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ADDITION OF 1-ACETOXY- and 1-TRIMETHYLSILYLOXY-BUTA-1,3-DIENES WITH α-OXO ESTERS; ENE AND DIELS-ALDER REACTIONS.

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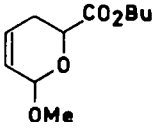
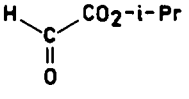
The addition of 1-acetoxy and 1-trimethylsilyloxy-3-methylbuta-1,3-diene with isopropyl glyoxylate and diethyl oxomalonate under thermal (110°C) and high-pressure (10 kbar) conditions was studied. It was found that silyloxy diene yielded only Diels-Alder adducts whereas acetoxy diene gave unsaturated esters. To rationalise the formation of the latter an ene addition was postulated as the first step of the reaction. High pressure conditions favoured Diels-Alder reaction. Small values of the anomeric effect of the $OSi(Me)_3$ (relative to OAc or OR) was noted.

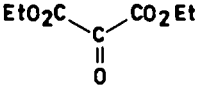
The utility of Diels-Alder reaction of dienophiles with activated carbonyl group for dihydropyran ring construction is amply documented[1]. The efficiency of the operation, which results from the regio- and stereo- selectivity of the addition rendered it an object of extensive studies in search of new methodologies for the total synthesis of natural products comprising a pyran moiety[2]. Thus for example 4+2 addition of butyl glyoxylate with 1-methoxybuta-1,3-diene readily furnished butyl 6-methoxy-3,6-dihydro-2H-pyran-2-carboxylate (1) [3] which in turn was used as a substrate in the total synthesis of monosaccharides[4].



(1)

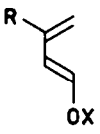


(2)

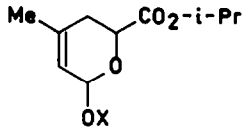


(3)

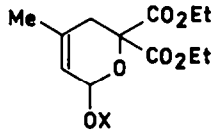
In connection with another project we required an analogue of 1 with methyl group at C-4 and easily removable protections of C-6 oxygen atom. For its synthesis we attempted the Diels-Alder reaction of isopropyl glyoxylate (2) with 1-acetoxy-3-methylbuta-1,3-diene (4). Instead of the desired adduct 8 an unsaturated oxo ester 12 was obtained.



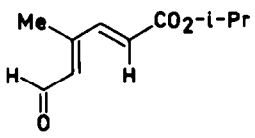
(4) R = Me, X = Ac
(5) R = Me, X = $Si(Me)_3$
(6) R = H, X = Ac
(7) R = H, X = $Si(Me)_3$



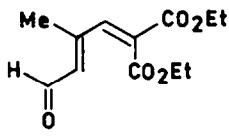
(8) X = Ac
(9) X = $Si(Me)_3$



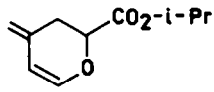
(10) X = Ac
(11) X = $Si(Me)_3$



(12)



(13)



(14)

An unexpected course of the reaction induced us to examine on one hand another dienophile with active carbonyl group - diethyl oxomalonate (3) and on the other a diene 5 with C-1 oxygen function protected as trimethylsilyl ether. For comparison purpose reactions of dienes 6 and 7 without C-3 methyl group with 2 (Scheme 2) were also examined.

Results and Discussion

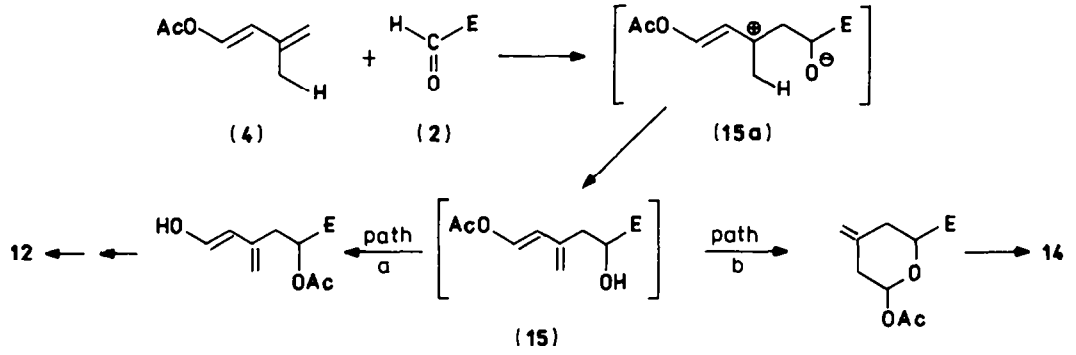
Both oxo esters 2 and 3 were reacted with 1.25 equiv. of a diene in toluene solution. In one series of experiments the reactions were carried out in refluxing toluene (bath temperature 120°C) and in the other under the high-pressure (10 kbar) at ambient temperature.

The structures of all obtained compounds were deduced unambigously from their analytical and spectroscopic data (Table 1 and 2).

1-Acetoxy-3-methylbuta-1,3-diene (4)

Oxo esters 2 and 3 in thermal reactions with 4 gave unsaturated oxo esters 12 and 13, respectively. Structures of the latter were immediately apparent from their ^1H NMR spectra which revealed the absence of the acetoxy group and the appearance of the aldehydic proton (δ 10.28 and 9.80) as well as three (for 12) or two (for 13) vinylic protons. Along with the ester 12 small amount of a side-product 14 was isolated. Its structure was evident from the ^1H NMR spectrum, which indicated the presence of four vinylic protons, two of which located at the terminal methylene group (δ 4.62 bs, 4.80 bs). Reported in the literature reactions of the diene 4 with different dienophiles yielded in all cases exclusively products of 4+2 cycloaddition[5]. The presence of 12 and 13 as well as 14 could be accounted for by the formation and subsequent

transformations of the not isolated ene adduct **15** (Scheme 1). Formation of the latter is a consequence of the propensity of carbonyl dienophiles for taking, besides cycloaddition, an ene route. E.g. the Lewis acid catalyzed reaction between unsubstituted isoprene and chloral gave predominantly ene adduct[6] whereas in the thermal reactions a mixture of ene and cycloadduct with predominance of the latter was obtained[7]. It could be presumed that diene **4** reacts with oxo ester **2** possibly *via* zwitterionic intermediate **15a** or close to it transition state to give a nondetected ene adduct **15**. The latter in a sequence of reactions, probably catalyzed by traces of adventitious acid undergoes either transacetylation followed by the proton shift and the elimination of acetic acid (Scheme 1, path a) to give **12** or cyclization and then elimination of acetic acid (Scheme 1, path b) to afford **14**.



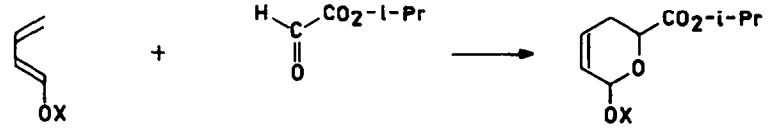
E = CO_2-isopropyl

Scheme 1

In the analogous fashion **13** can arise from diene **4** and diethyl oxomalonate (3)

We expected that by applying high-pressure conditions the reaction of 1-acetoxy-3-methylbuta-1,3-diene (**4**) with carbonyl dienophiles can be coaxed into following cycloaddition route (Scheme 1, path b) leading to the dihydropyran moiety. In fact we have been fully succesfull in case of diethyl oxomalonate (3) which under 10 kbar pressure at r.t. afforded cleanly the desired adduct **10**. Reaction of isopropyl glyoxylate (2) under these conditions led to a mixture which was not further examined. However the ^{1}H NMR spectra of the crude product suggested the presence of dihydropyran **8** as a main component.

To confirm the involvment of the C-3 methyl group in diverting the course of the reaction from the Diels-Alder path by making the ene route possible, the reaction of isopropyl glyoxylate (2) with 1-acetoxybuta-1,3-diene (**6**) was carried out. Indeed in this case thermal and high-pressure conditions alike gave only 4+2 adduct **16**, as a mixture of *cis* and *trans* isomers (Scheme 2).



(6) X = Ac (2) (16) X = Ac

(7) X = $Si(Me)_3$ (17) X = $Si(Me)_3$

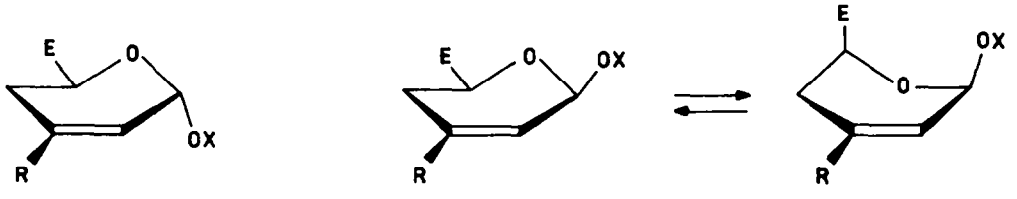
Scheme 2

1-Trimethylsilyloxy-3-methylbuta-1,3-diene (5)

In contrast to the diene 4 1-trimethylsilyloxy-3-methylbuta-1,3-diene (5) reacted smoothly with oxo esters 2 and 3 yielding dihydropyrans 9 and 11, respectively. In the case of compound 9 the preference of endo addition could be inferred (^1H NMR) from the ratio of *cis/trans* isomers amounting to 1:1.34 and 1:1.45, respectively for thermal and high-pressure reaction. No products which could be derived from the ene addition have been obtained showing that once acetyl group is substituted by trimethylsilyl one cycloaddition deceidedly prevails.

Configuration and conformation of dihydropyrans 9, 16 and 17.

Dihydropyrans 9, 16 and 17 analogues of 2,3-unsaturated glycosides occur in half-chair conformations[8] . Position of the conformational equilibrium depend on the steric and stereoelectronic interactions[9] .For *trans*-16 the equatorial position of CO_2-i-Pr and the anomeric effect of the pseudoaxial acetoxy group favour conformer $^0H_2$ (Scheme 3).



$^0H_2$ $^0H_2$ $^2H_0$

trans-9 R = Me, X = $Si(Me)_3$ *cis*-9

trans-16 R = H, X = Ac *cis*-16

trans-17 R = H, X = $Si(Me)_3$ *cis*-17

E = CO_2-isopropyl

Scheme 3

This is confirmed by the coupling constants values J_{23}=9.05 Hz, $J_{23'}$=6.40 Hz and J_{56}= 3.00 Hz (Table 2) indicating axial and pseudoequatorial position of H-2 and H-6 respectively. For the isomer *cis*-16 in which stabilization of the conformer $^2H_0$ due to the anomeric effect is opposed by the 1,3-diaxial interaction of CO_2-i-Pr and OAc groups an equilibrium between $^2H_0$ and $^0H_2$ should be possible. Similar coupling constants values: J_{23} = 5.58 Hz and $J_{23'}$= 5.92 Hz as well as J_{34} = 3.79 Hz and $J_{3',4}$ = 4.12 Hz

values indicate that the conformations $^{0}H_{2}$ and $^{2}H_{0}$ are nearly evenly populated (Scheme 3) These results are in accord with those found for analogous dihydropyrans with C-6 alkoxy substituent instead of OAc[8]. Consequently the assignment of *trans-cis* configuration of **16** was based on the H-2 coupling constants values.

A different conformational picture emerged for dihydropyrans **9** and **17** with $OSi(Me)_3$ substituent at C-2. Coupling constants values of H-2 (*trans*-**9**: J_{23} = 11.39 Hz, $J_{23'}$ = 4.04 Hz; *trans*-**17**: J_{23}= 9.51 Hz, $J_{23'}$ = 5.80 Hz; *cis*-**9**: J_{23} = 10.59 Hz $J_{23'}$ = 4.04 Hz; *cis*-**17**: J_{23} = 10.31 Hz, $J_{23'}$ = 3.92 Hz) revealed in each case its axial position, indicating that for both compounds not only *trans* but also *cis* isomer appears in $^{0}H_{2}$ conformation.

The change of the conformational equilibrium in case of *cis*-**9** and *cis*-**17** as compared to *cis*-**16** and other analogous dihydropyrans[8] results from the smaller anomeric effect of the $OSi(Me)_3$ group [9a] than that of Ac or OR groups. Hence 1,3-diaxial interaction of CO_2-i-Pr and $OSi(Me)_3$ shifts the equilibrium towards $^{0}H_{2}$ conformer. Since the configuration of compounds **9** and **17** could not be deduced from their ^{1}H NMR spectra the assignment is based on the equilibration experiments assuming *trans* isomers to be thermodynamically preferred.

Experimental

Melting points were determined on a Kofler hot stage microscope and are uncorrected. Boiling points refer to the air bath temperature. IR spectra were measured with Specord N-60 as films or in $CHCl_3$ solution. ^{1}H NMR spectra were recorded with Bruker MSL 300 and AM 500 and Varian EM 360 spectrometers in $CDCl_3$ solutions using TMS as internal standard. Column chromatography was carried out on Merck Kieselgel 60 (230-400 Mesh) with ethyl ether - petroleum ether mixture. TLC was performed on silica gel precoated plates.

Starting materials.

Isopropyl glyoxylate (**2**)[10], b.p. 34-36°C/18 Torr, diethyl oxomalonate (**3**)[11] b.p. 102-103°C/15 Torr, 1-acetoxybuta-1,3-diene (**6**)[12] b.p. 42-45°C/10 Torr, 1-acetoxy-3-methylbuta-1,3-diene (**4**) [13] b.p. 55-60°C/20 Torr, 1-trimethylsilyloxybuta-1,3-diene (**7**)[14] b.p. 53-55°C/25 Torr, 1-trimethylsilyloxy-3-methylbuta-1,3-diene (**5**)[14] b.p. 52-60°C/20 Torr, were obtained according to literature procedures and were distilled immediately before use. High-pressure reactions were carried out at ambient temperature in the piston-cylinder type apparatus[15]. The pressure inside the working volume was measured by a calibrated manganine coil with an accuracy of ca 0.1 kbar.

General Procedure for the Thermal Addition.

A mixture of 8 mmoles of an oxo ester (**2** or **3**) and 10 mmoles of a diene was dissolved in 5 ml of dry toluene which contained several crystals of hydroquinone. The mixture was heated under the atmosphere of nitrogen on the oil bath at 120°C for 3 hrs. Then the solvent was removed on the rotary evaporator and the residue

chromatographed on the silica gel column, eluted with ethyl ether - petroleum ether 15 : 85 mixture. Homogenous (TLC) products were distilled bulb-to-bulb under reduced pressure.

General Procedure for the High-Pressure Addition.

A stoppered teflon vessel (ca 5 ml volume) containing the reaction mixture prepared as in the thermal experiment was placed in the cylinder of the high-pressure apparatus filled with pentane, pressurized to 10 kbar and left for 20-24 hrs. After decompression the reaction mixture was worked up as described above. Yields and analytical data for the compounds obtained in thermal and high-pressure reactions are collected in Table 1.

Table 1

Substrates	Reaction Condition *)	Product	Yield %	B.p. °C/Torr
2 + 4	T	12 **)	48	110/0.2
2 + 5	T	9	65	100/0.15
2 + 5	P	9	58	100/0.15
3 + 4	T	13	42	110/0.15
3 + 4	P	10	54	110/0.2
3 + 5	T	11	85	110/0.2
2 + 6	T	16	50	100/0.2
2 + 6	P	16	22	100/0.2
2 + 7	T	17	71	85/0.1
2 + 7	P	17	60	85/0.1

Product *)	Molecular formula	Analyses % Calcd. C	H	Found C	H
12 T	$C_{10}H_{14}O_3$	65.91	7.74	65.98	7.65
9 T	$C_{13}H_{24}O_4Si$	57.32	8.88	56.98	8.92
9 P	$C_{13}H_{24}O_4Si$	57.32	8.88	57.12	8.80
13 T	$C_{12}H_{16}O_5$	59.99	6.71	60.09	7.01
10 P	$C_{14}H_{20}O_7$	55.94	6.71	55.85	6.79
11 T	$C_{15}H_{26}O_6Si$	54.52	7.93	54.49	7.91
16 T	$C_{11}H_{16}O_5$	57.89	7.07	57.66	7.06
16 P	$C_{11}H_{16}O_5$	57.89	7.07	57.46	7.26
17 T	$C_{12}H_{22}O_4Si$	55.78	8.58	55.54	8.72
17 P	$C_{12}H_{22}O_4Si$	55.78	8.58	55.62	8.85

*) T - thermal (110°C), P - high pressure (10 kbar).

**) Column chromatography afforded small amount of 14, characterised only by its ^1H NMR spectrum.

Table 2

IR and ^{1}H NMR data for adducts 9 - 17

Isopropyl *trans*-4-methyl-6-(trimethylsilyloxy)-3,6-dihydro-2H-pyran-2-carboxylate (*trans*-9): IR (film): ν_{max} 1756, 1732(>C=O), 1680(C=C) cm^{-1}; ^{1}H NMR (300 MHz): δ 0.18 (s, 9H, Si(CH_3)$_3$), 1.28 (d, J=6.28Hz, 6H, 2xCH_3), 1.75 (s, 3H, =C-CH_3), 1.95-2.39 (m, 2H, H-3, H-3'), 4.50 (dd, J_{23}=11.39Hz, $J_{23'}$=4.04Hz, H-2), 5.12 (sep, J=6.24Hz, O-CH<), 5.36-5.49 (m, 2H, H-5,H-6);

Isopropyl *cis*-4-methyl-6-(trimethylsilyloxy)-3,6-dihydro-2H-pyran-2-carboxylate (*cis*-9); IR (film): ν_{max} 1756, 1732(>C=O), 1680(C=C) cm^{-1}; ^{1}H NMR (300 MHz): δ 0.20 (s, 9H, Si(CH_3)$_3$), 1.27 (d, J=6.28Hz, 6H, 2xCH_3), 1.73 (s, 3H, =C-CH_3), 1.95-2.39 (m, 2H, H-3, H-3'), 4.24 (dd, J_{23}= 10.59Hz, $J_{23'}$=4.04Hz, H-2), 5.08 (sep J=6.24Hz, 1H, O-C<-H), 5.36-5.49 (m, 2H, H-5, H-6).

Diethyl 6-acetoxy-4-methyl-3,6-dihydro-2H-pyran-2,2-dicarboxylate (10): IR (film): ν_{max} 1750(C=O), 1695(C=C), 1230(C-O) cm^{-1}; ^{1}H NMR (60 MHz): δ 1.28 (t, J=7.0Hz, 6H, 2xCH_3), 1.85 (s, 3H, =C-CH_3), 2.00 (s, 3H, $COCH_3$), 1.80-2.30 (m, 2H, H-3, H-3'), 4.25 (q, J=7.0Hz, 4H, 2xOCH_2), 5.47 (bs, 1H, H-5), 6.45 (bs, 1H, H-6).

Diethyl 4-methyl-6-(trimethylsilyloxy)-3,6-dihydro-2H-pyran-2,2-dicarboxylate (11): IR (film) ν_{max} 1750(C=O), 1680(C=C), 1260(C-O), 1175(C-O) cm^{-1} ; ^{1}H NMR (300 MHz): δ 0.18 (s, 9H, Si(CH_3)$_3$), 1.26 (t, J=7.11Hz, 6H, 2xCH_3), 1.78 (bs, 3H, =C-CH_3), 2.36 (d, $J_{33'}$=17.13Hz, 1H, H-3), 2.64 (d, $J_{33'}$=17.13Hz, 1H, H-3,), 4.23 (q, J=7.15Hz, 2H, OCH_2), 4.28 (q, J=7.15Hz, 2H, OCH_2), 5.37 (m, 1H, H-6), 5.54 (m, 1H, H-5).

Isopropyl 4-methyl-6-oxohex-2,4-dienoate (12): IR (film): ν_{max} 1760, 1740, 1650, 1605 cm^{-1}; ^{1}H NMR (300 MHz): δ 1.30(d, J=6.26Hz, 6H, 2xCH_3), 2,12(d, J=1.13Hz 3H, =C-CH_3), 5.13 (sep, J=6.26Hz, 1H, O-C<-H), 6.08 (bd, J_{56}=7.98Hz, 1H, H-5), 6.22 (d, J_{23}=15.62Hz, 1H, H-2), 8.19 (d, J=15.63Hz, 1H, H-3), 10.28 (d, J_{56}=7.98Hz, 1H, H-6).

Diethyl 3-methyl-5-oxopent-1,3-diene-1,1-dicarboxylate (13): IR (film): ν_{max} 1755, 1745, 1730(>C=O), 1690(>C=O), 1680(C=C) cm^{-1}; ^{1}H NMR (60 MHz): δ 1.27 (t, J=7.0Hz, 3H, CH_3), 1.30(t, J=7.0Hz, 3H, CH_3), 2.10(bs, 3H, =C-CH_3), 4.20 (q, J=7.0Hz, 2H, O-CH_2), 4.27(q, J=7.0Hz, O-CH_2), 5.98(d, J_{34}=8.0Hz, 1H, H-3), 7.68(bs, 1H, H-2), 9.80(d, J_{34}=8.0Hz, 1H, H-4).

Isopropyl 4-methylene-3,4-dihydro-2H-pyrancarboxylate (14): ^{1}H NMR (300 MHz): δ 1.27 (d, J=6.23Hz, 6H, 2xCH_3), 2.64-2.80 (m, 2H, H-3, H-3'), 4.54 (dd, J_{23}=8.78Hz, $J_{23'}$=4.33Hz, 1H, H-2), 4.62 (bs, 1H, =C-H, H-7), 4.80 (bs, 1H, H-7,), 5.11 (sep, J=6.26Hz, 1H, O-C<-H), 5.44(d, J_{23}=6.01Hz, 1H, H-5), 6.49 (d, J=5.98Hz, 1H, H-6).

Isopropyl *trans*-6-acetoxy-3,6-dihydro-2H-pyran-2-carboxylate (*trans*-16). IR (film): ν_{max} 1760, 1740(C=O), 1655(C=C), 1235(C-O) cm^{-1}; ^{1}H NMR (500 MHz): δ 1.28 (d, J=6.28Hz, 3H, CH_3), 1.29 (d, J=6.28Hz, 3H, CH_3) 2.08 (s, 3H, $COCH_3$), 2.32-2.43(m, 2H, H-3, H-3'), 4.49(dd, J_{23}=9.05Hz, $J_{23'}$=6.39Hz, 1H, H-2), 5.13 (sep, J=6.28Hz, 1H, OCH<) 5.81 (dm, J=10.0Hz, 1H, H-4), 6.15 (m, 1H, H-5), 6.41 (dm, J=3.0Hz, 1H, H-6).

Isopropyl *cis*-acetoxy-3,6-dihydro-2H-pyran-2-carboxylate (*cis*-16). IR (film): ν_{max} 1760, 1740(C=O), 1655(C=C), 1235(C-O) cm^{-1}; ^{1}H NMR (500 MHz):

δ 1.27 (d, J=6.28Hz, 3H, CH_3), 1.28 (d, J=6.28Hz, 3H, CH_3), 2.11 (s, 3H, $COCH_3$), 2.40 (dddt, $J_{33'}$ =17.70Hz, J_{23}= 5.58Hz, J_{34}= 3.79Hz, J= 2.30Hz, 1H, H-3), 2.54 (dddt, $J_{33'}$=17.70Hz, $J_{23'}$=5.92Hz, $J_{3'4}$=4.12Hz, J=2.10Hz, 1H, H-3,), 4.47 (t, J=5.69Hz, 1H, H-2), 5.07 (sep, J=6.28Hz, 1H, O-C<-H), 5.71 (dq, J_{45}=10.23Hz, J=2.05Hz, 1H, H-5), 6.15 (dtd, J_{45}=10.27Hz, J=4.07Hz, J=1.25Hz, 1H, H-4), 6.35 (m, 1H, H-6).

Isopropyl *trans*-6-(trimethylsilyloxy)-3,6-dihydro-2H-pyran-2-carboxylate (*trans*-17): *IR (film):* ν_{max} 1760, 1740(C=O), 1650(C=C), 1130, 1070(C-O) cm^{-1}; ^1H NMR (500 MHz): δ 0.14 (s, 9H, $Si(CH_3)_3$), 1.23 (d, J= 6.26Hz, 3H, CH_3), 1.24 (d, J=6.26Hz, 3H, CH_3), 2.20-2.29 (m, 2H, H-3, H-3'), 4.44 (dd, $J_{23'}$=9.51Hz, $J_{23'}$=5.80Hz, 1H, H-2), 5.06 (sep, J=6.26Hz, 1H, OC<-H), 5.40 (dm, J_{56}=2.89Hz, 1H, H-6), 5.70 (dm, J_{45}=10.6Hz, 1H H-5), 5.84-5.92(m,1H, H-4).

Isopropyl *cis*-6-(trimethylsilyloxy)-3,6-dihydro-2H-pyran-2-carboxylate (*cis* - 17): IR (film): ν_{max} 1765, 1740(C=O), 1650(C=C), 1180, 1075(C-O)cm^{-1}; ^1H NMR (500 MHz): δ 0.16 (s, 9H, $Si(CH_3)_3$), 1.22(d, J=6.28Hz, 3H, CH_3), 1.23 (d, J=6.28Hz, 3H, CH_3), 2.18 (dm, $J_{33'}$=17.44Hz, 1H, H-3), 2.34 (ddq, $J_{33'}$= 17.44Hz, $J_{23'}$=10.43Hz, J=2.67Hz, 1H, H-3'), 4.24 (dd, J_{23}=10.31Hz, $J_{23'}$=3.92Hz, 1H, H-2), 5.03 (sep, J=6.28Hz, 1H, OCH<), 5.44 (tt, J=2.76Hz, J=1.20Hz, 1H, H-6), 5.62 (dtt, J_{45}=10.18Hz, J=1.48Hz, J=1.20Hz, 1H, H-5), 5.84-5.88 (m,1H,H-4).

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