1,3-Dioxolane Bearing Perfume and Herbicide Aldehyde Residues

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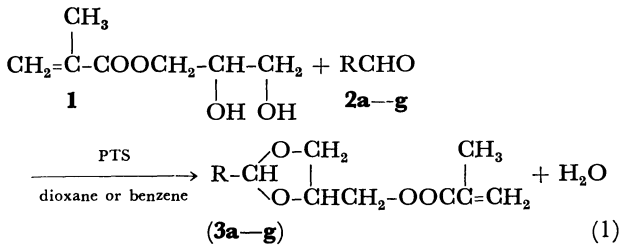
Synopsis. 4-Methacryloyloxymethyl-1,3-dioxolanes substituted at the 2 position with perfume and herbicide aldehyde residues were synthesized either by acetalization or by transacetalization involving 2,3-dihydroxypropyl methacrylate. The effect of the 2-substituent of the dioxolane ring on the rate of hydrolysis was remarkable.

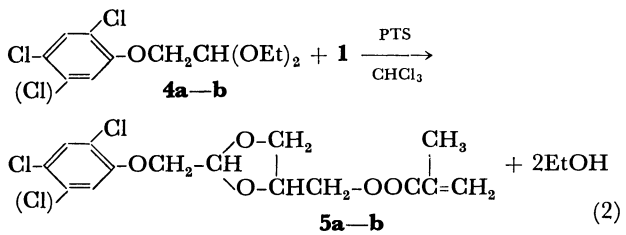
In the course of studies to synthesize polymerizable acetals bearing various functions capable of being released by hydrolysis, those from perfume and vitamin alcohols have been reported.[1,2] In the meantime, polyurethanes containing the acetal linkage in the principal chain[3] and polyamide attached with acetal side chains,[4] both containing a herbicide function, have also been reported.

In this note, we wish to report on novel acetals containing the 1,3-dioxolane unit composed of the perfume or herbicide aldehyde and 2,3-dihydroxypropyl methacrylate residues.

Acetals **3a**—**g** were synthesized by the acid-catalyzed acetalization of **1** and **2a**—**g** (Eq. 1), where R represents a perfume or herbicide residue in Table 1.



(1)

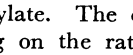
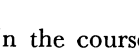
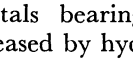
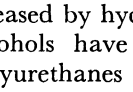
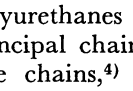
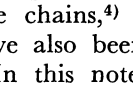
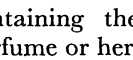


(2)

4a, **5a**: 2,4-Dichloro; **4b**, **5b**: 2,4,5-Trichloro

Diethyl acetals (**4a**—**b**) were also employed to conduct the *p*-toluenesulfonic acid (PTS)-catalyzed transacetalization as indicated in Eq. 2. A Soxhlet extractor, the thimble of which contained 4A or 5A molecular sieves for the removal of the ethanol produced, was employed in this case. Although the repetition of column chromatography decreased the yields of isolated products (9 and 11% for **5a** and **5b**, respectively), acetal conversions, calculated from the ^{1}H-NMR data for crude product **5a**, were 47 and 59% with 4A and 5A molecular sieves, respectively, on the basis of the starting **4a**, indicating advantage of the latter molecular sieves with larger micropores. The conversion for **5b** was 55% with 5A molecular sieves, also a much higher value than the yield (11%) of the purified product.

TABLE 1. ACETALS SYNTHESIZED ACCORDING TO Eq. 1

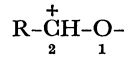
Abbreviation		Acetalization: Yield of 3a—g/%[a]	Acetalization: Solvent	Acetalization: Means of dehydration
2a, 3a		28	Dioxane	3A molecular sieves
2b, 3b		39	Dioxane	3A molecular sieves
2c, 3c		23	Dioxane	3A molecular sieves
2d, 3d		25	Dioxane	3A molecular sieves
2e, 3e		21	Dioxane	3A molecular sieves
2f, 3f		8	Benzene	Dean-Stark trap
2g, 3g		10	Benzene	Dean-Stark trap

a) Values for purified products.

TABLE 2. HYDROLYTIC RELEASE OF FUNCTIONAL ALDEHYDES FROM ACETALS

Acetals	Aldehyde released in: 2 h	Aldehyde released in: 24 h, %
3a	44	—
3d	Trace	—
3f	25	77
3g	27	—
5a	9	—

Novel 1,3-dioxolanes thus synthesized were subjected to acid hydrolysis, as exemplified in Table 2. The results indicate that the kind of 2-substituent of the dioxolane ring, *i.e.*, aldehyde residue, exerts a remarkable influence on the rate of hydrolysis: acetal **3a** bearing *p*-methoxyphenyl group as R which stabilizes the intermediate carbocation produced during the hydrolysis provides the highest rate, whereas, for **3d** and **5a** with aliphatic R, rates are much lower



than that for **3a** and even considerably lower than those for **3f** and **3g** with essentially the same release components as that in **5a**. This fact indicates that the release rate of the functional portion can be controlled here over a wide range by choosing the group neighboring to the C-2 atom of the 1,3-dioxolane ring.

Experimental

2,3-Dihydroxypropyl Methacrylate (**1**). A mixture of glycidyl methacrylate (14.2 g, 100 mmol), 4-*t*-butylcatechol (0.1 g), H_2SO_4 (concd, 0.2 ml), and water (100 ml) was stirred vigorously at room temperature for 24 h. The resulting clear solution was neutralized with an anion-exchange

resin (Diaion SA-10A) and freeze-dried to leave a liquid, which was distilled under reduced pressure to afford pure **1** as a colorless liquid (bp 115—120 °C/1.0 mmHg) in 60—70% yield. Found: C, 52.41; H, 7.74%. Calcd for $C_7H_{10}O_3$: C, 52.49; H, 7.55%. IR(CCl_4) 3500, 1720 cm^{-1}; NMR (D_2O) δ 2.0 (s, 3H, CH_3), 3.5—4.5 (m, 5 H, $-CH_2-CHCH_2$), 5.7 (s, 1H, $CH_2=$), 6.2 (s, 1H, $CH_2=$) ppm.

*2-(p-Methoxyphenyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3a**).* A solution of **1** (1.3 g, 8.1 mmol), *p*-anisaldehyde (**2a**; 1.1 g, 8.1 mmol), PTS (0.3 g), and phenothiazine (0.05 g) in dioxane (50 ml) was stirred at room temperature for 24 h under nitrogen in the presence of 3A molecular sieves. The reaction mixture was diluted with chloroform and neutralized with aq $NaHCO_3$ by shaking. The organic layer was dried over anhyd. Na_2SO_4 and evaporated *in vacuo* to leave an oil, which was chromatographed on alumina (Wako, 300 mesh, neutral). Methanol elution provided an oily product. Found: C, 64.26; H, 7.01%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%. IR ($CHCl_3$) 1710 cm^{-1}; NMR (CCl_4) δ 1.9 (s, 3H, CH_3), 3.3—4.5 (m, 5H, $-CH_2-CHCH_2$), 3.7 (s, 3H, OCH_3), 5.1—5.8 (m, 1H, acetal CH), 5.6 (s, 1H, $CH_2=$), 6.1 (s, 1H, $CH_2=$), 6.6—7.4 (m, 4H, ArH) ppm; Mass (*m/e*) 278 (M^+).

Products **3b**, **3c**, **3d**, and **3e**, each oily compound, were synthesized in the same manner.

*2-(3,4-Methylenedioxyphenyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3b**).* Found: C, 61.24; H, 5.92%. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H 5.52%. IR (CCl_4) 1710 cm^{-1}; NMR (CCl_4) δ 1.9 (s, 3H), 3.4—4.5 (m, 5H), 5.1—5.8 (m, 1H), 5.5 (s, 1H), 5.9 (s, 2H), 6.0 (s, 1H), 6.5—6.9 (m, 3H) ppm; Mass (*m/e*) 292 (M^+).

*2-Styryl-4-methacryloyloxymethyl-1,3-dioxolane (**3c**).* Found: C, 69.65; H, 7.02%. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%. IR ($CHCl_3$) 1710 cm^{-1}; NMR (CCl_4) δ 1.9 (s, 3H), 3.3—4.3 (m, 5H), 4.8—5.3 (b, 1H), 5.5 (s, 1H), 6.1 (s, 1H), 6.6—6.8 (d, 2H), 7.0—7.4 (s, 5H) ppm; Mass (*m/e*) 274 (M^+).

*2-(2,6-Dimethyl-5-heptenyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3d**).* Found: C, 68.65; H, 8.67%. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 8.86%. IR (CCl_4) 1720 cm^{-1}; NMR (CCl_4) δ 0.8—2.4 (m, 19H), 3.1—4.5 (m, 5H), 4.7—5.5 (m, 2H), 5.6 (s, 1H), 6.2 (s, 1H) ppm.

*2-(2,6-Dimethyl-1,5-heptadienyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3e**).* Found: C, 69.75; H, 8.48%. Calcd for $C_{17}H_{26}O_4$: C, 69.35; H, 8.90%. IR (CCl_4) 1730 cm^{-1}; NMR (CCl_4) δ 0.8—3.0 (m, 16H), 3.1—4.2 (m, 5H), 4.5—6.1 (m, 3H), 5.5 (s, 1H) 6.0 (s, 1H) ppm.

*2-(2,6-Dichlorophenyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3f**).* A mixture of **1** (1.6 g, 10 mmol), 2,6-dichlorobenzaldehyde (**2f**; 1.7 g, 10 mmol), hydroquinone (0.5 g), PTS (0.5 g), and benzene (100 ml) was refluxed for 2 h with a Dean-Stark trap fitted. The reaction mixture was washed with 5% aq K_2CO_3 (200 ml) and dried over anhyd. Na_2SO_4, followed by evaporation *in vacuo*. Silica gel (Wakogel C-300) column chromatography conducted on the crude product afforded pure **3f** as a viscous colorless oil (benzene eluate). Found: C, 52.61; H, 4.50%. Calcd for $C_{14}H_{14}O_4Cl_2$: C, 53.02; H, 4.45%. IR ($CHCl_3$) 1720 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, 3H, CH_3), 3.8—4.9 (m, 5H, $-CH_2-CHCH_2$), 5.7 (s, 1H, $CH_2=$), 6.2 (s, 1H, $CH_2=$), 6.3, 6.6, 6.7 (t, 1H, acetal CH), 7.2—7.5 (t, 3H, ArH) ppm; Mass (*m/e*) 317 (M^+).

*2-(2,4-Dichlorophenyl)-4-methacryloyloxymethyl-1,3-dioxolane (**3g**).* A viscous oil [hexane–benzene (1:4 v/v) eluate]. Found: C, 52.83; H, 4.41%. Calcd for $C_{14}H_{14}O_4Cl_2$: C, 53.02; H, 4.45%. IR ($CHCl_3$) 1720 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, 3H), 3.8—4.9 (m, 5H), 5.6 (s, 1H), 6.2 (s, 1H), 5.9, 6.2, 6.3 (t, 1H), 7.2—7.9 (m, 3H) ppm; Mass(*m/e*) 317 (M^+).

*(2,4-Dichlorophenoxy)acetaldehyde Diethyl Acetal (**4a**).* A solution of 2,4-dichlorophenol (16 g, 0.1 mmol) and potassium hydroxide (8 g) in methanol (100 ml) was evaporated *in vacuo* at 50—60 °C almost to dryness. The residue was dissolved in DMF (100 ml) and equimolar bromoacetaldehyde diethyl acetal (0.1 mol) was added, followed by stirring at 100 °C for 5 h under nitrogen. The reaction mixture was poured into excess aq $NaHCO_3$ (500 ml) and the oil thus separated was extracted with ether (200 ml). The ether extract was washed first with dil aq NaOH, then with water, dried over anhyd. Na_2SO_4, and concentrated *in vacuo*, followed by distillation under reduced pressure to afford **4a** as a light yellow oil (bp 121—122 °C/0.1 mmHg) in 33% yield. Found: C, 51.82; H, 5.70%. Calcd for $C_{12}H_{16}O_3Cl_2$: C, 51.79; H, 5.75%. NMR ($CDCl_3$) δ 1.2 (t, 6H, $2CH_3$), 3.2—4.2 (m, 6H, $3CH_2$), 4.8 (q, 1H, CH), 6.7—7.5 (m, 3H, ArH) ppm; Mass (*m/e*) 278 (M^+).

*(2,4,5-Trichlorophenoxy)acetaldehyde Diethyl Acetal (**4b**).* A light yellow oil of bp 135—137 °C/0.1 mmHg (30% yield). Found: C, 46.02; H, 4.94%. Calcd for $C_{12}H_{15}O_3Cl_3$: C, 46.15; H, 4.81%. NMR ($CDCl_3$) δ 1.3 (t, 6H), 3.5—4.2 (m, 6H), 4.9 (q, 1H), 7.3 (d, 2H) ppm; Mass (*m/e*) 312 (M^+).

*2-(2,4-Dichlorophenoxymethyl)-4-methacryloyloxymethyl-1,3-dioxolane (**5a**).* In a Soxhlet flask were placed **4a** (3.1 g, 10 mmol), **1** (3.2 g, 20 mmol), PTS (0.1 g), hydroquione (0.1 g), and chloroform (100 ml). The flask, fitted with a thimble containing 4A or 5A molecular sieves, was heated with stirring to reflux for 7 h. The reaction mixture was diluted with chloroform (50 ml), washed with aq Na_2CO_3, dried over anhyd. Na_2SO_4, and evaporated *in vacuo* to leave the crude product, which was chromatographed on silica gel (Wakogel C-300) to afford a viscous oil in 9% yield [benzene–ether (1:4 v/v) eluate]. Found: C, 51.94; H, 4.85%. Calcd for $C_{15}H_{16}O_5Cl_2$: C, 52.02; H, 4.62%. IR (CCl_4) 1720 cm^{-1}; NMR ($CDCl_3$+DMSO-d_6) δ 1.9 (s, 3H, CH_3), 3.1—4.3 (m, 7H, $3CH_2$+CH), 4.5—5.2 (b, 1H, acetal CH), 5.5 (s, 1H, $CH_2=$), 6.1 (s, 1H, $CH_2=$), 6.5—7.4 (m, 3H, ArH) ppm.

*2-(2,4,5-Trichlorophenoxymethyl)-4-methacryloyloxymethyl-1,3-dioxolane (**5b**).* A light yellow viscous oil [benzene–ether (4:1 v/v) eluate; 11% yield]. Found: C, 46.67; H, 4.12%. Calcd for $C_{15}H_{15}O_5Cl_3$: C, 47.18; H, 3.94%. IR (CCl_4) 1730 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, 3H), 3.5—4.3 (m, 7H), 4.6—5.2 (b, 1H), 5.6 (s, 1H), 6.2 (s, 1H), 6.6—7.5 (m, 2H) ppm; Mass (*m/e*) 381 (M^+).

Hydrolysis of the Acetals Synthesized. A solution of an acetal (1 mmol), PTS (0.05 g), and 4-*t*-butylcatechol (0.01 g) in THF–water (2:1 v/v; 30 ml) was let stand at 20 °C for 2 h. The solution was neutralized with solid Na_2CO_3, filtered, and evaporated *in vacuo*. The residue was extracted with $CHCl_3$– aq $NaHCO_3$. The organic layer was dried over anhyd. Na_2SO_4 and evaporated *in vacuo* to dryness. The relative strength of either the aldehyde signal produced or the remaining acetal CH in the ^1H-NMR ($CDCl_3$) was determined for the residue to calculate the value of % hydrolysis. Time of hydrolysis was also prolonged to 24 h.

References

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