THE JOURNAL OF Organic Chemistry

VOLUME 48, NUMBER 8 | APRIL 22, 1983

Lithium Tungsten Dioxide Promoted Claisen–Tishchenko Condensation of Aromatic and Aliphatic Aldehydes[1]

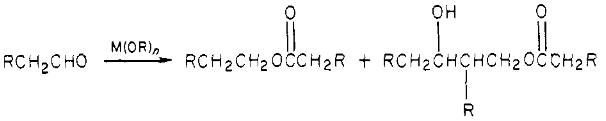
Gilberto M. Villacorta and Joseph San Filippo, Jr.*

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903

Received August 17, 1982

Lithium tungsten dioxide, $LiWO_2$, has been shown to be a useful catalyst for effecting the Claisen–Tishchenko condensation of aldehydes under heterogeneous conditions.

Nearly a century has passed since Claisen[2] discovered the alkoxide-induced condensation of benzaldehyde to benzyl benzoate. Somewhat later, Tishchenko[3] demonstrated that a similar condensation obtains with aliphatic aldehydes. Still later, Nord and co-workers[4] observed that, depending on the basicity of the metal alkoxide, the Claisen–Tishchenko condensation of simple aliphatic aldehydes bearing an α-hydrogen can also lead to glycol monoesters (eq 1). In addition to its considerable industrial importance,[5-11] the Claisen–Tishchenko reaction has recently been proposed to account for the observed reactivity of certain transition-metal formyl complexes[12] and may be a key step in the commercial Fischer–Tropsch process leading to the conversion of carbon monoxide into alkanes, alkenes, and alcohols over heterogeneous metal catalysts.



$$RCH_2CHO \xrightarrow{M(OR)_n} RCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_2R + RCH_2\overset{\overset{OH}{|}}{C}H\underset{\underset{R}{|}}{C}HCH_2O\overset{\overset{O}{\|}}{C}CH_2R \tag{1}$$

Table I. Product Distributions from the Reaction of Benzaldehyde with $LiWO_2$ in THF at 60 °C[a]

PhCHO/ $LiWO_2$ ratio	yield,[b] %			% PhCHO (recovered)
	$PhCO_2CH_2Ph$	PhC(O)-C(O)Ph	$PhCH_2OH$	
1:1	5	16	22	22
2:1	28	7	10	27
5:1	60	4	8	21
10:1	76	trace	5	12
20:1	89 (98)[c]	*d*	<1	8 (<1)[c]

[a] Reaction time 72 h. [b] Yields are based on starting amounts of PhCHO. [c] Yield after 72 h at 75 °C. [d] None detected.

Table II. Production of Benzyl Benzoate in THF as a Function of Temperature[a]

reaction bath temp, °C	% yield[b]	
	ester	PhCHO[b] (recovered)
40	23	54
50	34	47
60	60	21
75	66	15

[a] A 5:1 ratio of PhCHO/$LiWO_2$ was employed; reaction time 72 h. [b] Yields are based on starting amounts of PhCHO.

Past and current procedures for effecting Claisen–Tishchenko condensations have relied primarily on homogeneous promoters. We report here our observations related to the utilization of lithium tungsten(IV) oxide, $LiWO_2$, as an efficient agent for effecting the heterogeneous condensation of aromatic and aliphatic aldehydes.

Results and Discussion

Aromatic Aldehydes. Reaction of benzaldehyde with $LiWO_2$ in anhydrous tetrahydrofuran (THF) produces

---

(1) This work was supported by DOE Contract No. DE-AS05-80ER10662 and NSF Grant No. CHE 80-17045.

(2) Claisen, L. *Chem. Ber* **1887**, *20*, 646.

(3) Tishchenko, W. *Chem. Zentrable.* **1906**, *2*, 1309, 1552.

(4) Kulpinski, M. S.; Nord, F. F. *J. Org. Chem.* **1943**, *8*, 256. Villani, F. J.; Nord, F. F. *J. Am. Chem. Soc.* **1947**, *69*, 2605.

(5) Knopf, R. J.; Theiling, L. F., U.S. Patent 3 367 966 (Cl. 260-494).

(6) Lalk, R. *Pitture Vernici* **1972**, *48*, 55.

(7) Uchida, K.; Masaoka, S., Japanese Kokai 76 74 028 (C. CO9D5/02).

(8) Cerny, J. Ger. Offen. 2 605 794 (Cl. CO8L77/00).

(9) Minuto, M. U.S. Patent 3 803 077 (Cl. 260/30.8R; CO8f).

(10) Blomeyer, F.; Mennicken, G.; Uerdinger, W. Ger. 2 304 893 (Cl. CO9d).

(11) Von Bramer, P. T.; Whitley, M. R. *Off. Plast. Caoutch.* **1966**, *13*, 357.

(12) Hermann, W.; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117 and references therein.

0022-3263/83/1948-1151$01.50/0

Table III. Production of Aromatic Esters from the Reaction of ArCHO with $LiWO_2$ in THF at 60 °C

	% yield			
	ester		ArCHO[b]	
ArCHO	5:1[c]	20:1[c]	5:1[c]	20:1[c]
p-nitrobenzaldehyde	77		21	
benzaldehyde	60	89	21	8
p-tolualdehyde	40	79	48	15
p-anisaldehyde	31	32	60	68

[a] Reaction time 72 h. [b] Yield of recovered ArCHO. [c] Ratio of ArCHO/$LiWO_2$.

Table IV. Product Distribution Observed in the Reaction of RCHO with $LiWO_2$ (20:1) in THF at 40 °C[a]

RCHO	monoester, % yield[b,c]	diester, % yield[b]	% RCHO[b] (recovered)
n-butanal	**1a** + **2a**, 43 (2:1)	**3a**, *d*	*d*
isobutanal	**1b** + **2b**, 55 (2:1)	**3b**, 38[d]	*e*
n-heptanal	**1c** + **2c**, 93 (1.4:1)	**3c**, *d*	2

[a] Reaction time 24 h. [b] Yields are based on starting amounts of RCHO. [c] Numbers in parentheses indicate ratios of **1** and **2**, respectively. [d] None detected. [e] Not determined.

Table V. Effect of Concentration in Reaction of RCHO with $LiWO_2$ in THF at 30 °C[a]

RCHO	RCHO/ $LiWO_2$ ratio	monoester, % yield[b]	diester, % yield[b]
n-butanal	3:1	**1a** + **2a**, 65	**3a**, *c*
	5:1	**1a** + **2a**, 59	**3a**, *c*
	10:1	**1a** + **2a**, 51	**3a**, *c*
	20:1	**1a** + **2a**, 38	**3a**, *c*
isobutanal	20:1	**1a** + **2b**, 50	**3b**, 35
	200:1	**1b** + **2b**, 38	**3b**, *c*

[a] Reaction time 24 h. [b] Yields are based on starting amounts of RCHO. [c] None detected.

Table VI. Effect of Reaction Temperature on Product Distribution

$$\mathrm{RCHO} + \mathrm{LiWO_2}\ (20{:}1) \xrightarrow[24\ \mathrm{h}]{\mathrm{THF}} \text{products}$$

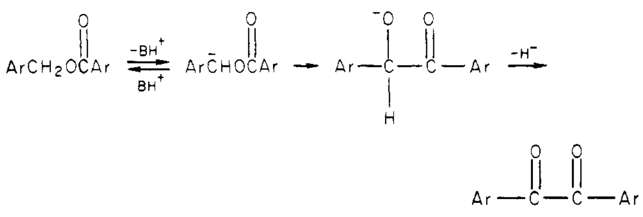
RCHO	temp, °C	monoester, % yield[a]	diester, % yield[a]
n-heptanal	30	**1c** + **2c**, *b*	**3c**, *b*
	40	**1c** + **2c**, 93	**3c**, *b*
n-butanal	30	**1a** + **2a**, 38	**3a**, *b*
	40	**1a** + **2a**, 43	**3a**, *b*
	55	**1a** + **2a**, 46	**3a**, *b*
	75	**1a** + **2a**, 50	**3a**, trace
isobutanal	30	**1b** + **2b**, 50	**3b**, 35
	40	**1b** + **2b**, 55	**3b**, 38
	55	**1b** + **2b**, 55	**3b**, 36

[a] Yields are based on starting amounts of RCHO. [b] None detected.

three products: benzyl alcohol, benzil, and benzyl benzoate. As Table I shows, the distribution of these products is strongly dependent on the ratio of reagents. Thus, a 1:1 ratio results in benzyl alcohol and benzil as the major products. This behavior is dramatically altered when the $PhCHO/LiWO_2$ ratio becomes ≥2:1, whereupon benzyl benzoate becomes the major product. Moreover, an examination of the reaction of various para-substituted benzaldehydes under equivalent conditions (Table III) reveals a reactivity pattern typically associated with reactions involving attack of a nucleophile at an electrophilic benzyl carbon center. The following overall order of reactivity is observed:

$$p\text{-}O_2N > H > p\text{-}CH_3 > p\text{-}CH_3O$$

We explored the possibility that benzil resulted from a Wittig-like rearrangement of benzyl benzoate,[13] as shown below. Specifically, we examined the reaction of benzyl



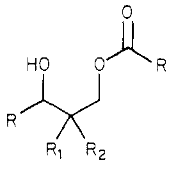
benzoate wiith $LiWO_2$ under typical reaction conditions. The resulting product mixture revealed a small amount (ca. 8%) of benzyl alcohol and benzoic acid (ca. 6%); the remainder of the starting material was recovered; no (<1%) benzil or benzoin was detected.

To determine the fate of the aldehydic hydrogen in the production of benzyl benzoate, the condensation of benzaldehyde-*1-d* was examined. Mass spectral analysis of the resulting product revealed it contained >97% d_2. Taken together with the related ^1H NMR analysis, these results establish that the overall transfer of the aldehydic hydrogen occurs as described in eq 2.

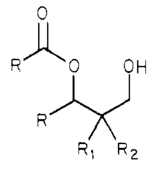
$$2PhCDO \xrightarrow[THF]{LiWO_2} PhCO_2CD_2Ph \tag{2}$$

In an effort to establish the position of the H-transfer step in the sequence of reactions comprising the overall condensation of benzaldehyde to benzyl benzoate, we examined the deuterium isotope effect associated with this reaction. Thus, an equimolar mixture of benzaldehyde and benzaldehyde-*1-d* was allowed to react with $LiWO_2$ under optimum experimental conditions and the subsequent product mixture subjected to isotopic analysis. The results revealed an essentially statistical isotopic distribution from which we conclude that the rupture of the carbon 1–hydrogen bond occurs after the overall rate-determining step.

Aliphatic Aldehydes. In contrast to the reaction of aromatic aldehydes, aliphatic aldehydes bearing at least one α-hydrogen yield products of multiple condensations leading to mixtures of the glycol monoesters **1** and **2**. A



1



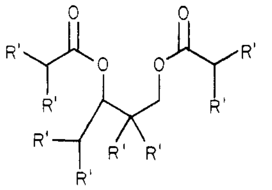
2

a, R = *n*-propyl; R_1 = H; R_2 = ethyl
b, R = isopropyl; R_1 = R_2 = methyl
c, R = *n*-hexyl; R_1 = H; R_2 = *n*-pentyl

number of parameters (Tables IV–VI)) influence the absolute and relative yields of **1** and **2**. For example, higher absolute yields obtain for R = n-C_6H_{13} than for R = n-C_3H_7, while the formation of a third product, the diester **3** which occurs at lower aldehyde-to-catalyst ratios when R′ = CH_3, is completely suppressed at higher aldehyde-

---

(13) Govindan, M.; Pinnick, H. W. *J. Org. Chem.* **1981**, *46*, 5011 and references therein.



3b, R' = CH_3

to-catalyst ratios. Also, in contrast to the reaction of aromatic aldehydes, higher reaction temperatures are distinctly deleterious to improved product yields. Finally, solvent has a significant influence on the course of the reaction of aliphatic aldehydes: curiously condensation does not proceed in ethylene glycol dimethyl ether (DME) or hexamethylphosphoric triamide (HMPA).

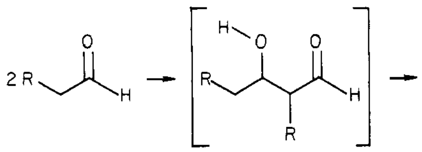
Not unexpectedly, the reaction of 2,2-dimethylpropanal (pivaldehyde) with LiWO$_2$ (eq 3) more closely paralells that

$$2CH_3C(CH_3)_2CHO \xrightarrow[75\ °C,\ 24\ h]{THF} CH_3C(CH_3)_2CH_2O_2CC(CH_3)_3\ (79\%) \quad (3)$$

of the aromatic aldehydes than of aliphatic substrates. However, unlike aromatic aldehydes, condensation in this instance does not obtain at reaction temperatures <70 °C.

The studies reported above reveal the utility of LiWO$_2$ as a catalyst for the condensation of aromatic and aliphatic aldehydes. Thus, the production of Claisen–Tischenko products is generally superior to that reported for other promoters. Moreover, product distribution can be selectively controlled through a judicious choice of reaction conditions.

Available evidence suggests that the mechanism(s) by which aliphatic aldehydes undergo LiWO$_2$-promoted condensation, although unknown in detail, is more complex than the corresponding reaction involving aromatic aldehydes. Still, several conclusions and reasonable speculations can be drawn at this point. Thus, we are in agreement with earlier[3] observations that condensation proceeds via an initial aldol reaction followed by a Claisen–Tishchenko condensation between the resulting aldol product and a third molecule of aldehyde to yield the observed mixture of glycol monoesters (eq 4). Undoubtedly, such transformations involve a multitude of complex equilibria (including transesterifications). Although the mechanism of aliphatic aldehyde condensation must be considered largely speculative at this point, the effectiveness of LiWO$_2$ as a catalyst capable of promoting such reactions is clearly indicated by the present study.



→ 1 and 2 (4)

Experimental Section

General Methods. All glassware was flame dried and allowed to cool under a stream of prepurified nitrogen prior to use. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride. Ethylene glycol dimethyl ether (DME) was distilled from a solution of disodium benzophenone dianion. Hexamethylphosphoric triamide (HMPA) was distilled from sodium in vacuo. Lithium (30% dispersion in mineral oil) was purchased from Lithium Corp. of America and tunsten(IV) oxide (WO$_2$) from Alfa Ventron. The aldehydes were purchased from either Eastman Kodak or Aldrich Chemical Co. and were purified by distillation, except *p*-nitrobenzaldehyde and pivalaldehyde which were used as received. Yields were determined by GLC using the internal standard method with response factors obtained from authentic samples. GLC analyses were carried out on a Varian Model 1400 gas chromatograph equipped with a flame-ionization detector and a Hewlett-Packard Model 3380A recorder–integrator. A variety of 0.125-in. columns was employed. High-performance liquid chromatography (HPLC) analyses were performed on Waters Associates HPLC equipment (M6000A pump and Model 440 UV detector) along with a Hewlett–Packard Model 3380A recorder–integrator. Optimum separation was achieved with a μ-Porasil column by using as an eluant a mixture of 7.5% THF in isooctane.

^{1}H NMR spectra were recorded on a Varian Model T-60 spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (Me$_4$Si). Infrared spectra were recorded on a Perkin-Elmer 727B spectrophotometer either as a liquid film or as KBr pellet samples. Mass spectra data were obtained on a Hewlett-Packard Model 5985 GC/MS spectrometer at 70 eV. ^{13}C NMR spectra were recorded on a Varian Model CFT-20 instrument. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of Lithium Tungten Dioxide (LiWO$_2$). In an argon-filled drybox were placed a 50-mL beaker, a flat spatula, and a 250-mL round-bottomed flask capped with a rubber septum and equipped with a sidearm and a Teflon-coated magnetic stirrer bar. Approximately 3 g of a 30% lithium dispersion in mineral oil was placed in the beaker and washed with 20 mL of dry, olefin-free pentane. By use of the spatula, the lithium was placed on a piece of weighing paper and the pentane allowed to evaporate, after which 0.78 g of dry lithium (112 mmol) was weighed out and placed in the 250-mL flask which was then stoppered with a rubber septum. The flask was removed from the drybox and THF (50 mL), followed by a solution of naphthalene (14.4 g, 112 mmol) in THF (35 mL), was added through a stainless steel cannula by employing a positive pressure of argon. Stirring was commenced, and additional THF (25 mL) was used to rinse the flask previously containing the naphthalene, and this residue was added to the now deep green solution of lithium naphthalide. After 1.5 h of stirring, the resulting solution of lithium naphthalide was transferred to a drybox and filtered through a plug of glass wool into a 250-mL round-bottomed flask charged with 22.0 g (102 mmol) of tungsten(IV) oxide (WO$_2$) and containing a Teflon-coated magnetic stirrer bar. The flask was capped with a rubber septum and removed from the drybox. An additional 50 mL of fresh THF was added to facilitate stirring which was continued for 3–4 h at ambient temperature.

At the end of this period, the contents of the flask were transferred through a stainless steel cannula into four, 60-mL flame-dried, argon-flushed centrifuge tubes, each capped with a rubber septum. After these tubes had been centrifuged for a few minutes, the supernatant from each was discarded, and the deep purple lithium tungsten oxide (LiWO$_2$) was shaken with 40 mL of a 20% solution of naphthalene in THF (to remove residual lithium), followed by repeated rinsings with THF until the supernatant solution remained clear. The remaining solvent was removed by cannula, and the LiWO$_2$ was dried under a stream of dry nitrogen. The isolated yield was 18–20 g. Lithium tungsten oxide can be stored indefinitely in the absence of moisture.

Reaction of Aromatic Aldehydes with Lithium Tungsten Oxide. The following is a general procedure used for the reaction of benzaldehyde, *p*-tolualdehyde, and *p*-anisaldehyde with LiWO$_2$.

In a drybox, 0.300 g (1.35 mmol) of LiWO$_2$ was placed in a 15-mL flask equipped with a Teflon-coated magnetic stirrer bar and capped with a rubber septum. After removal of the flask to the bench top, THF (5 mL) was added by syringe along with the desired amount of aldehyde and an appropriate internal standard. At this point a noticeable transformation in the catalyst ensued. Where the LiWO$_2$ was originally a solid, it was now replaced by a black liquid cushioned from the clear solvent above it by a deep yellow film. When stirred, the mixture appeared homogeneous. This transformation appeared to be crucial to the success of the catalyst, for when it failed to occur, the resulting product yields were insignificant. Thus, it is recommended that an initial addition of aldehyde be made without stirring and that stirring be commenced after the initial transformation has occurred (3–5 min). The remainder of the aldehyde may then be added dropwise. A 6-in. condenser capped with a rubber septum was then attached to the flask under a flush of dry nitrogen. The flask was placed in an oil bath and stirred for 72 h under a static head of nitrogen, following which the flask was cooled to room temperature and quenched with 0.2 mL of a saturated aqueous ammonium chloride solution. After the residual solid material was allowed to precipitate from solution, the contents of the flask were centrifuged. The yellow supernatant solution was transferred to a 25-mL Erlenmeyer flask, dried ($MgSO_4$), and filtered prior to analysis by GLPC.

Reaction of *p*-Nitrobenzaldehyde with $LiWO_2$. Into a flame-dried, nitrogen-flushed, 15-mL flask equipped with a Teflon-coated magnetic stirrer bar was quickly placed the desired amount of *p*-nitrobenzaldehyde. The flask was then transferred to a drybox where 0.300 g (1.35 mmol) of $LiWO_2$ was added. After the flask was capped with a rubber septum, it was removed to the bench top and freshly distilled THF (5 mL) introduced by syringe. A condenser was quickly attached, the flask was flushed with nitrogen before it was placed into a 60 °C oil bath, and the contents were stirred under a static head of nitrogen.

After the designated reaction time, the reaction mixture was allowed to cool, and an appropriate amount of internal standard was added followed by 0.2 mL of distilled water. After ca. 5 min, 5 mL of a 1:1 (v/v) solution of dry methylene chloride and tetrahydrofuran was added to the flask to dissolve the precipitated product mixture. The residual solid material was allowed to settle and the solution decanted into a 125-mL Erlenmeyer flask. The reaction pot was rinsed with 10-mL portions of the solvent until all of the yellow solid was removed (50–60 mL total). The combined rinsings and reaction mixture were then filtered through a glass-wool plug covered with ca. 25–30 mg of $MgSO_4$. The resulting filtrate was concentrated to dryness in vacuo. A small amount of the solid reaction mixture was dissolved in 4 mL of a 1:1 (v/v) solution of CH_2Cl_2/THF and analyzed by HPLC.

Pure *p*-nitrobenzyl *p*-nitrobenzoate was obtained by recrystallization of the reaction mixture from 95% ethanol. A HPLC analysis showed the absence of contaminants and spectral data confirmed the structure of the ester, mp 167–168 °C (lit.[14] mp 168 °C).

Reaction of Aliphatic Aldehydes with $LiWO_2$. The following procedure is typical of those used for the reaction of *n*-butanal, isobutanal, *n*-heptanal, and 2,2-dimethylpropanal with $LiWO_2$.

$LiWO_2$ (0.300 g, 1.35 mmol) was placed in a 25-mL round-bottomed flask containing a Teflon-coated magnetic stirrer bar. The flask was capped with a rubber septum and removed to the bench top where THF (5 mL), the desired amount of aldehyde, and a suitable GLC internal standard were added by syringe. In those instances where the desired reaction temperature exceeded 40 °C, the rubber septum was replaced by a 6-in. condenser which was capped with a rubber septum. The reaction flask was heated with stirring in an oil bath. (Unlike the corresponding reaction with aromatic aldehydes, $LiWO_2$ does *not* undergo a similar initial visual transformation when treated with an aliphatic aldehyde.) The resulting mixture was allowed to cool to ambient temperature, and aliquots were drawn out and centrifuged. The supernatant solution was analyzed by GLC without further treatment.

Isolation of Aliphatic Reaction Products. For purposes of identification, the glycol monoesters were isolated from their respective reaction mixtures by fractional distillation through a 36-in. Teflon annular spinning-band column. In the case of isobutyraldehyde, a distillation of the glycol diester was not attempted. Instead, this product was isolated by preparative gas chromatography with a 0.25-in. × 6 ft column of 10% SE-30 on Chromosorb P. The product of the pivalaldehyde reaction, products from the aromatic aldehydes (except *p*-nitrobenzaldehyde), and the base hydrolysis products of the glycol monoesters were all isolated for identification in a similar manner.

2-Ethyl-1,3-hexanediol monobutyrate (1a and 2a): bp 87 °C (0.2 torr)[lit.[15] bp 71–72 °C (0.03 torr)]; ^1H NMR ($CDCl_3$) 0.96 (t, J = 7 Hz, 9 H), 1.52 (m, 9 H), 2.32 (t, J = 7 Hz, 2 H), 2.85 (br, 1 H); IR (**1a** and **2a**, neat) 3420 (br, s), 2900 (s), 1719 (s), 1462 (m), 1380 (m), 1260 (m), 1185 (s), 1098 and 1010 (m), 860 (w), 783 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 173 (1.8), 143 (12.5), 89 (100.0), 71 (71.5), 56 (29.1), 55 (18.1).

2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (1b and 2b): bp 71–72 °C (0.4 torr) [lit.[16] of 124–126 °C (13 torr)]; ^1H NMR ($CDCl_3$) 0.87–1.28 (series of d, J = 7 Hz, 12 H), 0.96 (s, 6 H), 2.0 (m, 1 H), 2.63 (m, 1 H); IR (**1b** and **2b**, neat) 2960 (s), 2865 (m), 1720 (s), 1468 (s), 1388 (m), 1340 (w), 1265 (m), 1200 (s), 1162 (s), 1120 (w), 1080 (m), 981 (m), 919 (w), 765 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 173 (6.1), 143 (6.9), 98 (26.8), 89 (30.2), 83 (38.1), 71 (100.0), 56 (29.3), 55 (20.2).

2-Pentyl-1,3-nonanediol monoheptanoate (1c and 2c): bp 176–177 °C (0.35 torr) [lit.[15] bp 139–140 °C (0.1 torr)]; ^1H NMR ($CDCl_3$) 0.90 (m, 9 H), 1.35 (br, 27 H), 2.35 (t, J = 7 Hz, 2 H), 3.15 (br, 1 H); IR (**1c** and **2c**, neat) 3446 (br, m), 2935 (s), 2860 (s), 1730 (s), 1465 (m), 1380 (w), 1240 (m), 1175 (s), 1110 (w), 1039w), 731 (w) cm^{-1}.

2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (3): ^1H NMR ($CDCl_3$) 0.85–1.26 (series of d, J = 7 Hz, 18 H), 1.0 (s, 6 H), 2.0 (m, 1 H), 3.86 (s, 2 H), 4.8 (d, J = 3 Hz, 1 H); IR (neat) 2955 (s), 2870 (m), 1730 (s), 1469 (m), 1385 (m), 1340 (m), 1260 (m), 1195 and 1160 (s), 1075 (m), 962 (w), 760 and 753 (w) cm^{-1}.

2-Ethyl-1,3-hexanediol: ^1H NMR ($CDCl_3$) 0.95 (m, 6 H), 1.43 (m, 7 H), 3.34 (br, 2 H), 3.8 (m, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) 11.78, 12.33, 14.09, 18.37, 19.04, 19.58, 21.66, 35.72, 38.08, 46.41, 46.61, 63.82, 64.51, 74.94, 75.26; IR (neat) 3330 (br, s), 2960 (s), 2870 (s), 1465 (s), 1380 (m), 1225 (w), 1120 (m), 1079 (m), 1043 (s), 980 (m), 850 and 833 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 129 (0.7), 103 (25.9), 85 (18.5), 73 (64.4), 71 (17.6), 57 (35.0), 56 (100.0), 55 (66.9).

2,2,4-Trimethyl-1,3-pentanediol: ^1H NMR ($CDCl_3$) 0.93 (s, 6 H), ca. 1.0 (pair of d, J = 7 Hz, 6 H), 1.95 (m, 1 H), 3.46 (m, 5 H); IR (neat) 3350 (br, s), 2970 (s), 2880 (s), 1470 (s), 1391 and 1370 (m), 1277 (w), 1122 and 1120 (w), 1050 (s), 995 and 974 (m), 895 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 103 (14.3), 85 (21.9), 73 (32.1), 71 (28.6), 59 (13.6), 57 (49.5), 56 (100.0), 55 (42.5).

Reaction of Benzaldehyde-*1-d*. Benzaldehyde-*1-d* was prepared by the method of Seebach.[17] Deuterium incorporation in the starting material and the reaction products was determined by GC/MS and ^1H NMR spectrometry.

Belzaldehyde-*1-d* (>99% d_1, 0.7223 g, 6.75 mmol) was allowed to react with $LiWO_2$ (0.30 g, 1.35 mmol) in freshly distilled THF for 72 h under an atmosphere of dry nitrogen at reflux. The resulting reaction mixture was worked up as previously described.

A sample of the resulting ester was isolated by preparative gas chromatography with a 0.25 × 72 in. column of 10% SE-30 on Chromosorb P. Its ^1H NMR spectrum revealed the absence of the characteristic methylene proton resonance at 5.4 ppm. Mass sectral analysis revealed the following isotopic distribution: >97% d_2 and <3% d_1.

In a subsequent experiment, equivalent amounts of benzaldehyde-*1-d* and benzaldehyde were allowed to react with the catalyst in freshly distilled THF for 55 h at 60 °C. The reaction mixture was worked up in the usual manner and the sample analyzed immediately by GC/MS.

Registry No. **1a**, 18618-89-8; **1b**, 77-68-9; **1c**, 49562-88-1; **2a**, 18618-91-2; **2b**, 18491-15-1; **2c**, 55109-59-6; **3b**, 6846-50-0; $LiWO_2$, 69701-22-0; WO_2, 12036-22-5; 4-$O_2NC_6H_4CH_2O_2CC_6H_4NO_2$-4, 3481-11-6; $C_6H_5CH_2O_2CC_6H_5$, 120-51-4; 4-$CH_3C_6H_4CH_2O_2CC_6H_4CH_3$-4, 21086-87-3; 4-$CH_3OC_6H_4CH_2O_2CC_6H_4OCH_3$-4, 24318-43-2; $CH_3C(CH_3)_2CH_2O_2CC(CH_3)_3$, 5340-26-1; PhC(O)C(O)Ph, 134-81-6; $PhCH_2OH$, 100-51-6; $PhCO_2CD_2Ph$, 85029-27-2; lithium naphthalide, 27939-69-1; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; *p*-anisaldehyde, 123-11-5; *p*-nitrobenzaldehyde, 555-16-8; *n*-butanal, 123-72-8; isobutanal, 78-84-2; *n*-heptanal, 111-71-7; 2,2-dimethylpropanal, 630-19-3; 2-ethyl-1,3-hexanediol, 94-96-2; 2,2,4-trimethyl-1,3-pentanediol, 144-19-4; benzaldehyde-*1-d*, 3592-47-0.

---

(14) Lyons, E.; Reid, E. *J. Am. Chem. Soc.* **1917**, *39*, 1735.

(15) Pochini, A.; Salerno, G.; Ungaro, R., *Synthesis*, **1975**, 164.

(16) Schwenk, U.; Becker, A. *Justus Liebigs. Ann. Chem.* **1972**, *756*, 162.

(17) Seebach, D.; Erickson, B. W.; Singh, G. *J. Org. Chem.* **1966**, *31*, 4303.