[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXI. COMPARISON OF TENDENCIES OF SATURATED AND UNSATURATED ALDEHYDES TOWARD CYCLIC ACETAL FORMATION

BY HAROLD HIBBERT, EDWARD O. HOUGHTON[1] AND K. AUSTIN TAYLOR[2]

RECEIVED NOVEMBER 8, 1928 PUBLISHED FEBRUARY 5, 1929

Previous work on cyclic acetal formation carried out during the last few years[3] has dealt only with the cyclic acetals from saturated carbonyl derivatives. The tendency of unsaturated aldehydes toward cyclic acetal formation has apparently not been investigated.

The possibility that the lignin complex, as it occurs in wood, may contain an unsaturated aldehyde grouping,[4] and that in this case the latter may be linked up with a carbohydrate complex in the form of a cyclic acetal, or half acetal, pointed to the necessity for obtaining further information regarding the interaction of unsaturated aldehydes with polyhydroxy compounds.

In the present investigation experiments were carried out on the condensation of ethylene glycol with cinnamic aldehyde, α-monochlorocinnamic aldehyde, β-phenyl-α,β-dichloropropionaldehyde, α-methyl-β-ethylacrolein, crotonaldehyde, α-monochlorocrotonaldehyde and dichlorobutyraldehyde, using dilute sulfuric or phosphoric acid as catalyst.[5] The yields of cyclic acetal obtained provide a basis for comparison of the tendencies of saturated and unsaturated acetals toward cyclic acetal formation.

The unsaturated cinnamic and crotonaldehydes and α-methyl β-ethylacrolein, show practically no tendency to form cyclic acetals under the given experimental conditions, the yields obtained being almost negligible. In the case of cinnamic and crotonaldehydes, the yield of the cyclic acetals was not sufficiently high to enable them to be separated and identified as such. With α-methyl-β-ethyl-acrolein a yield of about 10% of an impure product was obtained, the analysis of which corresponded approximately to that of the acetal.

The unsaturated halogenated aldehydes, containing chlorine attached to the α-carbon atom, show a greater tendency toward cyclic acetal for-

---

[1] Holder of Bursary, Canadian National Research Council.

[2] Holder of Abitibi Power and Paper Company Research Fellowship.

The authors wish to express their thanks to the Canadian National Research Council, the Abitibi Power and Paper Company and the Canadian Pulp and Paper Association for the generous support accorded them.

[3] Hibbert and co-workers, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921); THIS JOURNAL **45**, 734, 2433, 3108, 3117, 3124 (1923); **46**, 1283 (1924); **50**, 1411, 2235, 2242 (1928).

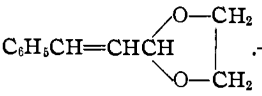
[4] Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, **1926**, pp. 277–285.

[5] Five-tenths to 1 cc. of the 40% acid was employed per mole of aldehyde used.

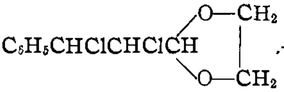
mation, apparently due to the activating influence exerted by the negative chlorine atom on the carbonyl group. Both α-monochlorocinnamic aldehyde and α-monochlorocrotonaldehyde, when condensed with ethylene glycol, gave a yield of 22% of the cyclic acetal.

The saturated aldehydes, *viz*, phenyldichloropropionaldehyde and dichlorobutyraldehyde, readily formed cyclic acetals with yields of 37 and 50%, respectively.[6]

Experimental Part

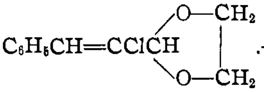


Cinnamylidene Ethylene Glycol, $C_6H_5CH{=}CHCH\left\langle\begin{array}{l}O-CH_2\\ \quad\;|\\ O-CH_2\end{array}\right.$.—Thirty-three grams (one-quarter mole) of cinnamic aldehyde, thirty-one grams (one-half mole) of ethylene glycol and three drops of 40% sulfuric acid as catalyst were heated to 100° on the water-bath for six hours. The reaction mixture was then neutralized with solid potassium carbonate, extracted with ether and the ether extract dried and distilled. A small yield of the acetal was indicated but could not be separated from the large amount of unchanged aldehyde present.



β-Phenyl-α,β-dichloropropylidene Ethylene Glycol, $C_6H_5CHClCHClCH\left\langle\begin{array}{l}O-CH_2\\ \quad\;|\\ O-CH_2\end{array}\right.$.—β-Phenyldichloropropionaldehyde was prepared according to the method of Naar.[7] Two hundred and three grams (1 mole) of the aldehyde was condensed with 124 g. (2 moles) of ethylene glycol by heating at 70° for four hours. The hydrochloric acid split off from the aldehyde was sufficient to bring about the condensation. The ether extract was shaken with saturated sodium bisulfite solution to remove any unchanged aldehyde, washed, dried and the recovered oil distilled; b. p. 164–166° at 8 mm.; yield, 37%.

Anal. Calcd. for $C_{11}H_{12}O_2Cl_2$: Cl, 28.74. Found: Cl, 28.88, 28.45.



α-Monochlorocinnamylidene Ethylene Glycol, $C_6H_5CH{=}CClCH\left\langle\begin{array}{l}O-CH_2\\ \quad\;|\\ O-CH_2\end{array}\right.$.—α-Monochlorocinnamic aldehyde (b. p. 132–134° at 8 mm.) was prepared by a modification of Naar's method by refluxing β-phenyldichloropropionaldehyde with aqueous sodium acetate. One mole of the chloro-aldehyde and two moles of ethylene glycol were heated at 130° for three hours, using three drops of 40% sulfuric acid as catalyst. The mixture was extracted in the usual manner, yielding an opaque, reddish oil which

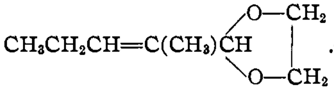
---

[6] From the recently published work of Adkins, This Journal, **49**, 2517 (1927), relating to equilibrium data on simple acetal formation, it is apparent that the tendency of unsaturated aldehydes to form acetals is very much less pronounced than that of the saturated, a fact which seems to point to the much lower stability of the acetals from the former. Possibly by working in a medium of much lower acid concentration it might be possible to isolate the cyclic acetals from unsaturated aldehydes. Experiments are in progress using other condensing agents such as copper sulfate, calcium chloride, zinc chloride, iodine, etc.

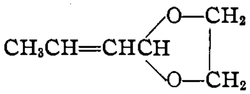
[7] Naar, *Ber.*, **24**, 244 (1891). A more convenient method of preparing the dichloro-aldehyde is to dissolve the theoretical amount of chlorine in carbon tetrachloride and to add this to the cinnamic aldehyde at −5°; yield, 72%; b. p. 94–97° (2 mm.).

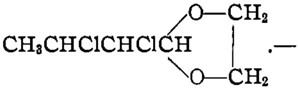
on cooling deposited the acetal in the form of fine, white crystals. These were recrystallized from benzene; m. p. 69–70°; yield, 22%. The crystals were readily soluble in alcohol, ether and benzene.

Anal. Subs.: 0.2110, 0.2017; CO_2, 0.4867, 0.4646; H_2O, 0.1023, 0.0960. Calcd. for $C_{11}H_{11}O_2Cl$: C, 62.70; H, 5.23; Cl, 16.86. Found: C, 62.90, 62.82; H, 5.38, 5.28; Cl, 17.72, 17.60.

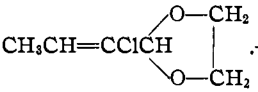
α-Methyl-β-ethylacrylidene Ethylene Glycol,  $CH_3CH_2CH{=}C(CH_3)CH\left<\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right.$.—Twenty grams of α-methyl-β-ethyl-acrolein, condensed in a similar manner with 25 g. of ethylene glycol, using three drops of 40% sulfuric acid as catalyst, gave a high-boiling fraction, b. p. 170–174° (12 mm.), which was free from aldehyde (semicarbazide reaction). This product is the acetal but is evidently contaminated with other products.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.60; H, 9.86. Found: C, 66.42, 66.74; H, 9.82, 9.55.

Crotylidene Ethylene Glycol,  $CH_3CH{=}CHCH\left<\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right.$.—One hundred and forty grams (two moles) of crotonaldehyde was heated with 186 g. (three moles) of glycol for four hours at 95°, using 2 cc. of 20% phosphoric acid as catalyst. Examination of the mixture showed that only a negligible amount of condensation had occurred.

Dichlorobutylidene Ethylene Glycol,  $CH_3CHClCHClCH\left<\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right.$.—Dichlorobutyraldehyde was prepared by passing the theoretical quantity of chlorine into crotonaldehyde at −5°. One hundred and forty-one grams (one mole) of the crude aldehyde was then condensed directly, without any further purification, with 91 g. (1.5 moles) of glycol by heating on the water-bath for one hour. No catalyst was added. The yield of acetal (b. p. 100–105°, 13–15 mm.) was 50.3%.

Anal. Calcd. for $C_6H_{10}O_2Cl_2$: Cl, 38.37. Found: Cl, 37.74.

α-Monochlorocrotylidene Ethylene Glycol,  $CH_3CH{=}CClCH\left<\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right.$.—α-Monochlorocrotonaldehyde (b. p. 147–150°, 760 mm.) was prepared by mixing dichlorobutyraldehyde with aqueous sodium acetate and steam distilling the product. Seventy grams (two-thirds mole) of the aldehyde was condensed with 62 g. (one mole) of glycol, using 1 cc. of 20% phosphoric acid as catalyst. Considerable polymerization occurred. After extraction, the acetal obtained was refractionated several times under reduced pressure; b. p. 76–80° (14 mm.); yield, 22%.

Anal. Calcd. for $C_6H_9O_2Cl$: Cl, 23.87. Found: Cl, 23.45, 23.58.

Summary

1. A comparison has been made of the tendency of saturated and unsaturated aldehydes to form cyclic acetals. The aldehydes were condensed with ethylene glycol, using dilute sulfuric or phosphoric acid as catalyst, and the yields of the resulting cyclic acetal determined.

2. The unsaturated aldehydes, cinnamic aldehyde, crotonaldehyde and

α-methyl-β-ethyl-acrolein show practically no tendency toward cyclic acetal formation under the experimental conditions used.

3. The unsaturated aldehydes containing chlorine attached to the α-carbon atom, namely, α-monochlorocinnamic aldehyde and α-monochlorocrotonaldehyde, give a yield of about 22% of the corresponding cyclic acetal. The greater tendency of these aldehydes to form cyclic acetals is probably due to the activating influence exerted by the negative chlorine atom on the carbonyl group.

4. The saturated aldehydes, *viz.*, phenyldichloropropionaldehyde and dichlorobutyraldehyde, show the normal tendency of saturated aldehydes to form cyclic acetals, the yields being 37 and 50%, respectively.

Pulp and Paper Research Institute
Montreal, Canada

[Contribution from the Department of Chemistry, University of Michigan]

SYNTHESIS OF CYCLOBUTANE ACIDS. I. NORPINIC ACID

By Carl A. Kerr

Received December 5, 1928 Published February 5, 1929

It is remarkable that while *cis*-cyclobutane-1,3-dicarboxylic acid,[1] methylcyclobutane[2] and 1,2-dimethylcyclobutane-3,4-dicarboxylic acid[3] have been synthesized from open-chain compounds, all attempts to effect cyclobutane ring closure in carbon chains having the *gem.*-dimethyl group as substituent have failed. This is particularly evident from the repeated failures to synthesize the well-known norpinic acid or 2,2-dimethylcyclobutane-1,3-dicarboxylic acid, which is a key acid formed in the oxidation of α- and β-pinene and some other terpene compounds. In an attempt to synthesize norpinic acid, Ganguly[4] found that ethyl α,α′-dibromo-β,β-dimethylglutarate did not react with methylene iodide in the presence of sodium to give the expected cyclobutane compound, while Vogel[5] showed that the disodium derivative of ethyl-β,β-dimethyl-α-cyanopropane-α,α′,α′-tricarboxylate failed to give a ring compound when treated with methylene iodide. Clemo and Welch[6] failed to get a cyclic compound from an attempted condensation of maleic or fumaric ester and dimethylketene, and further showed that the disodium derivative of β,β-dimethylpropane-α,α,α′,α′-tetracarboxylic ester did not react with methylene iodide to give a cyclobutane compound, as expected. Prior to the publication of Clemo

[1] Bottomley and Perkin, *J. Chem. Soc.*, **77**, 298 (1900); Simonsen, *ibid.*, **93**, 1778 (1908).

[2] Perkin, *ibid.*, **53**, 201 (1888).

[3] Vogel, *ibid.*, **129**, 1986 (1927).

[4] Ganguly, *J. Ind. Inst. Science*, **5**, 23 (1922).

[5] Vogel, *J. Chem. Soc.*, **130**, 2010 (1928).

[6] Clemo and Welch, *ibid.*, **130**, 2621 (1928).