A Facile, Selective Preparation of Monoketals from Pentaerythritol and Ketones

Marcelo C. Murguía,[1a] Santiago E. Vaillard,[1b] Ricardo J. Grau*[1c]

Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral and CONICET Güemes 3450, (3000) Santa Fe, Argentina
Fax +54(342)4551918; E-mail: cqfina@ceride.gov.ar

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Abstract: The selective preparation of monoketals **3a–f** from pentaerythritol **1** and cyclic, acyclic, aromatic, and aliphatic ketones **2a–f** was achieved by a facile method. The extreme polarity and low solubility of pentaerythritol in almost all organic solvents were the main difficulties to be overcome for the preparation of monoketals in good yields and high selectivity. A benzene–dimethylformamide (40:60) mixture proved to be excellent for the ketalization. The one-step procedure developed allowed the preparation of monoketals in good yields and good to excellent selectivity (higher than 90%).

Key words: pentaerythritol, 1,3-diols, monoketals, monoprotection, 1,3-dioxanes

Ketals find widespread applications in the pharmaceutical, phytopharmaceutical, fragrance, and lacquer industries.[2,3] They are of interest in synthetic steroid and carbohydrate chemistry.[4,5] In addition, ketals are useful in strategies for protecting groups of carbonyl, hydroxy and diol functions in organic synthetic sequences.[6,7] Particularly, protection for the hydroxyl groups of 1,2- and 1,3-diols can be accomplished by ketalization in acidic medium. On the other hand, the development of new amphipathic compounds derived from polyhydric alcohols has recently grown in importance because different surface and micellar properties can be expected for a molecule with distinct content of lipophilic and hydrophilic groups.[8,9] Pentaerythritol is one of the most common tetraols and it would be a useful symmetric 1,3-diol to synthesize novel amphipatic compounds bearing four lipophilic alkyl chains and four hydrophilic groups. This possibility prompted us to protect, in selective form, a pair of hydroxyl groups of pentaerythritol with ketones as the key step in the synthetic sequence to prepare well-defined amphipathic compounds.

In connection with the ketalization of pentaerythritol, numerous diketals have been reported.[10,11] However, an examination of the literature for the preparation of monoketals revealed that only few efforts have been made to obtain these synthetic intermediates, since Böeseken,[12] Orthner and Freyss,[13] and Orthner[14] published pioneer works regarding it. The extreme polarity of pentaerythritol and consequently its insolubility in almost all organic solvents appear to be the main difficulties found when dealing with the studies concerning the preparation of monoketals. If the ketalization is carried out under low solubility of pentaerythritol conditions, the diketal is mainly formed due to the presence of ketone in excess. All available methods give low yields of monoketals. Conrad et al.[10] have reported the preparation of monoketals from diketals by partial hydrolysis obtaining the monoketal of pentaerythritol and cyclohexanone in 12% yield. Schneider et al.[11] have described methods for preparation of the mono and diketals of pentaerythritol in benzene–dioxane (1:1) as solvent, but neither yields nor selectivities towards both ketalization products have been reported. Bonner et al.[15] have prepared the monoketal derived from acetone and pentaerythritol in 28% yield by a tedious procedure. Schaeffer and Stevens[16] have reported the preparation of the monoketal derived from the cyclohexanone in 3.5% yield by the Issidroides and Gulen procedure.

Our exploratory studies started with ketones since they might be less reactive than the analogous aldehydes. We report herein a one-step procedure to prepare monoketals **3a–f**, in good yields and good to excellent selectivities, from pentaerythritol **1** and cyclic, acyclic, aromatic, and aliphatic ketones **2a–f** in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate (Table 1, Scheme).

A solvent capable of dissolving both **1** and **2** was necessary for the success of the selective ketalization toward the monoketal **3** rather than the diketal **5**. Another key factor was to establish reaction conditions for removing the water formed to shift the equilibrium toward ketals, without losing the volatile ketones. Therefore, ketalization reactions were tried with benzene–DMF mixtures. Dimethylformamide was chosen as solvent because it dissolves both reagents and it allows, due to its low relative volatility, temperatures high enough to remove the water formed by reactive distillation. Benzene was used as recycling co-solvent to enhance the recovery of the volatile ketones, which might be lost together with water from the distillate. Upon varying the benzene–DMF molar ratio from 9:1 to 1:9, the selective preparation of the monoketals was best accomplished in a benzene–DMF (4:6) mixture. This composition was finally chosen since it makes it possible to carry out the ketalization reaction at temperatures in the 95−115 °C range, with high removal rates of the water formed and with high reflux rates of co-solvent, enhancing the recovery and recycling of the ketones evaporated. Three physical methods for the simultaneous re-

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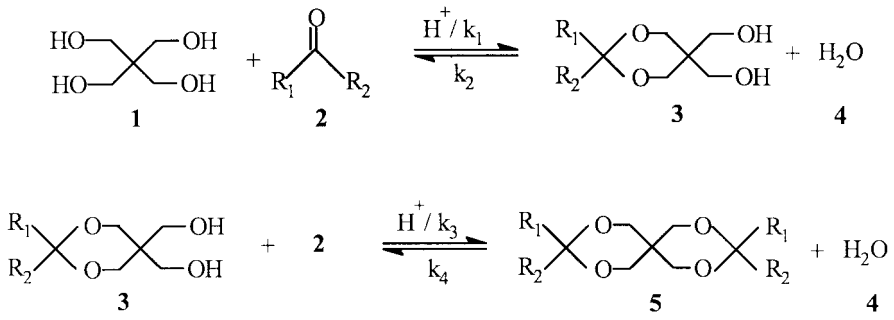
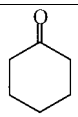
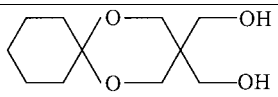
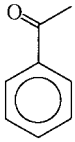
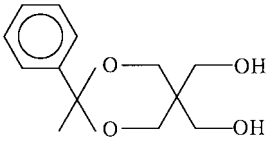
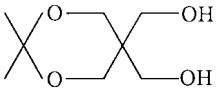
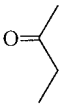
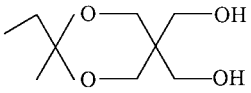
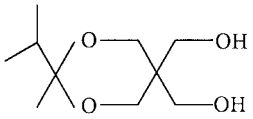
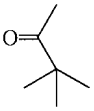
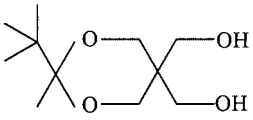


Scheme

Table 1 Monoketalization Reactions of Pentaerythritol **1** with Diverse Ketones **2**[a]

Entry	Ketones **2**	Reaction Conditions Temp.(°C)	Time (h)	Products **3**	Conv. (%)	Select. (%)	Yields (%)	Methods
1	 **2a**	115	48	 **3a**	99	92	90[b] (91)[c]	A
2	 **2b**	115	120	 **3b**	80	95	68.4[b] (76)[c]	A
3	 **2c**	90	48	 **3c**	64	95	56.7[b] (61)[c]	A, C
4	 **2d**	95	48	 **3d**	56	93	47[b] (52)[c]	B, C
5	 **2e**	110	96	 **3e**	48	94	41[b] (45)[c]	B
6	 **2f**	115	120	 **3f**	37	90	31[b] (33)[c]	B

[a] All acetalization reactions were carried out in benzene–DMF (40:60) in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate.
[b] Product quantified by isolation.
[c] Product quantified by GC analysis using the method of internal standard.

moval of the water formed were used (see experimental, preparation of ketals).

When cyclohexanone **2a** was reacted with a solution of pentaerythritol **1** and benzene–DMF (40:60), in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate (0.1 equivalent of $TsOHH_2O$ for 1 equiva-

lent of ketone) for 48 hours at 115 °C, **3a** was obtained in 90% yield, with 99% conversion and 92% selectivity (entry 1, Table 1). Under the same conditions and long enough reaction times (greater than 120 hours), acetophenone **2b** gave the corresponding monoketal **3b** in 68.4% yield, with 80% conversion and 95% selectivity (entry 2, Table 1). Despite the lower yield, in comparison with **3a**, the selectivity towards the monoketal was successfully higher (95%). As expected, **2b** is less reactive than **2a**. In both cases, the monoketal to diketal ratio attained was high (92:8 and 95:5, respectively), and nearly constant from the beginning of the reaction (Table 2). This unexpected result suggested that the ability of a pair of hydroxyls groups of **1** to undergo ketal formation is much greater than those of **3**, and that the hydrolysis rates of **3** and **5** are negligible with respect to the ketalization rates of **1** and **3**, respectively. If both conditions are fulfilled, the monoketal to diketal molar ratio must be nearly constant during the ketalization reaction as it can be seen by inspection of the kinetic equations of reaction rates.

Table 2 Ketalization Reaction of Pentaerythritol with **2b**[a]

Entry	**3b**, Conversion (%)	**3b**, Yield (%)	**5b**, Yield (%)	**3b**, Selectivity (%)	Reaction time (h)
1	27	26	0.6	97.8	24
2	41	39	2.1	94.9	48
3	67	63	4.7	93.1	94
4	80	76	4.0	95.0	120
5	81	76	5.7	93.0	164

[a] Reaction carried out in benzene–DMF (4:6) in the presence of 0.1 equiv $TsOHH_2O$ for 1 equiv of **2b,** at 115 °C. All values were calculated by GC using the method of internal standard.

The reaction rates of monoketal and diketal are given by

$$\frac{d}{dt}[\mathbf{3}] = k_1[\mathbf{1}][\mathbf{2}] - k_2[\mathbf{3}][\mathbf{4}] - k_3[\mathbf{2}][\mathbf{3}] + k_4[\mathbf{4}][\mathbf{5}]$$

$$\frac{d}{dt}[\mathbf{5}] = k_3[\mathbf{2}][\mathbf{3}] - k_4[\mathbf{4}][\mathbf{5}]$$

Equation 1

Thus, if the hydrolysis reaction rates are negligible with respect to the ketalization ones, the rate of the change of the diketal to monoketal ratio reduces to

$$\frac{d}{dt}\frac{[\mathbf{5}]}{[\mathbf{3}]} = \frac{k_3[\mathbf{3}]}{k_1[\mathbf{1}] - k_3[\mathbf{3}]}$$

Equation 2

and if the ketalization rate of pentaerythritol is much greater than the monoketal one $k_1[\mathbf{1}][\mathbf{2}] >> k_3[\mathbf{2}][\mathbf{3}]$, then $d\{[\mathbf{5}]/[\mathbf{3}]\}/dt \rightarrow 0$.

Therefore, no change in the [**5**]/[**3**] ratio would be expected, as observed experimentally. This result may be explained by considering that the ketalization rate is critically dependent on the relative positions of the pair of hydroxyls and hence the stereochemistry and the conformational stability of the ketal produced. Preliminary Molecular Modeling based on semi empirical calculations by the AM1 method showed that one of the hydroxyl groups in the optimized structure of **3** would be highly hindered by the six-membered ring, consequently **3** has a much lesser ability than **1** to undergo ketalization reaction.

The above procedure (Method A) failed when applied to the preparation of aliphatic ketals. In this case, the water formed during the ketalization reaction was removed inefficiently by means of a Dean-Stark trap. It seemed that the greater content of volatile ketones in the recycling current dissolved some water, which was consequently recycled from the trap to the reaction medium. Therefore, poor yields and worse selectivities of monoketals were obtained; accordingly, these compounds are unstable in the presence of water.[10] Instead, the use of a jacket containing anhydrous magnesium sulfate as dehydrating agent proved successful (Method B). In this way, monoketals **3c** to **3f** were selectively prepared from acetone (**2c**), 2-butanone (**2d**), 3-methyl-2-butanone (**2e**), and 3,3-dimethyl-2-butanone (**2f**), respectively (entries 3–6, Table 1). After little experimentation, we were able to obtain acetone, cyclic 2,2-bis(hydroxymethyl)trimethylene ketal **3c** in 56.7% yield and high mono-/diketal product ratio (95:5) (entry 3, Table 1). 2-Butanone, cyclic 2,2-bis(hydroxymethyl)trimethylene ketalt **3d** was obtained from **2d** in 47% yield and high selectivity (93:7) (entry 4). Likewise, 2-methyl-2-(1-methylethyl)-1,3-dioxane-5,5-dimethanol (**3e**) (41%, 94:6 selectivity), and 2-methyl-2-(1,1-dimethylethyl)-1,3-dioxane-5,5-dimethanol (**3f)** (31%, 90:10 selectivity), were prepared (entries 5 and 6).

The conversion of the aliphatic ketones decreased in the order: acetone > 2-butanone > 3-methyl-2-butanone > 3,3-dimethyl-2-butanone. A reaction time of 48 hours (at 90 °C) was required for 64% conversion of **3c**; 48 hours (at 95 °C) for 56% conversion of **3d**; 96 hours (at 110 °C) for 48% conversion of **3e**; and 120 hours (at 115 °C) 37% conversion of **3f**. The sterical hindrances might account for this observed sequence. Some improvement of reaction time was corroborated by carrying out the ketalization reaction in the lower container of a Soxhlet apparatus (Method C).

In conclusion, several monoketals from pentaerythritol and cyclic, acyclic, aromatic and aliphatic ketones were easily obtained in good yields and good to excellent selectivities. A benzene–DMF (40:60) mixture proved excellent for the selective ketalization reaction. Currently, further ketalization of more complex ketones and diverse aldehydes are in progress to extend this simple protocol to

the selective preparation of monoketals as intermediates to be used in strategies of the synthesis of well-defined amphiphatic compounds.

Mps (uncorrected) were determined on a Büchi 510 micro melting point apparatus. IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-200 spectrometer, using $(CD_3)_2SO$ as solvent. Chemical shifts (δ) are reported in ppm relative to internal TMS. Mass spectra were performed on a Shimadzu GCMS-QP 5000 spectrometer. Elemental analyses were performed at the Galbraith Laboratories, Inc., Knoxville, U.S.A. GLC analyses were performed on a Shimadzu GC-17AATF chromatograph equipped with a methyl silicone capillary column (30 m × 0.32 mm, 0.25 μm film thickness) and flame ionization detector. Isolated and authenticated compounds were used as internal standard to perform quantitative GC analyses. Column chromatography was performed on silica gel (70−230 mesh ASTM).

All reactants and solvents were of analytical grade. Benzene and DMF were double distilled and stored on molecular sieves (4 Å). High purity *p*-toluenesulfonic acid monohydrate was dried at 100 ° C under vacuum prior to use. Pentaerythritol was purified by sublimation according to a reported procedure.[17] Cyclohexanone, acetophenone, acetone, 2-butanone, 3-methyl-2-butanone and 3,3-dimethyl-2-butanone were distilled and dried as previously reported.[17,18]

Preparation of Ketals; General Procedure

Method A: Synthesis of ketals attended by reactive distillation.
The reaction was carried out in a 100-mL three-neck round-bottomed flask equipped with a magnetic stirring bar and a Dean-Stark trap topped with a condenser. A catalytic amount of *p*-toluenesulfonic acid monohydrate (5% w/w relative to the ketone) was added to a dispersion of pentaerythritol (22 mmol) and benzene–DMF (40:60, 50 mL) at r.t. The well-stirred dispersion was warmed to 80 °C until complete dissolution, and the ketone (15 mmol) was added dropwise while the reaction mixture was heated to 115 °C. The H_2O formed during the reaction was removed by reactive distillation and collected in the Dean-Stark trap. The reaction was stopped when there was no further increase in the collected H_2O. After cooling, the reaction mixture was poured into H_2O (30 mL), neutralized with K_2CO_3 and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo. Compounds **3a** to **3c** were isolated as white solids by Kugelrohr distillation and purified by column chromatography on silica gel (Et_2O–light petroleum, 80:20). Conversions, selectivities and yields are summarized in Table 1 (entries 1 to 3).

Method B: Synthesis of ketals attended by a dehydrating agent.
The upper part of the apparatus described above was provided with a jacket containing anhyd $MgSO_4$ to remove the H_2O formed during the reaction by means of a dehydrating agent. The reaction was carried out as above, starting from the same amount of reagents and solvents. Compounds **3d** to **3f** were obtained as white solids. Conversions, selectivities and yields are summarized in Table 1 (entries 4 to 6).

Method C: Synthesis of ketals using a Soxhlet apparatus.
Pentaerythritol (22 mmol), benzene–DMF (40:60, 50 mL) and a catalytic amount of *p*-toluenesulfonic acid monohydrate (5% w/w relative to the ketone) were placed into the lower container of a Soxhlet apparatus. The upper part of the apparatus was provided with a jacket containing anhyd $MgSO_4$. The mixture was heated to 80 °C until complete dissolution, then the ketone (15 mmol) was added dropwise, and finally the reaction mixture was kept at 115 °C. Then the reaction mixture was treated as described above. Compounds **3c** and **3d** were obtained as white solids. Conversions, selectivities and yields are summarized in Table 1 (entries 3 and 4).

1,5-Dioxaspiro[5.5]undecande-3,3-dimethanol (**3a**)
Mp 123−124 °C (Lit.[11] mp 123 °C).

IR (KBr): ν = 920.0, 1039.6, 1062.7, 1107.1, 1369.4, 2856.4, 2922.0, 3273.0 cm^{-1}.

^{1}H NMR [200 MHz, $(CD_3)_2SO$]: δ = 1.31–1.57 (m, 6H), 1.61–1.78 (m, 4H), 3.27–3.48 (m, 4H), 3.61 (s, 4H), 4.47 (t, 2H).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 22.11, 25.19, 32.25, 60.63, 60.79, 61.19, 96.88.

MS: *m/z* (%) = 216 (M^+, 6), 187 (13), 173 (96), 160 (4), 125 (5), 101 (6), 99 (14), 83 (34), 71 (40), 55 (100), 41 (72).

Anal. Calcd for $C_{11}H_{20}O_4$ (216.3): C, 61.08; H, 9.32; O, 29.59. Found: C, 61.01; H, 9.61; O, 29.38.

2-Methyl-2-phenyl-1,3-dioxane-5,5-dimethanol (**3b**)
Mp 126–127 °C.

IR (KBr): ν = 675.0, 707.8, 871.8, 1001.0, 1019.8, 1040.0, 1407.9, 2871.8, 2954.7, 3323.1 cm^{-1}.

^{1}H NMR [200 MHz, $(CD_3)_2SO$]: δ = 1.41 (s, 3H), 3.07–3.67 (m, 6H), 4.10–4.23 (m, 2H), 4.27 (t, 1H, *J* = 6.0 Hz), 4.55 (t, 1H, *J* = 6.0 Hz), 7.33–7.48 (m, 5H).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 31.31, 45.46, 59.77, 61.06, 61.20, 63.11, 99.47, 126.20, 127.55, 128.60, 141.06.

MS: *m/z* (%) = 223 (M^+ – 15, 11), 161 (14), 121 (11), 105 (38), 71 (10), 44 (64), 32 (100).

Anal. Calcd for $C_{13}H_{18}O_4$ (238.3): C, 65.52; H, 7.61; O, 26.86. Found: C, 65.31; H, 7.84; O, 26.85.

2,2-Dimethyl-1,3-dioxane-5,5-dimethanol (**3c**)
Mp 125–126 °C (Lit.[15] mp 126–127 °C).

IR (KBr): ν = 673.1, 827.4, 1002.9, 1020.1, 1041.2, 1369.4, 2877.6, 2941.2, 2995.2, 3323.1 cm^{-1}.

^{1}H NMR [200 MHz, $(CD_3)_2SO$]: δ = 1.31 (s, 6H), 3.34–3.39 (m, 6H), 3.60 (s, 2H), 4.23 (t, 1H, *J* = 5.9 Hz), 4.50 (t, 1H, *J* = 5.9 Hz).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 23.78, 45.54, 60.47, 61.03, 61.65, 97.04.

MS: *m/z* (%) = 161 (M^+ – 15, 11), 113 (3), 83 (5), 71 (21), 59 (60), 43 (100).

Anal. Calcd for $C_8H_{16}O_4$ (176.2): C, 54.52; H, 9.15; O, 36.32. Found: C, 54.47; H, 9.51; O, 36.02.

2-Ethyl-2-methyl-1,3-dioxane-5,5-dimethanol (**3d**)
Mp 73–74 °C.

IR (KBr): ν = 721.3, 866.0, 898.8, 1042.8, 1043.4, 1365.5, 2881.5, 2925.8, 2974.0, 3259.5 cm^{-1}.

^{1}H NMR [200 MHz, $(CD_3)_2SO$]: δ = 0.85 (t, 3H, *J* = 7.0 Hz), 1.27 (s, 3H), 1.57–1.69 (m, 2H), 3.33–3.43 (m, 4H), 3.53–3.69 (m, 4H), 4.38–4.52 (m, 2H).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 7.72, 19.80, 30.12, 60.33, 60.79, 61.11, 61.38, 98.55.

MS: *m/z* (%) = 175 (M^+ – 15, 22), 161 (51), 127 (2), 101 (9), 83 (34), 73 (61), 71 (55), 57 (68), 55 (43), 43 (100).

Anal. Calcd for $C_9H_{18}O_4$ (190.2): C, 56.82; H, 9.54; O, 33.64. Found: C, 56.52; H, 9.79; O, 33.69.

2-Methyl-2-(1-methylethyl)-1,3-dioxane-5,5-dimethanol (**3e**)
Mp 76–77 °C.

IR (KBr): ν = 549.7, 771.5, 852.5, 896.8, 1038.2, 1062.5, 1379.0, 1440.7, 2877.6, 2960.0, 3182.3 cm^{-1}.

^1H NMR [200 MHz, $(CD_3)_2SO$]: δ = 0.86 (s, 3H), 0.90 (s, 3H), 1.21 (s, 3H), 1.99 (dd, 1H), 3.28–3.72 (m, 8H), 4.43–4.50 (m, 2H).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 15.46, 16.67, 34.38, 38.66, 60.25, 61.03, 61.22, 100.06.

MS: *m/z* (%) = 189 (M^+ – 15, 5), 161 (17), 141 (2), 119 (2), 101 (3), 87 (9), 83 (10), 71 (15), 55 (10), 43 (100).

Anal. Calcd for $C_{10}H_{20}O_4$ (204.3): C, 58.79; H, 9.87; O, 31.33. Found: C, 58.68; H, 10.15; O, 31.17.

2-Methyl-2-(1,1-dimethylethyl)-1,3-dioxane-5,5-dimethanol (**3f**)
Mp 145–146°C.

IR (KBr): ν = 669.3, 873.7, 1016.4, 1041.5, 1407.9, 2885.3, 2943.2, 3327.0 cm^{-1}.

^1H NMR [200 MHz, $(CD_3)_2SO$]: δ = 0.93 (s, 9H), 1.31 (s, 3H), 3.39 (s, 8H), 4.09–4.31 (m, 2H).

^{13}C NMR [50 MHz, $(CD_3)_2SO$]: δ = 24.65, 45.46, 59.98, 61.17, 61.55.

MS: *m/z* (%) = 203 (M^+ – 15, 13), 161 (39), 119 (5), 101 (20), 88 (6), 83 (27), 71 (31), 57 (71), 43 (100).

Anal. Calcd for $C_{11}H_{22}O_4$ (218.3): C, 60.52; H, 10.16; O, 29.32. Found: C, 60.28; H, 10.41; O, 29.31.

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