Preparation of Some Ethyl Higher-Alkyl Acetals and Their Conversion to Vinyl Ethers[1]

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Unsymmetrical acetals were prepared from stearyl, oleyl, and the mixed alcohols, derived from linseed oil, by the acid-catalyzed addition of each alcohol to ethyl vinyl ether.

Stearyl, oleyl, and linseed-alkyl vinyl ethers were obtained by cleavage of ethanol from the respective unsymmetrical acetals over alkali-metal bisulfates, sulfanilic acid, or aniline sulfate-sulfuric acid. Yields of the higher alkyl vinyl ethers were moderate due to disproportionation and formation of ethyl vinyl ether from the acetals.

VINYL ETHERS may be prepared by reaction of alcohols with acetylene (1) or vinyl chloride (2), by vinyl interchange reactions between alcohols and vinyl ethers (3) or vinyl esters (4), by dehydrohalogenation of β-haloethers (5), and by cleavage of alcohols from acetals (6). In connection with work on the preparation of a number of higher alkyl vinyl ethers (7,8) we have investigated the preparation of some ethyl higher alkyl acetals of acetaldehyde and their conversion to vinyl ethers.

The unsymmetrical acetals were prepared by the acid-catalyzed addition of alcohols to ethyl vinyl ether (Equation 1). The acetals were dealcoholized to yield the higher alkyl vinyl ethers (Equation 2).

$$(1)\quad ROH+CH_3CH_2OCH{=}CH_2 \rightleftarrows RO(CH_3CH_2O)CHCH_3$$

$$(2)\quad RO(CH_3CH_2O)CHCH_3 \rightleftarrows ROCH{=}CH_2+CH_3CH_2OH$$

Stearyl, oleyl, and a mixture of unsaturated alcohols (largely linoleyl and linolenyl alcohols) obtained by reduction of linseed oil were used in these studies. We refer to the mixture of unsaturated alcohols as linseed alcohols.

Summary and Discussion

Preparation of Unsymmetrical Acetals. The acid-catalyzed addition of an alcohol to a vinyl ether to form an unsymmetrical acetal has been previously reported (9). Hydrochloric and *p*-toluenesulfonic acids were used as catalysts. In our initial preparations stoichiometric amounts of fatty alcohol and ethyl vinyl ether were mixed with a catalytic amount of *p*-toluenesulfonic acid, or hydrochloric acid, dissolved in water or benzene. Two days were allowed for the reaction. After catalyst neutralization and distillation *in vacuo* of the low-boiling substances, a crude mixture apparently containing 86% unsymmetrical acetal was obtained. Distillation of these mixtures showed that they contained unreacted fatty alcohol, unsymmetrical acetal, and symmetrical acetal corresponding to the fatty alcohol employed. In one preparation 35% of the residue obtained after distillation of the highly volatile materials was symmetrical acetals.

The symmetrical acetals are probably formed by Equilibrium Reactions 3 and 4.

$$(3)\quad ROH+CH_3CH_2O(RO)CHCH_3 \rightleftarrows (RO)_2CHCH_3+CH_3CH_2OH$$

$$(4)\quad CH_3CH_2OH+CH_3CH_2O(RO)CHCH_3 \rightleftarrows (CH_3CH_2O)_2CHCH_3+ROH$$

If reactions 3 and 4 occur, then excess ethyl vinyl ether or diethyl acetal should increase unsymmetrical acetal yield. These reactions may have the vinyl ether as an intermediate.

A 100% excess of ethyl vinyl ether resulted in a reaction which easily went out of control unless the reaction flask was placed in an ice bath. Cooling greatly reduced the amount of symmetrical acetal formed. Temperatures as low as 0–5° were employed. The rate of Reactions 3 and 4 apparently depends greatly upon temperature. Further increases in yield were obtained with a 200% excess of ethyl vinyl ether. The best yields of unsymmetrical acetals were 81–84% (Table I).

TABLE I

Typical Yields in Preparation of Unsymmetrical Acetals Under Various Conditions

$$ROH+CH_3CH_2OCH{=}CH_2 \longrightarrow CH_3CH_2O(RO)CHCH_3$$

R =	Molar ratio vinyl ether: ROH	Catalyst mg./mole: ROH	Reaction time (hr.)	Reaction temp., °C.	Unsym. acetal yield, %
Oleyl	3	PTSA[a] 400	2	−1 to 2	82
Oleyl	3	PTSA 400	2	5–10	73
Oleyl	1	PTSA 190	0.25	to 82	40
Stearyl	3	PTSA 400	1	15–20	84
Stearyl	1	HCl 300	22	Ambient slight exotherm	75
Stearyl	1	HCl 68	2	Ambient slight exotherm	73
Linseed alkyl	2	PTSA 200	1.25	15–20	82
Linseed alkyl	2	PTSA 400	3	5–10	71
Linseed alkyl	1	HCl 21	120	Exotherm	59

[a] *p*-Toluenesulfonic acid.

Dealcoholization of Unsymmetrical Acetals. Voronkov (10) reported preparation of vinyl ethers by dealcoholization of symmetrical acetals, using sodium bisulfate, sulfanilic acid, or aniline sulfate as catalysts. Several patents have been issued for the vapor phase preparation of vinyl ethers from symmetrical acetals (11). Relatively little has been reported on the cleavage of alcohols from unsymmetrical acetals. Deschamps (12) reported that the lower-molecular-weight alcohol was preferentially cleaved from unsymmetrical acetals by passing their vapors over kaolin at elevated temperatures.

Attempts to bring about cleavage of ethanol from ethyl fatty acetals by passing their vapors over bentonite or kaolin at temperatures ranging from 195–350° were unsuccessful. The highest yield obtained was 12% with the bentonite catalyst at 250–300°. In view of the low yields the question arose as to whether fatty vinyl ethers were stable over these catalysts. When linseed vinyl ethers were passed over bentonite

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under conditions similar to those used in the attempt to prepare vinyl ether from acetal, the vinyl ethers were largely converted to a mixture of linseed alcohols and olefins. For example, the vinyl ether content of linseed vinyl ethers was reduced to 37% by passage over bentonite at 360°. The product contained 19% linseed alcohols. An olefin mixture which had an iodine value of 249 (Wijs) also was isolated.

The passage of ethyl linseed acetals over the silver catalyst described by Baur (11) at 360° gave a mixture containing about 56% unchanged acetals. 25% linseed alcohols, and 22% linseed vinyl ethers.

The catalysts mentioned by Voronkov (10) were also investigated. The procedure was to add the catalyst to the unsymmetrical acetal and then vacuum-distill the mixture. The distillate was collected over an alkaline substance, such as alkali-metal hydroxide or carbonate, as indicated by Voronkov. Linseed vinyl ethers were obtained in a yield of 51.8% with aniline sulfate as catalyst and in a yield of 45.5% with sulfanilic acid as a catalyst. The sulfanilic acid was activated by recrystallization from 10% sulfuric acid; otherwise it was not effective.

Yields in these reactions were reduced by the formation of symmetrical acetals. Diethyl acetal together with ethanol and ethyl vinyl ether was obtained from a trap cooled by a mixture of dry ice and acetone. Presumably the diethyl acetal is formed via Reaction 3. When a sample of ethyl stearyl acetal was heated with a catalytic amount of *p*-toluenesulfonic acid at temperatures of 130–135° for 1 hr. under a pressure of 0.2–4.0 mm. so that no fatty vinyl ether would distill, the material collected in the cold trap contained 93% diethyl acetal and only 6.4% ethanol. If distillation is not sufficiently rapid, unsymmetrical acetal will be largely converted to symmetrical difatty acetal; the diethyl acetal will be removed as it is formed. Should this reaction occur to the maximum extent, the theoretical yield of fatty vinyl ether obtainable would be reduced to one-half of the value, based on dealcoholization of the unsymmetrical acetal.

Cleavage of alcohol occurs only under conditions where the vinyl ether may be distilled from the mixture whereas conversion of unsymmetrical acetals to symmetrical acetals occurs at temperatures as low as room temperature. Rapid establishment of conditions favorable to cleavage might therefore minimize acetal interconversion and increase the yield of fatty vinyl ether. In one experiment ethyl stearyl acetal was stirred in a flask equipped for distillation and heated *in vacuo* to 135°. Sulfanilic acid was added. Considerable foaming occurred, and care was necessary to prevent foaming into the condenser. The distillate contained 47.9% stearyl vinyl ether, 15.8% recovered acetal, and 34.2% stearyl alcohol. This technique offered little improvement over the previous method.

Experimental

Analytical Procedures. The method of hydrolytic oximation was used for the determination of acetals. The procedure of Mitchell (13) was modified by using a 1-hr. reflux in the place of pressure bottles and by adding 1% of pyridine to the reagent to give improved reproducibility.

Vinyl ether content was determined by an iodiometric procedure previously described (7).

Alcohols were determined by the method of phthalation (14).

Preparation of the Acetal

Acetaldehyde Ethyl Oleyl Acetal. In a 1-liter, 3-necked flask fitted with mechanical stirrer, thermometer, and ice-salt bath were placed 268.5 g. (1 mole) of oleyl alcohol (Cachalot 0–8, M. Michel and Company) and 216.9 g. (3 moles) of ethyl vinyl ether. The mixture was stirred and brought to 0°. Then 0.40 g. *p*-toluenesulfonic acid monohydrate was added. The temperature was maintained at 0–3° for 2 hrs. Then 250 ml. of 10% sodium hydroxide solution were added, and stirring was continued for ½ hr.

The mixture was transferred to a separatory funnel, and the aqueous layer was drawn off. The acetal layer was washed with three 250-ml. portions of 10% sodium hydroxide solution, then dried over sodium sulfate. The solution was filtered, and the excess vinyl ether was distilled *in vacuo*. The residue distilled from 2 g. of potassium carbonate with mechanical stirring *in vacuo* gave 278.1 g. (81.8%) acetal b.p. 166°/0.45 mm.–184°/1.2 mm., n_D^{30} 1.4432. Analysis showed approximately 1.4% alcohol and 98% acetal. A sample was redistilled through an 8-in. Vigreaux column, and the fraction having a b.p. 161°/0.6 mm. and n_D^{30} 1.4448 was collected as pure ethyl oleyl acetal. Acetal analysis indicated 100% purity.

Anal. Calcd. for $C_{22}H_{44}O_2$: C, 77.58; H, 13.01. Found: C, 76.71; H, 12.64.

The analysis is low in carbon apparently because of the presence of stearyl alcohol in the oleyl alcohol used. The iodine value (Wijs) of the oleyl alcohol was 83.4 whereas theory is 94.5. The hydroxyl equivalent weight was 268.5 (theory 268.5).

Acetaldehyde Ethyl Stearyl Acetal. This acetal was obtained in a yield of 84% by reacting stearyl alcohol (Eastman White Label) with ethyl vinyl ether in benzene in a manner similar to the procedure for the preparation of ethyl oleyl acetal. The stearyl acetal had b.p., 142–142.5°C./0.15 mm. and n_D^{30} 1.4372.

Anal. Calcd. for $C_{22}H_{46}O_2$: C, 77.13; H, 13.54. Found: C, 76.82; H, 13.35.

To prepare ethyl stearyl acetal with hydrogen chloride as catalyst, 270.4 g. (1 mole) of stearyl alcohol, 72.1 g. (1 mole) of ethyl vinyl ether, 400 ml. of benzene, and 15 ml. of 0.19 *N* hydrogen chloride in benzene were placed in a 1-liter flask. The mixture was allowed to stand with occasional shaking. After 16 hr. a sample removed and stripped *in vacuo* contained 86.9% ethyl stearyl acetal by analysis. After 40 hr. a similar sample contained 85.6% ethyl stearyl acetal. After 44 hr. the mixture was washed with three portions of saturated sodium bicarbonate, then with water. After drying over potassium carbonate and filtering, 40 g. of potassium carbonate were added and the solvents were removed by distillation *in vacuo*.

Distillation from carbonate gave 205 g., b.p. 134°/0.1 to 155°/0.8 mm. of crude ethyl stearyl acetal and 77.0 g. residue (distearyl acetal). The crude ethyl stearyl acetal was dissolved in 250 ml. of petroleum ether, chilled to 0°, and filtered. The filtrate, stripped *in vacuo,* gave 97.5% pure ethyl stearyl acetal.

A sample of the residue (distearyl acetal) from the distillation was recrystallized from acetone, then from petroleum ether, m.p. 40–41° (corrected).

Anal. Calcd. for $C_{38}H_{78}O_2$: C, 80.49; H, 13.87. Found: C, 79.90; H, 13.77.

Acetaldehyde Ethyl Linseed Acetals. In a 2-liter, 3-necked flask equipped with a thermometer and mechanical stirrer were placed 528 g. (2 moles) of linseed alcohols (Unadol 90)[12] and 432.6 g. (6 moles) of ethyl vinyl ether. The reactants were stirred and brought to 15° by means of an ice bath. *p*-Toluenesulfonic acid monohydrate (0.2 g.) was then added. The mixture was stirred at about 12° for 75 min. and was treated with 200 ml. of 10% NaOH. After the mixture was stirred for an additional 10 min., it was transferred to a separatory funnel. The layers were separated, and the acetal layer was washed successively with 500 ml. of 10% NaOH and two 500-ml. portions of water. After drying over anhydrous sodium sulfate and filtering, the mixture was stripped *in vacuo* on the steam bath. A sample taken for analysis contained 96.4% acetal calculated as ethyl linseed acetals. The mixture was distilled from potassium carbonate with continuous stirring; b.p. 152°/0.25 mm. to 172°/0.05 mm. The distillate weighed 545.4 g. (81.7%) and contained 100% ethyl linseed acetal by analysis.

Dealcoholization of the Acetals with Acid Catalysts. The following examples illustrate the method when sodium bisulfate, sulfanilic acid, aniline sulfate, or *p*-toluenesulfonic acid is used as a catalyst for the dealcoholization of the acetals.

Ethyl Linseed Acetals. A 250-ml. flask equipped for vacuum distillation was charged with 141.0 g. (0.41 mole) of ethyl linseed acetals and 0.25 g. of sulfanilic acid (recrystallized from 10% H_2SO_4). The mixture was distilled *in vacuo.* Extensive fuming accompanied the distillation. The distillate (99.0 g. collected over potassium carbonate) had b.p. 144–154°/0.25 mm. and contained 56% linseed vinyl ethers and 44% linseed alcohols.

Ethyl Stearyl Acetal. In a 500-ml., 3-necked flask equipped with a mechanical stirrer, thermometer, and head for vacuum distillation were placed 149.8 g. (0.43 mole) of ethyl stearyl acetal and 0.13 g. of aniline sulfate. The stirrer was started, the system was evacuated, and the mixture was heated as rapidly as possible to distillation temperature. In 12 min. the temperature of the reaction mixture had reached 135°, and fuming began. After 24 min. distillation started. The distillate, b.p. 162°/0.35–169°/0.15 mm., was collected over potassium carbonate. Analysis showed the distillate to contain 47.9% stearyl vinyl ether and 48.2% stearyl alcohol.

Dealcoholization in the Vapor Phase over Solid Catalysts

Over Bentonite. A glass tube approximately 60 x 1 cm. in diameter equipped with 2 thermocouple wells. dividing the column into thirds, was wrapped in an insulated electric heating jacket. The tube was charged with about 25 g. of bentonite (giving a neutral aqueous extract) to form a layer about 0.5 in. deep when the tube was mounted at an angle of 30° with the horizontal. A distillation flask containing 72.0 g. of ethyl linseed acetals was connected by a still head to the catalyst tube. A condenser and vacuum receiver were attached to the lower end of the column. The catalyst was heated at 250–300° and 0.3–3.6 mm. for about 3 hr. to remove water. Then with the column maintained at about 350° and 14 mm., the acetal was distilled into the tube, b.p. 220–223°. The distillate, 36 g., contained 5.7% linseed vinyl ether, 40.8% linseed alcohol, and 9.2% acetal. Only a sufficient portion of the acetal was distilled to allow analysis of distillate obtained under stable operations. The material collected in a dry ice-cooled trap separated into aqueous and acetal layers upon warming.

Stability of Linseed Vinyl Ether Over Bentonite. Linseed vinyl ether was distilled over bentonite at 360° and 2–4 mm. until 31.7 g. of distillate collected. Analysis showed that the distillate contained 36.9% linseed vinyl ethers and 19.0% linseed alcohols.

Twenty-two grams of the distillate were refluxed for 1 hr. in 100 ml. of 90% aqueous methanol containing 5 drops of concentrated hydrochloric acid to hydrolyze the vinyl ether. The product was extracted with ether, and the ether solution was washed with water and dried. Evaporation of ether left a residue (19 g.), which was warmed on a steam bath for 1 hr. with 70 ml. of 1 M phthalic anhydride in pyridine. The excess anhydride was hydrolyzed by warming with a few milliliters of water. The mixture was neutralized with sodium hydroxide solution and was extracted with 100 ml. of petroleum ether. The petroleum ether layer was extracted with hydrochloric acid to remove the pyridine, then with twelve 250-ml. portions of 0.5 N sodium hydroxide in 25% aqueous ethanol, dried over Drierite, and filtered. The solvent was stripped *in vacuo.* The infrared spectrum of the residue, 5.68 g., showed no absorption bands for alcohol or vinyl ether. The spectrum was consistent with that of an olefin. The iodine value (Wijs) was 249.0.

Over Silver. The silver catalyst on clay shards described by Baur (8) was prepared and charged into a 16 x 3 in. glass tube, equipped with a thermocouple well and heating jacket. The depth of the catalyst was 9–10 in. The remainder of the tube was filled with Raschig rings. The tube was mounted at an angle of about 20° with the horizontal. A flask containing 150.4 g. of ethyl nonconjugated-linseed acetal and a head for distillation were connected to the catalyst tube. The column was heated to 270 ± 15°, and the acetal was distilled at 213°/18 mm. into the column. When 35.0 g. of distillate (40.1 g. distilled) collected, the distillation was stopped. Analysis showed the distillate to contain 56% of ethyl linseed acetal, 25% of linseed alcohols, and 22% of linseed vinyl ethers. From a trap in the vacuum line, cooled by dry ice, was obtained 3.4 g. of a mixture which contained 47% of ethyl vinyl ether and 48% of ethanol. Since the material from the cold trap contained little diethyl acetal, little disproportionation of the unsymmetrical acetal occurred.

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