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-

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(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); (b) Michael, *J. prakt. Chem.*, [2] **44**, 113 (1891); (c) Montemartini, *Gazz. chim. ital.*, [II] **27**, 176 (1897).

fore, obvious. The data herein communicated represent an attempt to accomplish this end for all of the alkyl esters of levulinic acid heretofore reported,[1] the 2,4-dinitrophenylhydrazone providing the point of departure.

The glaring discrepancy in the melting points of the corresponding derivative of levulinic acid as reported from two different laboratories, 92°[2d] and 203°,[2e] respectively, made a reinvestigation of this compound desirable in the hope of verifying one or the other value. The results of this study, which confirms the latter value and demonstrates a probable error in the experimental procedure by which the former was obtained, have been made part of this communication.

Experimental

The alkyl esters of levulinic acid were part of the material prepared for vapor pressure measurements.[1] The hydrazine reagent was made from hydrazine sulfate and 2,4-dinitrochlorobenzene by the method of Purgotti[5] as modified by Allen.[2d]

2,4-Dinitrophenylhydrazones of Alkyl Levulinates.—From preliminary experiments it was observed that the reaction between the ester and the hydrazine reagent can be carried out in 15% aqueous acetic acid solution, 1% aqueous hydrochloric acid solution, or in ethyl alcohol to which a small amount of hydrochloric acid (sp. gr. 1.18) has been added. Preference was given the last in this phase of the study because of its superiority as a solvent for the reactants, besides which it is an excellent medium from which to precipitate the reaction product.

Partial solution of 0.3 g. of 2,4-dinitrophenylhydrazine in 25 cc. of anhydrous ethyl alcohol was effected by boiling the mixture. The solution was allowed to cool somewhat, whereupon a slight excess over the calculated amount of ester necessary for complete reaction was added. The solution was again brought to boiling and 0.1 cc. of hydrochloric acid (sp. gr. 1.18) was added. Boiling was continued until the color changed from red to orange and the undissolved reagent had gone into solution. This usually required one minute. The hydrazone was then precipitated by cooling the solution, an ice–salt bath being used when necessary. The isoamyl, *n*-octyl, *n*-nonyl and *n*-decyl derivatives separated as liquids and crystallized only after being set aside overnight in a refrigerator (4°). Careful reprecipitation of these derivatives from ethyl alcohol, however, gave crystalline products. Each derivative with the exception of that of levulinic acid and its methyl ester was recrystallized from alcohol to a constant melting point (Table I and fig.). In the case of the exceptions noted chloroform was

TABLE I

MELTING POINTS OF THE 2,4-DINITROPHENYLHYDRAZONES OF CERTAIN ALKYL ESTERS OF LEVULINIC ACID, $CH_3C{=}[NNHC_6H_3(NO_2)_2]CH_2CH_2COOR$

When R is	Melting point, °C.	Nitrogen, %		When R is	Melting point, °C.	Nitrogen, %	
		Calcd.	Found			Calcd.	Found
n-CH_3	141.2	18.07	18.11	*n*-C_8H_{17}	44.0	13.72	13.92
n-C_2H_5	101.0	17.29	17.55	*n*-C_9H_{19}	41.4	13.27	13.51
n-C_3H_7	63.0	16.57	16.62	*n*-$C_{10}H_{21}$	49.6	12.84	12.98
n-C_4H_9	65.8	15.91	16.11	*iso*-C_3H_7	90.9	16.57	16.60
n-C_5H_{11}	84.2	15.30	15.52	*iso*-C_4H_9	55.6	15.91	16.04
n-C_6H_{13}	56.6	14.74	14.82	*iso*-C_5H_{11}	50.5	15.30	15.59
n-C_7H_{15}	79.0	14.22	14.50				

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(5) Purgotti, *Gazz. chim. ital.*, [I] **24**, 555 (1894).

used as solvent. The pure compounds are yellow or orange in color, the shade apparently depending to a considerable extent on the size of the crystals obtained. They are stable in air at ordinary temperatures, and are insoluble in water, but soluble in ethyl ether, chloroform, benzene and petroleum ether. Hot ethyl alcohol dissolves them readily, cold but slightly.

2,4-Dinitrophenylhydrazone of Levulinic Acid.—Because the use of ethyl alcohol as a solvent in the preparation of this substituted hydrazone, as has been suggested,[2d] seems illogical in view of the possibility of concomitant esterification, water was substituted for it as solvent for the reactants in this case. Otherwise, the details of procedure were essentially the same as those given above for the preparation of the ester derivatives. The hydrazone, after recrystallization from chloroform, melted at 206.5°.

Anal. Calcd. for $C_{11}H_{12}N_4O_6$: N, 18.92. Found: N, 18.92.

When ethyl alcohol was used as solvent, the resulting product varied with the time of heating of the reaction mixture. Three preparations, made under different conditions, led to the following results. (1) The reaction was carried out with as little heating as possible (boiling for one minute), after which the reaction product was separated from the solvent by fractional precipitation. One fraction, after recrystallization from chloroform, melted at 202°. Analysis showed it to be the derivative of levulinic acid. The other proved to be a mixture, its melting point lying between 175 and 185°. It was not appreciably purified by recrystallizations, four of which were made. (2) The reaction mixture was subjected to two heatings, one during the period of reaction and the other after a precipitate had formed. The effect of this treatment was to dissolve the latter. From this solution there were subsequently obtained by fractional precipitation two products, one (m. p. 100°) the derivative of ethyl levulinate, the other, as before, a mixture. (3) The reaction mixture was held at its boiling temperature for twenty minutes. The resulting product was a mixture melting at about 98°. It was evidently largely composed of the ethyl levulinate derivative.

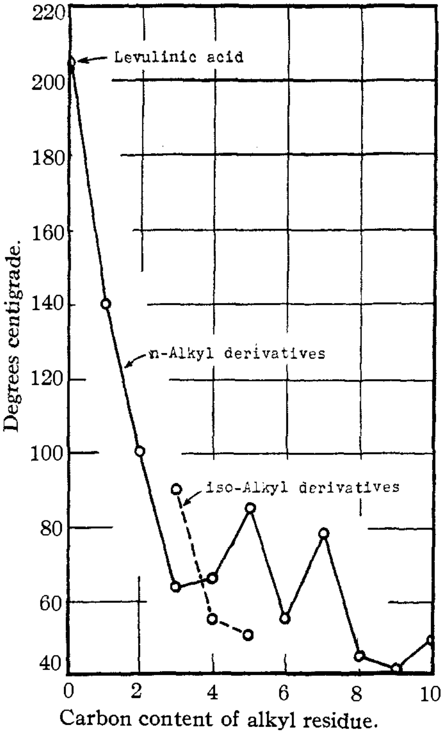

Fig. 1.—Melting points of the 2,4-dinitrophenylhydrazones of levulinic acid and its alkyl esters.

These experiments demonstrate that it is inadvisable because of esterification to use ethyl alcohol as a solvent when combining levulinic acid with 2,4-dinitrophenylhydrazine. The melting point of the resulting phenylhydrazone (206.5°) when a 1% hydrochloric acid solution is used as solvent is in fair agreement with that obtained by Pummerer and co-workers[2e] (203°), who carried out the reaction in acetic acid solution (1 + 1).

Analysis of the 2,4-Dinitrophenylhydrazones.—The nitrogen content of the 2,4-

dinitrophenylhydrazones was determined by a modified Dumas procedure using an apparatus of semi-micro proportions. The suggestions of Pregl for micro analysis by the Dumas method were followed closely. Resort was not made, however, to his empirical method for correcting the volume of nitrogen obtained as it is probably not applicable to the larger type of apparatus used by us. It was found that our procedure could be closely standardized as to the time and the amount of carbon dioxide used in an analysis and that by a blank on the apparatus it was possible to determine a correction factor for the small amount of residual gas in the carbon dioxide. This was subsequently applied to all of the analyses.

Summary

The 2,4-dinitrophenylhydrazones of ten normal alkyl and three isoalkyl esters of levulinic acid have been prepared and their melting points determined. Experimental data are offered in explanation of conflicting reports in the literature on the melting point of the corresponding levulinic acid derivative.

MADISON, WISCONSIN

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Chemistry of Lignin. VIII. The Oxidation of Alkali Lignin

BY MAX PHILLIPS AND M. J. GOSS

Oxidation, probably the most common method used for the degradation of an organic compound for the purpose of ascertaining its structure, has thus far afforded no interesting results on the structure of lignin. The products of oxidation have been, with one or two exceptions, simple organic acids. A review of the literature on this subject up to 1926 is given by Fuchs.[1] Some of the more recent articles are those of Rassow and Zickmann,[2] Schaarschmidt, Nowak and Zetzsche,[3] and Horn.[4] Fischer, Schrader and Freiedrich[5] subjected lignin to what these investigators designate as "pressure oxidation," and obtained, in addition to some simple aliphatic acids, small quantities of aromatic acids. However, in view of the rather drastic method of oxidation employed by Fischer and co-workers, it seems doubtful whether their results can be interpreted as definitely indicating that an aromatic nucleus is present in the lignin molecule.

The present paper concerns itself with the oxidation of alkali lignin isolated from corn cobs. It has been found that this lignin when subjected to oxidation affords chiefly oxalic acid. However, when the lignin is first

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(1) Walter Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926.

(2) Rassow and Zickmann, *J. prakt. Chem.*, [2] **123**, 216 (1929).

(3) Schaarschmidt, Nowak and Zetzsche, *Z. angew. Chem.*, **42**, 618 (1929).

(4) Horn, *Brennstoffchem.*, **10**, 364 (1929).

(5) Fischer, Schrader and Friedrich, *Gesamm. Abhand. Kenn. Kohle*, **6**, 1 (1923).