Syntheses of Polymerizable Acetals. I. Vinylbenzaldehyde Acetals with Perfume Alcohols

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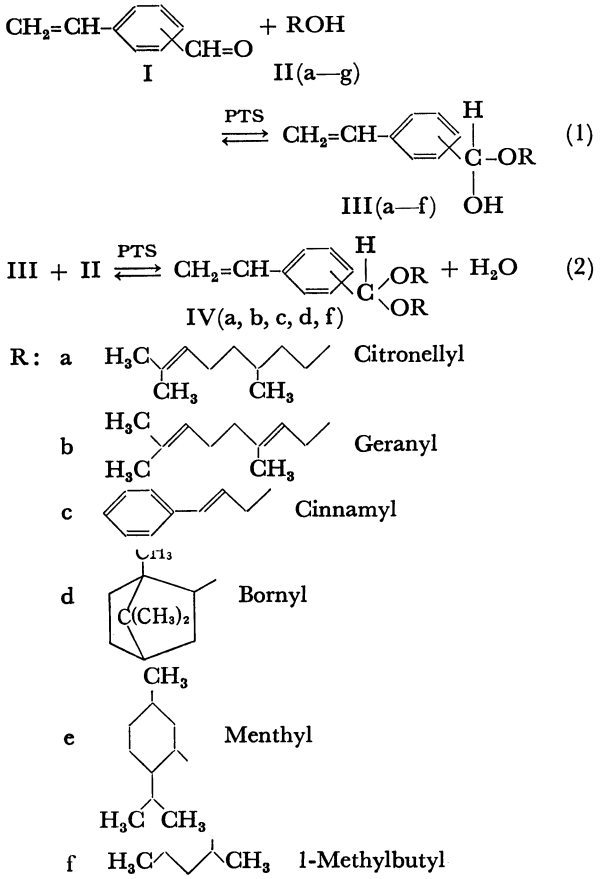
Several acetal monomers and a hemiacetal monomer of vinylbenzaldehydes were synthesized from the reaction with some perfume alcohols in the presence of *p*-toluenesulfonic acid as an acid catalyst. It was found that primary alcohols such as citronellol and geraniol with the exception of cinnamyl alcohol afforded acetal monomers in high yields, secondary alcohols such as borneol and menthol in low yields, with the latter affording only hemiacetal monomer, and linalool, a tertiary alcohol, neither acetal nor hemiacetal monomers. The radical polymerizations of the acetal and hemiacetal monomers synthesized provided soluble polymers which easily release perfume alcohols under mild acidic conditions.

Acetals are well-known for their easily hydrolyzable properties under acidic conditions in spite of their stabilities in neutral or alkaline media. This outstanding characteristic can be utilized for the syntheses of the readily hydrolyzable polymers which might find their use in liberating their functional groups gradually under acidic conditions.

With such intentions, Kamogawa[1] prepared vinyl polymers containing the isoalloxazine functional group in side chains through hemiacetal linkage.

As the first attempt to incorporate functional groups into the side chains of vinyl polymers through pure acetal linkages for the above-mentioned purpose, vinylbenzaldehyde acetals with perfume alcohols were synthesized using *p*-toluenesulfonic acid (PTS) as a catalyst.

Acetal monomers were synthesized as follows:



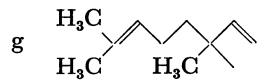


Table 1 shows the analytical results obtained for the acetal monomers synthesized. Since the starting chloromethylstyrene (I) was an unseparable mixture of para- and meta-isomers (40/60), the acetal monomers obtained should also be mixtures of para- and meta-isomers, presumably thereby having an oily appearance in spite of the absence of low-molecular weight impurities, as ascertained by gas chromatograph. The isomers could not be separated; the ratios of the para- to meta-isomers could not be determined.

As is generally recognized in acetal synthesis from aldehydes and alcohols under acidic conditions,[2] primary alcohols such as citronellol and geraniol gave high yields of acetals (IV-a and IV-b); secondary alcohols such as borneol and the reference, 2-pentanol, gave low yields (IV-d and IV-f). 3,7-Dimethyl-1,6-octadien-3-ol (linalool, II-g), a tertiary alcohol, gave neither acetal nor hemiacetal monomers, presumably due to the large steric hindrance exerted against the reaction. Similarly, *l*-menthol, a more sterically hindered secondary alcohol as compared with borneol, only gave a hemiacetal monomer (III-e). The fact that the yield of the monomer IV-c prepared with cinnamyl alcohol, a primary alcohol, was low (26.1%) may denote that steric hindrance is fairly large in this case, owing to the coplanar character of the styryl portion of the alcohol residue due to resonance.

The radical polymerization of acetal monomers appears to be almost unaffected by the kind of alcohol residue of the acetal monomers, as recognized from the results in Table 2. The polymer of III-e (a hemiacetal) is soluble in polar solvents such as alcohol due to the presence of pendant polar hydroxyl groups, but is insoluble in nonpolar petroleum ether, while the other polymers (acetals) are insoluble in alcohol but are soluble in petroleum ether.

The IR spectra of all polymers indicated no absorptions due to the double bond of the vinyl group (disappearance of the 910 cm^{-1} band) but indicated strong $-CH_2-$ absorption characteristic of the back-bone chains of vinyl polymers at 2930 and 2860 cm^{-1}.

The hydrolyses of the acetal polymers with liberation of perfume alcohol and the formyl group in the polymer during storage are dependent upon the extent of contact

TABLE 1. ANALYTICAL RESULTS OF THE SYNTHESIZED ACETAL MONOMERS

Monomer	Yield	Elemental analysis C[a)]%	Elemental analysis H[a)]%	IR (CCl_4) cm^{-1}	Mass peak *m/e*
IV-a	52.3	81.82 (81.69)	10.58 (10.79)	2860—2970(alkyl), 1610 (aryl), 1440 (CH), 1100 and 1060 (ether), 990 and 910 (vinyl)	426 (M^+)
IV-b	61.8	81.44 (82.46)	10.89 (9.95)	2850—2960 (alkyl), 1615 (aryl), 1430 (CH), 1100 and 1060 (ether), 985 and 905 (vinyl)	422 (M^+)
IV-c	26.1	85.51 (84.82)	6.72 (6.80)	3030 and 1610 (aryl), 2850—2950 (alkyl), 1440 (CH), 1120 and 1070 (ether), 980 and 910 (vinyl)	382 (M^+)
IV-d	22.4	81.90 (82.46)	9.98 (9.95)	2870—2980 (alkyl), 1610 (aryl), 1440 (CH), 1060 and 1040 (ether), 990 and 910 (vinyl)	422 (M^+)
IV-f	37.8	78.14 (78.62)	10.20 (10.34)	2870—2960 (alkyl), 1610 (aryl), 1440 (CH), 1080 and 1030 (ether), 990 and 910 (vinyl)	290 (M^+)

a) The figures in the parentheses indicate calcd values.

TABLE 2. POLYMERIZATION BEHAVIOR OF ACETAL MONOMER[b)]

Monomer	Precipitant for polymer	Conversion %	Polymer $[\eta]$[a)]dl/g	Polymer Appearance	Polymer Solubility
IV-a	Methanol	92	0.32	Glassy	Sol. in pet. ether
IV-b	Methanol	34	0.22	Glassy	Sol. in pet. ether
IV-c	Methanol	84	0.25	White powder	Sol. in pet. ether
IV-d	Methanol	91	0.25	White powder	Sol. in pet. ether
III-e	Pet. ether	58	0.43	White solid	Sol. in ethanol
IV-f	Methanol	78	0.34	Glassy	Sol. in pet. ether

a) Intrinsic viscosity in THF at 30 °C. b) Initiator (AIBN), 0.005 g/l ml THF; monomer, 0.5 g/1ml THF; 70 °C × 48 h.

with moisture, as well as the acidity. Thus, a polymer of IV-a in a carbon tetrachloride solution indicated almost no change in the IR spectrum even after storage of several weeks in air; storage in the solid state, especially in a fluffy powder (*e.g.* the polymer of IV-d), caused considerable change in the IR spectrum even within a week with the appearance of a 1700 cm^{-1} band (formyl groups in polymer), thereby indicating that hydrolysis was in progress.

Experimental

IR, ^{1}H-NMR, and mass spectra were obtained with a Hitachi EPI-G spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively, under standard measurement conditions. Elemental analyses were carried out using a Perkin-Elmer 240 instrument.

Vinylbenzaldehyde (I). The Sommlet reaction[3,4] was applied for the synthesis. Thus, from chloromethylstyrene (Seibi Chem. Co., a 40/60% mixture of para- and meta-isomers) and an equimolar amount of hexamethylenetetramine vinylbenzaldehyde was obtained in 45—50% yields after refluxing in chloroform for 2—4 h and subsequent steam distillation of the resulting hexaminium salt in the presence of a polymerization inhibitor (*e.g.* 4-(*t*-butyl) catechol). Bp, 54—56 °C/0.2—0.3 mmHg. Elemental analysis, IR (CCl_4), and ^{1}H-NMR (CCl_4) demonstrated structure I. Para/meta= 40/60 by NMR.

Vinylbenzaldehyde Dicitronellyl Acetal (IV-a). A solution of 3.0 g (0.023 mol) of vinylbenzaldehyde, 7.2 g (0.046 mol) of citronellol, 0.03 g of 4-(*t*-butyl) catechol, and 0.15 g of *p*-toluenesulfonic acid (PTS) as a catalyst in 30 ml of anhydrous chloroform was refluxed with stirring for 7 h with the addition of a molecular sieve 3A (1/16) as dehydrating agent. Upon cooling the solution was evaporated *in vacuo* at 40 °C leaving an oil, which was extracted with aqueous sodium carbonate and 100 ml of ether. The organic layer was then dried over anhydrous potassium carbonate, filtered, and evaporated *in vacuo* at 40 °C to obtain a crude acetal monomer. The crude product was chromatographed on an alumina column eluted by petroleum ether to afford a colorless oil in a 52.3% yield. The product was soluble in common organic solvents, including petroleum ether, but was insoluble in water.

NMR (CCl_4, Me_4Si): δ 7.26 (d 4H aromatic), 6.77 (q, 1H vinyl), 5.78 (d 1H vinyl), 5.39 (s, 1H acetal), 5.29 (d 1H vinyl), 3.8—0.5 (b 38H dicitronellyl) ppm. [No -CHO peak].

Other acetal monomers, *i.e.*, vinylbenzaldehyde digeranyl acetal (IV-b), dicinnamyl acetal (IV-c), dibornyl acetal (IV-d), and bis(1-methylbutyl) acetal (IV-f), were synthesized in the same manner to provide oily products even after chromatographic purification (Table 1).

Vinylbenzaldehyde Menthyl Hemiacetal (III-e). The same reaction procedure was adopted as that for the synthesis of monomer IV-a, except that methanol was employed as the eluting agent of the alumina column. Thus, from 3.0 g (0.023 mol) of vinylbenzaldehyde and 7.4 g (0.046 mol) of *l*-menthol, a colorless viscous oil was obtained in a 22.4% yield. The product was soluble in common organic solvents and was insoluble in water.

Found: C, 79.31; H, 9.57%. Calcd for $C_{19}H_{28}O_2$ (hemiacetal): C, 79.16; H, 9.72%. IR (CCl_4): 3610 (OH), 2850—2960 (alkyl), 1610 (aryl), 990 and 910 cm^{-1} (vinyl). Mass spectrum *m/e* 288 (M^+). NMR (CCl_4, Me_4Si): δ 7.17 (d, 4H aromatic), 6.62 (q, 1H, vinyl), 5.63 (d, 1H, vinyl), 5.15 (d, 1H, vinyl), 4.53 (s, 1H, OH), 3.0—0.5 (b, 19H, menthyl) ppm. [No -CHO in IR and NMR].

Other acetal monomers synthesized also indicated characteristic peaks in NMR at δ 7.1—7.3 (aryl) and 5—7 (styrenic vinyl) together with peaks of the alcohol residues, the integrator calculations indicating that the monomers were

apparently pure, without any splitting of the singlet peaks due to the presence of isomers.

Polymerization. A conventional procedure for free-radical polymerizations was adopted. In a typical example conforming to the polymerization conditions in Table 2, 0.5 g of monomer IV-d and 0.005 g of α,α′-azobisisobutyronitrile (AIBN) were dissolved in 1 ml of tetrahydrofuran (THF). The solution was put into a glass ampoule, which was evacuated and sealed-off, and left standing for 48 h at 70 °C. Upon cooling, the viscous solution was poured into a large quantity of methanol to afford a white precipitate, which was freeze-dried from dioxane.

References

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