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1,3-Dichloropropene as a Source of the 1,3-Dianion Derived from Propene: Synthesis of Unsaturated 1,5-Diols and Dihydropyrans[1]

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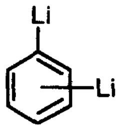
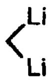
Abstract: The reaction of 1,3-dichloropropene (**1**, *ca.* 1/1 *Z/E* mixture) with an excess of lithium powder and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB, 5 mol %) in the presence of an electrophile [Me_2CO, Et_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, Bu^tCHO, Me_3SiCl] in THF at 0°C affords, after hydrolysis with water, the expected unsaturated 1,5-diols **3** as a *Z/E* mixture or disilane (*E*)-**4**. Treatment of isolated compounds (*Z*)-**3** with 85% phosphoric acid gives the expected dihydropyrans **5**.

INTRODUCTION

Polilithiated intermediates[2] are interesting reagents in synthetic organic chemistry due to their capability to give directly polyfunctionalised molecules by reaction with electrophilic reagents. In general, they are of difficult access because of their high instability even at low temperatures. Three main ways have been used for the preparation of this type of reactive intermediates: (a) direct deprotonation, (b) halogen-lithium exchange, and (c) mercury- and tin-lithium transmetallation[3]. Concerning the most general methodology involving lithiation of halogenated starting materials (route b), the main difficulty to be overcome is how to avoid either elimination processes or Wurtz-type coupling reactions. Recently we could prepare very reactive dianions synthons by combining an arene-catalysed lithiation[4] at low temperature with carrying out the process under Barbier-type reaction conditions. With this methodology we could use dichlorinated compounds such as dichlorobenzenes[5a], dichloromethane[5b], 2,3-dichlorpropene[5c], 3-chloro-2-(chloromethyl)propene[5d,e] and 1,2- or 1,4-dichlorobutenes[5f] as synthons of the corresponding dilithiated species **I**-**V**, respectively[6]. In the present paper we apply this methodology employing 1,3-dichloropropene as the synthon of the corresponding dianionic intermediate.



I



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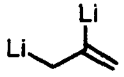

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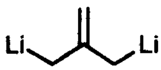
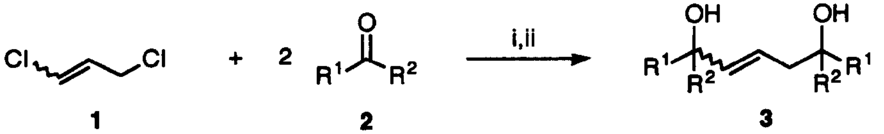


IV

V

RESULTS AND DISCUSSION

The reaction of commercially available 1,3-dichloropropene **1** (*ca.* 1/1 diastereoisomeric mixture) with an excess of lithium powder [1/7 molar ratio (theoretic 1/4 molar ratio)] and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 1/0.05 molar ratio, 5 mol %[7]) in the presence of a carbonyl compound **2** in THF at 0°C led, after hydrolysis with water, to the corresponding *Z/E* mixture of unsaturated 1,5-diols **3** (Scheme 1 and Table 1). Both diastereoisomers were easily separated by flash chromatography (Table 1, footnotes b and c) except in the case of product **3a**, where the corresponding (*E*)-diastereoisomer decomposed during the chromatographic separation (Table 1, entry 1). On the other hand, when pivalaldehyde (**2e**) was used as electrophilic reagent, the expected mixture of diastereoisomers correponding to each *Z*- and *E*-**3e** was isolated (Table 1 entry 5 and footnote d).



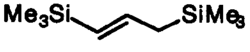
Scheme 1. ***Reagents and conditions:*** i, Li powder, DTBB cat. (5 mol %), THF, 0°C, 1 h; ii, H_2O.

Table 1. Preparation of Compounds **3**

Entry	Carbonyl compound **2** No.	R^1	R^2	Product **3**[a] No.	Yield (%)[b]	*Z/E* ratio[c]
1	**2a**	Me	Me	**3a**	72	1.3/1
2	**2b**	Et	Et	**3b**	60	1.6/1
3	**2c**	$-[CH_2]_4-$		**3c**	67	1.9/1
4	**2d**	$-[CH_2]_5-$		**3d**	50	1.3/1
5	**2e**	Bu^t	H	**3e**	64	1.1/1[d]

[a] All isolated products **3** were >95% pure (300MHz ^1H NMR and GLC). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**. [c] The *E/Z* ratio was deduced from the crude product **3** by ^1H NMR and was essentially the same (≤5%) for the isolated diastereoisomers after flash chromatography except for compound **3a** (see text); the corresponding stereochemistry was assigned on the basis of their spectroscopic data (see Experimental). [d] A mixture of diastereoisomers corresponding to each (*Z*)- and (*E*)-**3e** was obtained: (*Z*)-**3e**, 8/3; (*E*)-**3e**, 7/5 (300 MHz ^1H NMR).

When the same process described in Scheme 1 was carried out using chlorotrimethylsilane as electrophile, the corresponding product **4** with *E*-geometry ($J_{CH=CH}$=18.5 Hz; n.O.e. experiments) was the only reaction product isolated.

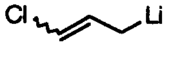


4 (76%)

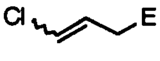
It is worthy to note that the process described above for preparing compounds **3** has to be carried out under Barbier-type reaction conditions: the two-steps procedure (catalytic lithiation followed by reaction with the electrophile), even at -90°C, gave only volatile products (C_3 and C_6 hydrocarbons; GLC) resulting from the decomposition of the mono or dilithiated intermediates initially formed (see below).

One experiment was performed in order to study the relationship between the stereochemistry of the starting materials and the isolated products. Thus, *ca.* 2/1 and 1/2 mixtures of diastereoisomers **1** were obtained by careful distillation (vigreux column) of the commercially mixture (*ca.* 1/1) and submitted separately to the reaction shown in Scheme 1, using 3-pentanone as electrophile: in both cases *the same* Z/E *diastereoisomeric ratio was isolated*, so demonstrating that the stereochemistry of the final products **3** is independent of the geometry of the starting materials **1**. The same experiment with chlorotrimethylsilane as electrophilic component gave also the (*E*)-derivative **4** as the only reaction product, leading to the same conclusion as above.

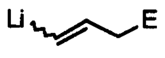
Concerning a possible mechanistic pathway, we think that the first lithiation yields probably to the intermediate **VI**, which can follow two different routes: (a) reaction with the electrophile present in the reaction media to give **VII**, followed by tandem lithiation to **VIII**, and final coupling with a second molecule of the electrophile affording the reaction product **3** or **4**, or (b) a new lithiation of **VI** yields the dilithiopropane **IX**, which traps two molecules of electrophile giving the corresponding reaction products. Although species of the type **IX** or **X** have been formulated in the lithiation of propene[8] or by calculations[9], respectively, we think that the most probable pathway involves the intermediates **VI**-**VIII**: the main argument in favour of that is the necessity of carrying out the reaction in the presence of the electrophile (Barbier-type conditions). In the absence of this reagent intermediate **VI**, which is very unstable, suffers elimination (α, β or γ) or coupling reactions, or abstracts a proton from the reaction media[10].



VI



VII



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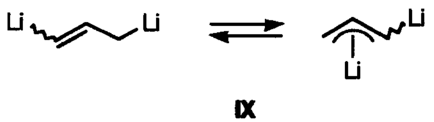
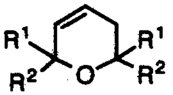


IX

X

Finally, we studied the obtention of dihydropyrans by dehydration of diols **3**. Thus, while isolated compounds (*E*)-**3** gave an intractable mixture by treatment with 85% phosphoric acid, the corresponding products (*Z*)-**3a-d** yielded, under the same reaction conditions, the expected substituted dihydropyrans **5**.



5a: $R^1=R^2=Me$ (99%)
5b: $R^1=R^2=Et$ (93%)
5c: R^1-$R^2=[CH_2]_4$ (75%)
5d: R^1-$R^2=[CH_2]_5$ (92%)

From the results described here we conclude that commercially available 1,3-dichloropropene is an adequate precursor for the synthon $^-CH_2CH=CH^-$ in the reaction with carbonyl compounds or chlorotrimethylsilane under Barbier-type reaction conditions. Moreover, the obtained unsaturated 1,5-diols in the *Z* form (once separated by flash chromatography) can be easily transformed into substituted dihydropyrans **5** under acidic conditions.

EXPERIMENTAL PART

General.- M.p.s are uncorrected and were measured on a Reichert thermovar apparatus. IR spectra were determined with a Pye Unicam SP3-200 spectrometer. ^1H and ^{13}C NMR spectra were recorded in a Bruker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (*J*) are measured in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. MS (EI) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m HP-1 capillary column (0.2 mm diam, 0.33 μm film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=275°C, T_{column}=60°C (3 min) and 60-270°C (15°C/min); retention times (t_r) are given under these conditions. Thin layer chromatography (TLC) was carried out on Scheleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Microanalyses were performed by the Microanalyses Service of the University of Alicante. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Solvents were dried by standard procedures[11]. Lithium powder (Strem), starting chlorinated material **1** as well as DTBB and the electrophiles used were commercially available (Aldrich, Fluka), the last ones being dried by conventional methods[11].

***Lithiation of 1,3-Dichloropropene under Barbier-type Reaction Conditions. Isolation of Compounds* 3 *and* 4. *General Procedure*.**- To a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol) in THF (5 ml) was slowly added (*ca.* 1 h) a solution of 1,3-dichloropropene (Aldrich; 1/1 *Z*/*E* mixture; 2 mmol) and the corresponding electrophile (4 mmol) in THF (5 ml) at 0°C. Then the reaction mixture was hydrolysed with water (10 ml) and successively extracted with diethyl ether (2x10 ml) and ethyl acetate (2x10 ml). The organic layer was dried over Na_2SO_4 and evaporated (15 Torr) giving a residue, which was purified by flash chromatography (silica gel, hexane/ethyl acetate) affording pure compounds **3** or **4**. Yields and products ratio are given in Table 1. Analytical, physical and spectroscopic data follow.

(Z)-*2,6-Dimethyl-3-hepten-2,6-diol* [(*Z*)-**3a**]: t_r=6.99 min, R_f=0.27 (hexane/ethyl acetate: 3/2), mp 73-74°C ($CHCl_3$); ν_{max} (film) 3280 (OH), 1650, 710 (HC=C), 1180 and 1120 cm^{-1} (CO); δ_H 1.25, 1.34 (12H, 2s, 4xCH_3), 2.53 (2H, dd, *J*=8.5, 0.9, CH=CHCH_2), 2.65, 3.40 (2H, 2 br s, 2xOH), 5.44 (1H, dt, *J*=11.8, 8.5, CH=C*H*CH_2) and 5.65 (1H, dt, *J*=11.8, 0.9, C*H*=CHCH_2); δ_C 29.55 (2C), 31.5 (2C) (4xCH_3), 40.25 (C=CCH_2), 70.45, 71.85 (2xCO), 124.0 and 140.2 (C=C); *m*/*z* 143 (M^+-CH_3, 1%), 82 (54), 67 (43), 59 (59), 43 (100) and 41 (27) (Found: C, 67.3; H, 11.5. $C_9H_{18}O_2 \cdot 0.1H_2O$ requires C, 67.54; H, 11.46).

(Z)-*3,7-Diethyl-4-nonen-3,7-diol* [(*Z*)-**3b**]: t_r=11.19 min, R_f=0.67 (hexane/ethyl acetate: 3/2), mp 40-42°C ($CHCl_3$); ν_{max} (film) 3320 (OH), 1650, 700 (HC=C), 1170 and 1160 cm^{-1} (CO); δ_H 0.87, 0.90 (12H, 2t, *J*=7.5, 7.4, 4xCH_2CH_3), 1.50 (8H, m, 4xC$H_2$$CH_3$), 2.40, 3.50 (2H, 2 br s, 2xOH), 2.48 (2H, d, *J*=8.5, CH=CHCH_2), 5.40 (1H, d, *J*=12.1, C*H*=CHCH_2) and 5.52 (1H, dt, *J*=12.1, 8.5, CH=C*H*CH_2); δ_C 7.95 (2C), 8.05 (2C) (4x$CH_2$$CH_3$), 30.95 (2 C), 34.55 (2C) (4x$CH_2$$CH_3$), 35.25 (C=C$CH_2$), 74.7, 77.2 (2xCO), 125.0 and 137.9 (C=C); *m*/*z* 185 (M^+-C_2H_5, 17%), 158 (12), 167 (80), 149 (44), 111 (17), 110 (100), 109 (12), 99 (10), 97 (14), 95 (44), 87 (31), 81 (74), 69 (26), 67 (10), 57 (80), 55 (12), 45 (19), 43 (19) and 41 (17) (Found: C, 69.8; H, 12.45. $C_{13}H_{26}O_2 \cdot 0.5H_2O$ requires C, 69.91; H, 12.18).

(E)-*3,7-Diethyl-4-nonen-3,7-diol* [(*E*)-**3b**]: t_r=11.31 min, R_f=0.40 (hexane/ethyl acetate: 3/2), mp 52-53°C (diethyl ether); ν_{max} (film) 3400 (OH), 1665, 975 (HC=C), 1145 and 1035 cm^{-1} (CO); δ_H 0.86, 0.88 (12H, 2t, *J*=7.5, 7.5, 4xCH_2CH_3), 1.50 (10H, m, 4xC$H_2$$CH_3$, 2xOH), 2.20 (2H, dd, *J*=7.2, 0.8, CH=CHCH_2), 5.48 (1H, dt, *J*=15.6, 0.8, C*H*=CHCH_2) and 5.64 (1H, dt, *J*=15.6, 7.2, CH=C*H*CH_2); δ_C 7.7 (2C), 7.85 (2C) (4x$CH_2$$CH_3$), 30.9 (2C), 33.1 (2C) (4xC$H_2$$CH_3$), 41.35 (C=C$CH_2$), 74.35, 75.4 (2xCO), 123.7 and 139.15 (C=C); *m*/*z* 213 (M^+-1, 0.1%), 167 (13), 149 (14), 110 (100), 99 (34), 95 (21), 87 (49), 81 (40), 69 (14), 57 (38), 45 (14) and 43 (11) (Found: C, 70.1; H, 12.4. $C_{13}H_{26}O_2 \cdot 0.5H_2O$ requires C, 69.91; H, 12.18).

(Z)-*1,3-Bis-(1-hydroxycyclopentyl)propene* [(*Z*)-**3c**]: t_r=12.71 min, R_f=0.48 (hexane/ethyl acetate: 3/2), mp 79-80°C ($CHCl_3$); ν_{max} (film) 3240 (OH), 3010 (HC=C), 1200 and 995 cm^{-1} (CO); δ_H 1.50-1.90 (16H, m, 8xring CH_2), 2.63 (2H, dd, *J*=8.4, 1.2, CH=CHCH_2), 2.60, 3.30 (2H, 2 br s, 2xOH), 5.52 (1H, dt, *J*=11.7, 8.4, CH=C*H*CH_2) and 5.75 (1H, dt, *J*=11.7, 1.2, C*H*=CHCH_2); δ_C 23.45 (2C), 23.55 (2C), 39.6 (2C), 41.85 (2C) (8xring CH_2), 39.05 (C=CCH_2), 81.5, 81.9 (2xCO), 126.0 and 139.1 (C=C); *m*/*z* 192 (M^+-H_2O, 2%), 163 (11), 111 (17), 108 (72), 98 (40), 97 (11), 95 (19), 94 (20), 93 (80), 91 (15), 85 (31), 83 (18), 81 (16), 80 (11), 79 (40), 77 (17), 69 (18), 68 (17), 67 (70), 65 (12), 57 (22), 56 (13), 55 (100), 53 (18), 43 (48), 42 (29), and 41 (89) (Found: C, 73.8; H, 10.8. $C_{13}H_{22}O_2$ requires C, 74.24; H, 10.54).

(E)-*1,3-Bis-(1-hydroxycyclopentyl)propene* [(*E*)-**3c**]: t_r=12.71 min, R_f=0.23 (hexane/ethyl acetate: 3/2), mp 66-

67°C (CHCl$_3$); ν_{max} (film) 3350 (OH), 3030, 970 (HC=C), 1190, 1080 cm^{-1} (CO); δ_H 1.55-1.90 (18H, m, 8xring CH$_2$, 2xOH), 2.32 (2H, m, CH=CHC*H*$_2$) and 5.77 (2H, m, CH=CH); δ_C 23.6 (2C), 23.85 (2C), 39.4 (2C), 40.5 (2C) (8xring CH$_2$), 44.2 (C=C*C*H$_2$), 81.65, 81.75 (2xCO), 122.95 and 140.3 (C=C); *m/z* 192 (M$^+$-H$_2$O, 6%), 174 (10), 163 (27), 135 (12), 111 (39), 108 (100), 98 (63), 95 (19), 94 (20), 93 (86), 91 (14), 85 (23), 83 (16), 81 (11), 80 (11), 79 (32), 77 (11), 69 (11), 67 (43), 57 (10), 55 (35), 43 (13) and 41 (25) (Found: C, 73.6; H, 10.9. C$_{13}$H$_{22}$O$_2$·0.1H$_2$O requires C, 73.61; H, 10.55).

(Z)-*1,3-Bis-(1-hydroxycyclohexyl)propene* [(*Z*)-**3d**]: t_r=14.51 min, R_f=0.58 (hexane/ethyl acetate: 3/2), mp 81-82°C (CHCl$_3$); ν_{max} (film) 3300 (OH), 1650, 710 (HC=C) and 1060 cm^{-1} (CO); δ_H 1.25-1.80 (20H, m, 10xring CH$_2$), 2.40, 3.10 (2H, 2 br s, 2xOH), 2.53 (2H, d, *J*=8.6, CH=CHC*H*$_2$), 5.47 (1H, dt, *J*=11.9, 8.6, CH=C*H*CH$_2$) and 5.67 (1H, d, *J*=11.9, C*H*=CHCH$_2$); δ_C 22.2 (2C), 22.3 (2C), 25.4, 25.75, 37.7 (2C), 39.5 (2C), (10xring CH$_2$), 39.2 (C=C*C*H$_2$), 71.3, 72.55 (2xCO), 124.25 and 139.95 (C=C); *m/z* 238 (M$^+$, 1%), 123 (10), 122 (100), 107 (21), 99 (12), 93 (14), 81 (23), 79 (18) and 55 (15) (Found: C, 75.6; H, 11.0. C$_{15}$H$_{26}$O$_2$ requires C, 75.58; H, 10.99).

(E)-*1,3-Bis-(1-hydroxycyclohexyl)propene* [(*E*)-**3d**]: t_r=14.51 min, R_f=0.20 (hexane/ethyl acetate: 3/2), mp 126°C (CHCl$_3$); ν_{max} (film) 3300 (OH), 1660, 955 (HC=C) and 1060 cm^{-1} (CO); δ_H 1.20-1.80 (22H, m, 10xring CH$_2$, 2xOH), 2.18 (2H, d, *J*=6.7, CH=CHC*H*$_2$), 5.65 (1H, d, *J*=15.5, C*H*=CHCH$_2$) and 5.75 (1H, dt, *J*=15.5, 6.7, CH=C*H*CH$_2$); δ_C 22.15 (2C), 22.2 (2C), 25.5, 25.75, 37.4 (2C), 38.1 (2C) (10xring CH$_2$), 45.2 (C=C*C*H$_2$), 71.15, 71.4 (2xCO), 122.55 and 142.05 (C=C); *m/z* 220 (M$^+$-H$_2$O, 0.1%), 122 (100), 107 (18), 99 (16), 81 (19) and 79 (10) (Found: C, 75.3; H, 11.0. C$_{15}$H$_{26}$O$_2$ requires C, 75.58; H, 10.99).

(Z)-*2,2,8,8-Tetramethyl-4-nonen-3,7-diol* -[(*Z*)-**3e**]: t_r=10.90 min, R_f=0.60 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3380 (OH), 3010, 1650, 790 (HC=C), 1070 and 1000 cm^{-1} (CO); δ_H 0.91, 0.93 [36H, 2s, 4x(CH$_3$)$_3$C], 2.11, 2.16 (2H, 2m, 2xCH=CHC*H*H), 2.20, 2.40 (2H, 2m, 2xCH=CHCH*H*), 2.80 (4H, br s, 4xOH), 3.20, 3.29 (2H, 2m, 2xCH$_2$C*H*OH), 4.01, 4.04 (2H, 2d, *J*=8.6, 7.9, 2xCH=CHC*H*OH) and 5.56-5.78 (4H, 2m, 2xCH=CH); δ_C (major diastereoisomer) 25.5 (3C), 25.75 (3C) [2x(*C*H$_3$)$_3$C], 30.0 (C=C*C*H$_2$), 34.35, 34.9 [2x (CH$_3$)$_3$*C*], 73.7, 78.35 (2xCO), 131.05 and 132.25 (C=C); *m/z* 196 (M$^+$-H$_2$O, 0.1%), 157 (20), 139 (28), 121 (21), 110 (29), 95 (60), 87 (48), 83 (17), 71 (100), 70 (29), 69 (41), 57 (78), 55 (15), 45 (11), 43 (28) and 41 (43) (Found: C, 69.6; H, 12.4. C$_{13}$H$_{26}$O$_2$·0.5H$_2$O requires C, 69.91; H, 12.18).

(E)-*2,2,8,8-Tetramethyl-4-nonen-3,7-diol* [(*E*)-**3e**]: t_r=11.11 min, R_f=0.53 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3320 (OH), 1660, 970 (HC=C), 1070 and 1000 cm^{-1} (CO); δ_H 0.91, 0.92 [36H, 2s, 4x(CH$_3$)$_3$C], 1.85 (4H, br s, 4xOH), 1.98 (2H, m, 2xCH=CHC*H*H), 2.35 (2H, m, 2xCH=CHCH*H*), 3.25 (2H, m, 2xCH$_2$C*H*OH), 3.72, 3.74 (2H, 2d, *J*=5.5, 6.2, 2x CH=CHC*H*OH) and 5.55-5.80 (4H, 2m, 2xCH=CH); δ_C (major diastereoisomer) 25.75 (6C) [2x(*C*H$_3$)$_3$C], 34.65, 34.7 [2x(CH$_3$)$_3$*C*], 35.15 (C=C*C*H$_2$), 78.55, 80.85 (2xCO), 130.95 and 133.05 (C=C); *m/z* 196 (M$^+$-H$_2$O, 0.2%), 157 (26), 139 (20), 121 (14), 110 (33), 95 (47), 87 (55), 83 (12), 71 (100), 70 (20), 69 (31), 57 (42), 43 (13) and 41 (23) (Found: C, 72.8; H, 12.0. C$_{13}$H$_{26}$O$_2$ requires C, 72.84; H, 12.22).

(E)-*1,3-Bis(trimethylsilyl)propene* (**4**)[12]: t_r=5.15 min, R_f=0.72 (hexane); ν_{max} (film) 3040, 1585, 685 (HC=C), 1250 and 840 cm^{-1} (SiCH$_3$); δ_H -0.02, 0.01 [18H, 2s, 2x(CH$_3$)$_3$Si], 1.61 (2H, dd, *J*=7.8, 1.3, CH=CHC*H*$_2$), 5.41 (1H, dt, *J*=18.4, 1.3, C*H*=CHCH$_2$) and 6.00 (1H, dt, *J*=18.4, 7.8, CH=C*H*CH$_2$); δ_C -2.0 (3C), -0.95 (3C) [2x(CH$_3$)$_3$Si], 28.35 (C=C*C*H$_2$), 128.05 and 143.65 (C=C); *m/z* 187 (M$^+$+1, 1%), 186 (M$^+$, 3), 98 (40), 83 (13), 73 (100), 59 (12), 45 (30) and 43 (16).

*Dehydration of Compounds (Z)-***3***. Isolation of Dihydropyrans* **5***. General Procedure.-* To a solution of the corresponding diol (*Z*)-**3** (1 mmol) in hexane (40 ml) was added 85% phosphoric acid (3 or 4 drops). After *ca.* 15 min stirring the reaction mixture was decanted and the organic layer was evaporated (60 Torr). The resulting residue was purified by flash chromatography (silica gel, pentane) (products **5b-d**) or distilled (product **5a**) to give pure products **5**. Yields are given in the text. Analytical, physical and spectroscopic data follow.

*2,2,6,6-Tetramethyl-5,6-dihydro-*2H*-pyrane* (**5a**): t_r=3.15 min, R_f=0.43 (hexane/ethyl acetate: 19/1); ν_{max} (film) 3060, 1660, 710 (HC=C), 1165 and 1010 cm^{-1} (CO); δ_H 1.24 (12H, 2s, 4xCH_3), 1.94 (2H, m, CH=CHCH_2) and 5.67 (2H, m, CH=CH); δ_C 29.45 (2C), 30.15 (2C) (4xCH_3), 35.65 (C=C$\mathit{C}H_2$), 70.4, 71.55 (2xCO), 120.7 and 134.0 (C=C); *m/z* 141 (M^++1, 1%), 140 (M^+, 5), 126 (11), 125 (100), 107 (39), 83 (40), 82 (49), 81 (13), 67 (63), 55 (11), 43 (73), and 41 (16).

*2,2,6,6-Tetraethyl-5,6-dihydro-*2H*-pyrane* (**5b**): t_r=8.83 min, R_f=0.66 (hexane/ethyl acetate: 19/1); ν_{max} (film) 3020, 1660, 700 (HC=C), 1050 and 1005 cm^{-1} (CO); δ_H 0.83, 0.84 (12H, 2t, *J*=7.5, 7.5, 4xC$\mathit{H}_3$$CH_2$), 1.51 (8H, m, 4x$CH_3C\mathit{H}_2$), 1.90 (2H, dd, *J*=4.6, 1.8, CH=CHCH_2), 5.57 (1H, dt, *J*=10.4, 1.8, C*H*=CHCH_2) and 5.81 (1H, dt, *J*=10.4, 4.6, CH=C*H*CH_2); δ_C 8.05 (2C), 8.1 (2C) (4xCH_3), 30.2 (C=C$\mathit{C}H_2$), 32.1 (2C), 32.4 (2C), (4x$CH_3$$\mathit{C}H_2$), 75.8, 74.7 (2xCO), 122.45 and 131.4 (C=C); *m/z* 169 (M^+-C_2H_3, 1%), 168 (M^+-C_2H_4, 11), 167 (M^+-C_2H_5, 100), 149 (30), 109 (13), 97 (12), 95 (11), 81 (12) and 57 (39) (Found: M^+-C_2H_5, 167.1436. $C_{11}H_{19}O$ requires M, 167.1436).

6-Oxadispiro[4.1.4.3]-12-tetradecene (**5c**): t_r=10.02 min, R_f=0.56 (hexane/ethyl acetate: 19/1); ν_{max} (film) 3020, 1655, 700 (HC=C), 1070 and 1040 cm^{-1} (CO); δ_H 1.56, 1.78 (16H, 2m, 8xring CH_2), 2.03 (2H, dd, *J*=3.6, 1.2, CH=CHCH_2), 5.66 (1H, dt, *J*=10.2, 1.2, C*H*=CHCH_2) and 5.72 (1H, dt, *J*=10.2, 3.6, CH=C*H*CH_2); δ_C 23.0 (2C), 23.7 (2C), 38.4 (2C), 40.4 (2C) (8xring CH_2), 34.15 (C=C$\mathit{C}H_2$), 81.6, 82.5 (2xCO), 121.15 and 133.35 (C=C); *m/z* 193 (M^++1, 5%), 192 (M^+, 30), 174 (13), 164 (10), 163 (54), 149 (20), 135 (17), 131 (10), 121 (13), 112 (15), 111 (100), 108 (28), 107 (25), 98 (88), 97 (13), 95 (33), 94 (27), 93 (53), 91 (25), 83 (18), 82 (13), 81 (19), 80 (14), 79 (54), 77 (26), 69 (10), 67 (42), 66 (10), 65 (12), 55 (35), 53 (11), and 41 (22) (Found: M^+, 192.1501. $C_{13}H_{20}O$ requires M, 192.1514).

7-Oxadispiro[5.1.5.3]-14-hexadecene (**5d**): t_r=12.40 min, R_f=0.68 (hexane/ethyl acetate: 19/1); ν_{max} (film) 3010, 1650, 695 (HC=C), 1040 and 1010 cm^{-1} (CO); δ_H 1.22-1.82 (20H, m, 10xring CH_2), 1.93 (2H, m, CH=CHCH_2) and 5.69 (2H, m, CH=CH); δ_C 22.25 (2C), 22.4 (2C), 25.8, 26.3, 38.0 (2C), 38.75 (2C) (10xring CH_2), 35.3 (C=C$\mathit{C}H_2$), 71.2, 71.8 (2xCO), 120.85 and 133.5 (C=C); *m/z* 222 (M^++2, 1%), 221 (M^++1, 10), 220 (M^+, 79), 205 (22), 178 (14), 177 (100), 163 (18), 149 (20), 125 (30), 122 (45), 121 (44), 112 (30), 109 (13), 108 (27), 107 (46), 97 (15), 95 (30), 93 (24), 91 (22), 83 (18), 81 (33), 80 (13), 79 (50), 77 (23), 69 (12), 67 (22), 55 (31), 53 (11), and 41 (23) (Found: M^+, 220.1822. $C_{15}H_{24}O$ requires M, 220.1827).

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