ClCH_2C_4H_3O \longrightarrow C_6H_5C{\equiv}CCH_2C_4H_3O + MgBrCl \quad (1)$$

Incidentally, the reduction product of the phenyl-2-furfurylacetylene was shown to be identical with the reduction product[1] of Carlina-oxide: namely, 1-phenyl-3-α-furylpropane, $C_6H_5CH_2CH_2CH_2C_4H_3O$. Such identity was established not only by a comparison of physical constants, but more particularly by the method of mixed melting points of the monomercurial, $C_6H_5CH_2CH_2CH_2C_4H_2OHgCl(\alpha)$.

We have shown that phenylacetic acid (identified as the *p*-toluidide) is a product of ozonolysis. The formation of phenylacetic acid rules out Formulas (A) and (C) and leaves (B) (benzyl-2-furylacetylene) as the structure of Carlina-oxide. The critical experiments of ozonolysis assume that there is no rearrangement with ozone, and there is no present decisive information of such rearrangement. Indirect supporting evidence for Formula (B) is to be observed in the Diels–Alder[2] reaction with maleic anhydride. Phenyl-2-furfurylacetylene (A) forms an addition compound with maleic anhydride. However, we have not succeeded in obtaining an addition compound from Carlina-oxide and maleic anhydride. In view of the recent study by Van Campen and Johnson,[3] it appears quite unlikely that either Carlina-oxide or the isomeric allene (C) would give such an addition compound. They found that although furfuryl compounds (of which (A) is a type) do give addition compounds, other substituted furans containing a carbethoxyl, cyano, nitro or ethylenic group attached directly to the furan nucleus form no addition compound. Both (B) and (C) have

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(1) Semmler, *Ber.*, **39**, 726 (1906); Semmler and Ascher, *ibid.*, **42**, 2355 (1909).

(2) Diels and Alder, *ibid.*, **62**, 554 (1929).

(3) Van Campen and Johnson, THIS JOURNAL, **55**, 430 (1933).

an unsaturated group attached directly to the critical α-position of the furan nucleus.

Experimental Part

Phenyl-2-furfurylacetylene (A).—A solution of 42.1 g. (0.36 mole) of furfuryl chloride in 125 cc. of ether was added slowly (three hours) to an equivalent solution of phenylacetenylmagnesium bromide [Reaction (I)] in 400 cc. of ether. Reaction set in at once, and subsequent to the addition the refluxing was continued for fifteen minutes by external heating. A negative color test showed the Grignard reagent to be used up. Hydrolysis was effected by a 10% ammonium chloride solution, and after steam distillation the dried ethereal extract was fractionally distilled to give 22.7 g. of a 34.6% yield of phenyl-2-furfurylacetylene: b. p. 160–161° (20 mm.); n^{17}_{D} 1.5833; d^{17}_{17} 1.0683 and d^{17}_{4} 1.0696.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.68; H, 5.54. Found: C, 85.55; H, 5.65.

α-(γ-Phenylpropyl)-α'-furylmercuric Chloride, $C_6H_5(CH_2)_3C_4H_2OHgCl$.—The 1-phenyl-3-$\alpha$-furylpropane, $C_6H_5(CH_2)_3C_4H_3O$, was prepared in 15% yield in accordance with the directions of Semmler[1] by the sodium and alcohol reduction of furfuralacetophenone. A solution of 0.983 g. of the phenylfurylpropane in 10 cc. of alcohol was added to an aqueous solution of 1.59 g. of mercuric chloride and 3.2 g. of sodium acetate, and the mixture shaken for two days in a small flask. By working up in a customary manner for furan mercurials[4] a 20% yield of purified mercurial was obtained. It melted at 94–95° after crystallization from ethyl alcohol.

Anal. Calcd. for $C_{13}H_{13}OClHg$: Hg, 49.28. Found: Hg, 49.01, 48.93.

In a like manner, 10 g. of phenyl-2-furfurylacetylene (A) was reduced to give 3.4 g. or a 34% yield of 1-phenyl-3-α-furylpropane. Its mercurial melted at 94–95° and showed no depression in a mixed melting point determination with the mercurial obtained by the reduction of furfuralacetophenone.

The 1-phenyl-3-α-furylpropane obtained by the above two reductions was like that obtained in 25% yield by the reduction of 12.9 g. of Carlina-oxide which was isolated by fractionation of the oil obtained from Schimmel and Co., Leipzig. This 1-phenyl-3-α-furylpropane was also characterized and identified by means of its mercurial and the method of mixed melting points.

Ozonization of Carlina-oxide.—A solution of 2.4 g. of Carlina-oxide in 50 cc. of glacial acetic acid was ozonized at room temperature for twelve hours. After heating the resulting solution on a water-bath at 100°, the acetic acid was removed by distillation under reduced pressure. The resulting oil was treated with a 10% solution of sodium bicarbonate and, after extraction with ether, the aqueous solution was concentrated under reduced pressure and then acidified with hydrochloric acid. The ensuing dark, oily acid mixture had an odor remindful of phenylacetic acid. When heated with 30 cc. of water, part of it dissolved and this solution (after separation from the undissolved oil) was concentrated under reduced pressure. The oily acid which separated was taken up in ether, dried with sodium sulfate, and the ether removed by distillation. A portion of the oil was heated with *p*-toluidine in accordance with the directions of Bischoff and Walden[5] for the preparation of phenylacet-*p*-toluidide. The phenylacet-*p*-toluidide obtained after several crystallizations from alcohol was shown to be identical by a mixed melting point determination with an authentic specimen prepared in the same manner.[5] Mixed melting point determinations were also carried out with acet-*p*-toluidide and benz-*p*-toluidide and the authentic phenacet-*p*-toluidide to show

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(4) Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

(5) Bischoff and Walden, *Ann.*, **279**, 128 (1894).

that such possible *p*-toluidides were not present in the finally purified *p*-toluidide from Carlina-oxide.

The results of ozonolysis were checked with another specimen of Carlina-oxide.

The addition compound obtained from phenyl-2-furfurylacetylene (A) and maleic anhydride in benzene melted at 112° when recrystallized from benzene. It assumes a light brown color on standing. Several unsuccessful attempts were made to prepare an addition compound from maleic anhydride and Carlina-oxide.

Summary

Evidence is presented to show that Carlina-oxide is benzyl-2-furylacetylene, and not the isomeric phenyl-2-furfurylacetylene (which was synthesized) nor the isomeric allene.

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Levulinic Acid. V. The 2,4-Dinitrophenylhydrazones of Certain of its Alkyl Esters

BY MILFORD A. COWLEY AND H. A. SCHUETTE

Certain characteristics, such as the simpler physical constants, the vapor pressure and the molar entropy, of each of the first ten homologous normal and the first three iso alkyl esters of levulinic acid have been described in earlier communications[1] from this Laboratory. With the completion of the series to this point there arises the need of chemical means for characterizing the compounds in question. A search of the literature revealed the fact that although there have been described numerous compounds[2] by which levulinic acid itself may be identified—for example, its phenylhydrazone,[2a] *p*-nitrophenylhydrazone,[2b] semicarbazone,[2i] or oxime[2j]—yet, except for the report by Sah and Mah[3a] on the phenylhydrazones and semicarbazones of certain of its lower esters, there is no evidence that anyone has ever extended the list of any of its carbonyl derivatives beyond that of the amyl compound. Aside from their work, only scattered, and often incidental, references[2a,2j,3b,4] to derivatives of levulinic acid esters are to be found. The desirability of filling the gaps in the record is, there-

(1) Schuette and Cowley, THIS JOURNAL, **53**, 3485 (1931); Cowley and Schuette, *ibid.*, **55**, 387 (1933).

(2) (a) Fischer, *Ann.*, **236**, 126 (1886); (b) Fiest, *Ber.*, **33**, 2098 (1900); (c) Mungiolo, *Gazz. chim. ital.*, **45**, [II] 299 (1915); (d) Allen, THIS JOURNAL, **52**, 2955 (1930); (e) Pummerer, Ebermayer and Gerlach, *Ber.*, **64B**, 804 (1931); (f) Seka and Heilperin, *Monatsh.*, **57**, 45 (1931); (g) Borsche, *Ber.*, **49**, 2538 (1916); (h) Fargher and Furness *J. Chem. Soc.*, **107**, 688 (1915); (i) Blaise, *Bull. soc. chim.*, [3] **21**, 647 (1899); (j) Müller, *Ber.*, **16**, 1617 (1883); (k) Bennett, THIS JOURNAL, **50**, 1747 (1928).

(3) (a) Sah and Mah, THIS JOURNAL, **52**, 4880 (1930); (b) *Science, Repts. Tsing Hua Univ.*, Ser. **A**, **1**, 259 (1932).

(4) (a) Pummerer and Gump, *Ber.*, **56B**, 999 (1923); (h) Michael, *J. prakt. Chem.*, [2] **44**, **113** (1891); (c) Montemartini, *Gazz. chim. ital.*, [II] **27**, 176 (1897).