Lewis Acid-Catalyzed Hetero-Diels–Alder Reactions of Methyl 2-Oxo-3-alkenoates with Alkenes

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Lewis acid-catalyzed cycloadditions of 4-substituted methyl 2-oxo-3-butenoates and -3-pentenoates with alkenes took place with high regio- and stereoselectivities to afford substituted 6-methoxycarbonyl-3,4-dihydro-2*H*-pyrans in good to moderate yields. None of the ene products were produced. Similar reactions of methyl 3-phenyl-2-oxo-3-butenoate with alkenes afforded both the corresponding 3,4-dihydro-2*H*-pyrans and a dimeric cycloadduct of the diene component. The regio- and stereoselectivities of the present inverse-electron-demand cycloadditions indicated that the reactions proceeded through a concerted exo transition state.

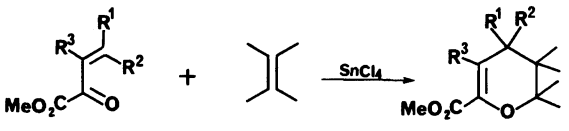
Inverse electron demand hetero-Diels–Alder reactions of 1-oxa-1,3-dienes (α,β-unsaturated carbonyl compounds) with enol ethers have become a promising strategy in the syntheses of polyfunctional compounds,[1] because the reactions can construct a C–C bond and a C–O bond with satisfactory regio- and stereoselectivities. Recent examples have demonstrated that the reactions are of potential value in the syntheses of carbohydrates[2—5] and bicyclic acetals.[6—8] However, the low diene reactivity of 1-oxa-1,3-dienes has restricted the choice of dienophiles. Thus, in most of the cycloadditions of 1-oxa-1,3-dienes, enol ethers,[2,4,9,10] enediol diethers,[11] or ketene acetals[12] have been employed as dienophiles. Even with electron-rich dienophiles, simple 1-oxa-1,3-dienes were not sufficiently reactive, so that reactions at high temperatures[13] or under high pressures[14] were employed to accomplish the reactions in satisfactory yields. In selected instances, the modification of 1-oxa-1,3-diene structures by introducing hetero atoms or electron-withdrawing substituents at the C-3 and/or C-4 positions of the dienes has been shown to increase the rates of the cycloadditions.[1] However, little is known about the cycloadditions of 1-oxa-1,3-dienes bearing a C-2 electron-withdrawing group.[15—18] Boger and Robarge[18] have reported that methyl 4-methoxy- and 4-phenyl-2-oxo-3-butenoates reacted thermally with enol ethers and ketene acetals to give substituted 6-methoxycarbonyl-3,4-dihydro-2*H*-pyrans. This paper concerns the regio- and stereoselective cycloaddition of methyl 2-oxo-3-alkenoates **1** with simple alkenes catalyzed by tin(IV) chloride.[19]

Although numbers of cycloadditions of 1-oxa-1,3-dienes with electron-rich dienophiles have been documented,[1] only a few examples have been reported for those with simple alkenes. Thus, Smith, Norton, and Ballard[20] have reported that thermal reactions of acrylaldehyde with 1-hexene and 2-methylpropene took place to give 2-alkyl-3,4-dihydro-2*H*-pyrans, albeit in poor yields. Highly reactive quinonemethides were reported to react with 2-methylpropene to produce the corresponding 2*H*-1-benzopyrans.[21] Likewise, the cycloadditions of (arylmethylene)malonaldehyde with 2-methylpropene and cyclohexene,[22] and of 3-methyl-2-butenoyl cyanide with 2-methylpropene[17] have also been reported. Recently, Tietze and Kiedrowski[23] described an intramolecular hetero-Diels–Alder reaction of an alkylidene Meldrum's acid to afford a tricyclic cycloadduct. Similar intramolecular cycloadditions of 2,6-dimethyl-2,7-octadienal,[24] and of methyl 4-[2-(3-methyl-2-butenyloxy)phenyl]-2-oxo-3-butenoate[25] leading to bicyclic dihydropyrans were recently reported.

In the presence of tin(IV) chloride, methyl 4-phenyl-2-oxo-3-butenoate (**1a**) reacted with simple alkenes to give substituted 4-phenyl-6-methoxycarbonyl-3,4-dihydro-2*H*-pyrans **2a**—**e** in good to moderate yields (Scheme 1). The reactions did not take place without the catalyst. The reaction of **1a** with cyclohexene yielded a chlorocyclohexane derivative **3** as well as the expected bicyclic adduct **2f**. However, **1a** was found to react as a dienophile in the reaction with 2-methyl-1,3-butadiene to give a cyclohexene derivative **4**. The results are tabulated in Table 1.

With 1-hexene, **1a** afforded a *trans*-2-butyldihydropyran derivative **2a**, but no 3-butyldihydropyran was produced at all (Entry 1). Similarly, with 2-methylpropene a 2,2-dimethyldihydropyran derivative **2b** was obtained as a sole product (Entry 2). Thus, the reaction of **1a** with 1-alkenes showed high regioselectivity.[26]

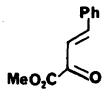
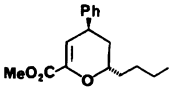
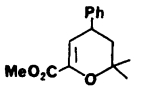
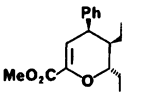
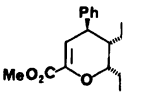
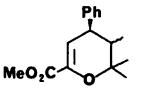
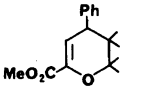
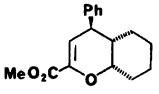
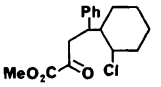
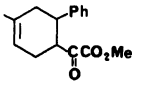
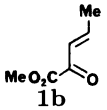
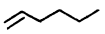
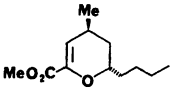
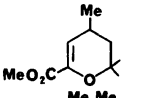
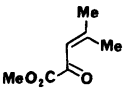
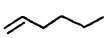
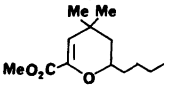
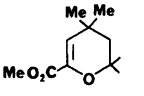
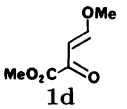
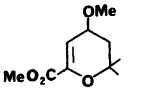
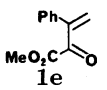
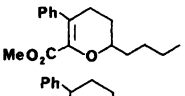
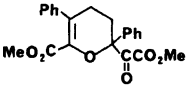
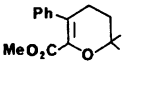
The stereochemistry of the cycloadducts **2a,c,f** was determined by inspecting the observed proton–proton coupling constants (J values) of the ^{1}H NMR spectra of the cycloadducts. The configuration of each cyclo-



	R^1	R^2	R^3
1a	Ph	H	H
b	Me	H	H
c	Me	Me	H
d	MeO	H	H
e	H	H	Ph

Scheme 1.

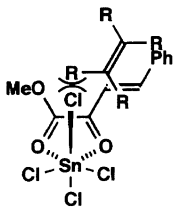
Table 1. Tin(IV) Chloride-Catalyzed Diels–Alder Reactions of Methyl 2-Oxo-3-alkenoates **1** with Alkenes[a)]

Entry	Diene	Dienophile	Products and Yields/%[b)]
1	 **1a**		 **2a** (63.3)[c)]
2	**1a**		 **2b** (84.9)[d)]
3	**1a**		 *trans*-**2c** (34.3)[e)]
4	**1a**		 *cis*-**2c** (19.6)[f)]
5	**1a**		 **2d** (92.8) [*cis* : *trans*=3 : 1]
6	**1a**		 **2e** (95.7)
7	**1a**		 **2f** (57.0)
			 **3** (23.8)
8	**1a**		 **4** (76.0)
9	 **1b**		 **2g** (21.7)
10	**1b**		 **2h** (74.0)
11	 **1c**		 **2i** (29.6)[g)]
12	**1c**		 **2j** (77.6)
13	 **1d**		 **2k** (14.6)
14	 **1e**		 **2l** (34.8)
			 **5** (51.8)
15	**1e**		 **2m** (36.2)
			5 (41.1)

a) Conditions: molar ratio of **1** : alkene : $SnCl_4$ = 1 : 2 : 0.9, in dichloromethane at 0 °C for 3 h.
b) Isolated yields. c) 36.2% by $TiCl_4$ catalyst. d) 70.5% by $TiCl_4$ catalyst. e) For 8 h.
f) For 12 h. g) 1.73 Molar $SnCl_4$ was used at room temperature for 3 h.

adduct was deduced by considering the following diagnostic J values.[15] A large ($J=3.4$—4.3 Hz) or small ($J=2.3$—2.4 Hz) coupling involving protons on C-4 and C-5 indicates the presence of an axial or an equatorial proton on C-4. By the same token, the values of the coupling constants observed for sets of protons on C-2 and C-3, and on C-3 and C-4, indicate the stereochemistry of the substituents on those carbon atoms [representative J values (Hz): $3_{ax}/4_{ax}=10.8$—12.3; $3_{ax}/4_{eq}$ and $3_{eq}/4_{ax}=3.8$—6.0; $2_{ax}/3_{ax}=7.8$—8.3; $2_{ax}/3_{eq}$ and $2_{eq}/3_{ax}=2$—2.3]. An inspection of the NMR data revealed that all of the cycloadducts **2a,c,f** have the *trans*-C-2/C-4 configuration, which must have resulted from addition through an *exo* transition state (Entries 1, 3, 4, 7). In addition, the observed exclusive preservation of the starting alkene geometry (*trans*- and *cis*-3-hexenes) in the cycloadducts (*trans*- and *cis*-**2c**) is characteristic of a concerted [4+2] cycloaddition (Entries 3 and 4).

Hence, the reaction proceeded with high regio- and stereoselectivities through a concerted *exo* transition state. The 1-oxa-1,3-diene **1a** was reported to undergo *endo* selective $LUMO_{diene}$-controlled Diels–Alder additions with electron-rich dienophiles to give cycloadducts having the *cis*-C-2/C-4 configuration,[18] which should predominate over the *trans*-C-2/C-4 cycloadducts, due to the more favored secondary orbital interaction in the transition state. However, there is no such orbital interaction in the present cycloaddition of **1a** with simple alkenes. Recently, Roush and Brown[27] observed a significant preference for *exo* cycloaddition in the reactions of cyclopentadiene with conformationally restricted cyclic 1-oxa-1,3-dienes. The high *exo* selectivity of the reaction was speculated to originate in a difference in the dipole moments of the *exo* and *endo* transition states. However, no dipole moment difference could be anticipated in the reaction of **1a** with simple alkenes. For the present *exo* selective $LUMO_{diene}$-controlled cycloaddition, we assume a transition state in which one of the chlorine atoms of the **1a**–$SnCl_4$ complex[28] sterically controls the approach of the alkene molecule (Scheme 2). Thus, in the reaction of **1a** with 1-alkenes, the interaction between an axially oriented chlorine atom and an alkyl group disfavors the endo transition state leading to the *cis*-C-2/C-4 cycloadduct, so that a cycloadduct having the *trans*-C-2/C-4 configuration was produced overwhelmingly through the less-hindered *exo* transition state.



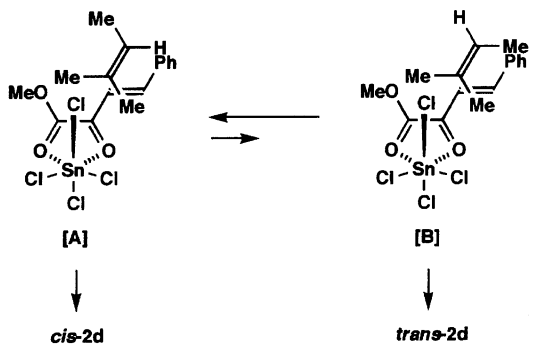
Scheme 2.

The reaction of **1a** with 2-methyl-2-butene yielded an isomeric cycloadduct mixture, in which *cis*-**2d** predominated over *trans*-**2d** (Entry 5). The former, a predominant, but less-stable stereoisomer possessing an axial methyl group on C-3 and a quasi-equatorial phenyl group on C-4, is produced through a transition state in which the terminal methyl group (C-4 of 2-methyl-2-butene) holds an endo orientation (Scheme 3, [A]). Contrarily, although a transition state having an exo-oriented terminal methyl group leads to *trans*-**2d** (Scheme 3, [B]), it may suffer steric overcrowding between the methyl group and the phenyl group. A similar steric interaction between the phenyl group of **1a** and an ethyl group makes the *cis*-3-hexene less reactive than *trans*-3-hexene (Entries 3 and 4).[29]

Although the formation of **2f** from cyclohexene is explained by the *exo* transition state, this reaction may have an ionic character to some extent because an ionic addition product **3** was also isolated.

Other methyl alkenoates **1b**—**d** also showed high regio- and stereoselectivities in reactions with simple alkenes (Entries 9—13). However, the reactions of methyl 3-phenyl-2-oxo-3-butenoate (**1e**) with alkenes yielded mixtures of the expected cycloadduct **2l,m** and a cyclic dimer **5** of **1e** (Entries 14 and 15). Although the thermal dimerization to give 3,4-dihydro-2*H*-pyrans has been well known for substituted acrylaldehydes and alkyl or aryl vinyl ketones,[13] an intriguing observation is that the presence of a substituent on C-3 of 1-oxa-1,3-diene prefers the formation of a dimeric product. Jellal and Santelli[30] reported a similar reaction; that is, an attempted preparation of methacryloyl cyanide from the reaction of methacryloyl chloride with copper(I) cyanide resulted in the formation of 2-cyano-3,6-dimethyl-4*H*-pyran (60%), which was supposed to be produced by the elimination of carbon monoxide and hydrogen cyanide from 6-cyano-3-cyanocarbonyl-2,5-dimethyl-3,4-dihydro-2*H*-pyran (a cyclic dimer of methacryloyl cyanide).

The reaction of **1a** with styrene revealed the other stereoselectivity (not fully concerted). The results will be reported elsewhere.



Scheme 3.

Experimental

Infrared spectra were recorded on a JASCO IRA-3 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX 90Q and Bruker AM-250 spectrometers. The chemical shifts are given in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on an ESCO EMD-05A spectrometer. Melting points were measured on a Yanaco micro-hot-plate apparatus, and are uncorrected.

Substituted methyl 2-oxo-3-alkenoates **1a**—**d** were prepared by methods described in the literature.[31] Methyl 3-phenyl-2-oxo-3-butenoate (**1e**) was prepared by MnO_2 oxidation of methyl 2-hydroxy-3-butenoate: colorless oil; IR (neat) 1740, 1690, 1275 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.18 (5H, s), 6.13 (1H, s), 6.08 (1H, s), and 3.77 (3H, s).

Dichloromethane was dried over calcium hydride and distilled before use.

Tin(IV) Chloride Catalyzed Reaction of Methyl 2-Oxo-3-alkenoates 1 with Alkenes. General Procedure. Tin(IV) chloride (0.01 mL, 0.09 mmol) was added through a syringe to a solution of **1** (1.5 mmol) and an alkene (3.0 mmol) in dichloromethane (20 mL) cooled in an ice bath; the mixture was stirred under a nitrogen atmosphere. After 3 h, the reaction was quenched by adding a small portion of saturated aqueous sodium hydrogencarbonate solution. The mixture was brought to room temperature and the organic layer was separated, washed with a saturated sodium hydrogencarbonate solution, and dried over sodium sulfate. The solvent was removed under reduced pressure to give an oil. The crude material was chromatographed on a silica gel column with dichloromethane as an eluent to give products.

***trans*-2-Butyl-6-methoxycarbonyl-4-phenyl-3,4-dihydro-2*H*-pyran (2a):** Yellow oil; IR (neat) 1740 and 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.2—7.4 (5H, m), 6.16 (1H, q, J=4.3 and 0.7 Hz), 3.91 (1H, m, J=8.3 and 2.8 Hz), 3.83 (3H, s), 3.62 (1H, m, J=6.0, 4.3, and 3.8 Hz), 1.96 and 1.86 (2H, m, J=14.0, 8.3 and 6.0 Hz; and 14.0, 3.8, and 2.8 Hz), and 1.2—1.6 (6H, m); ^{13}C NMR ($CDCl_3$) δ=163.59, 144.74, 144.52, 128.51, 128.00, 127.62, 111.72, 73.06, 52.07, 36.15, 35.17, 33.98, 27.45, 22.63, and 13.94; MS m/z 274 (M^+), 227, 216, and 215. Found: C, 74.39; H, 8.03%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%.

2,2-Dimethyl-6-methoxycarbonyl-4-phenyl-3,4-dihydro-2*H*-pyran (2b): Colorless crystals from CCl_4; mp 79 °C; IR (Nujol) 1720 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.0—7.5 (5H, s), 6.05 (1H, br s), 3.78 (3H, s), 3.4—3.8 (1H, m), 1.95 (1H, dq, J=15.4, 6.4, and 1.3 Hz), 1.63 (1H, q, J=15.4 and 12.3 Hz), 1.40 (3H, s), and 1.32 (3H, s); ^{13}C NMR ($CDCl_3$) δ=163.77, 143.59, 143.16, 128.69, 127.42, 126.77, 112.22, 76.20, 52.06, 42.42, 36.70, 29.42, and 23.54; MS m/z 246 (M^+), 228, 213, and 187. Found: C, 73.23; H, 7.31%. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37%.

***r*-2,*t*-3-Diethyl-6-methoxycarbonyl-*t*-4-phenyl-3,4-dihydro-2*H*-pyran (*trans*-2c):** Colorless oil; IR (neat) 1732 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.2—7.4 (5H, m), 6.17 (1H, dd, J=3.4 and 0.8 Hz), 4.20—4.26 (1H, q, J=7.8 and 4.0 Hz), 3.83 (3H, s), 3.77—3.82 (1H, q, J=5.8 and 3.4 Hz), 1.75—1.88 (1H, m), 1.6—1.7 (2H, m), 0.8—1.2 (2H, m), 1.07 (3H, t, J=7.0 Hz), and 0.78 (3H, t, J=7.0 Hz); ^{13}C NMR ($CDCl_3$) δ=163.55, 142.46, 140.91, 128.25, 128.59, 128.18, 126.51, 111.61, 77.85, 52.11, 40.85, 38.36, 25.04, 19.41, 11.83, and 9.83; MS m/z 274 (M^+), 243, and 215. Found: C, 74.38; H, 8.29%. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39%.

***r*-2,*c*-3-Diethyl-6-methyoxycarbonyl-*t*-4-phenyl-3,4-dihydro-2*H*-pyran (*cis*-2c):** Colorless oil; IR (neat 1738 and 1648 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.2—7.4 (5H, m), 6.08 (1H, dd, J=4.3 and 0.6 Hz), 3.86—3.90 (1H, m), 3.83 (3H, s), 3.37 (1H, t, J=4.5 and 4.3 Hz), 1.85—1.72 (1H, m), 1.72—1.60 (2H, m), 1.49—1.18 (2H, m), 0.98 (3H, t, J=7.3 Hz), and 0.96 (3H, t, J=7.3 Hz); ^{13}C NMR δ= 163.55, 144.09, 143.78, 128.49, 128.13, 126.65, 112.04, 77.43, 52.23, 44.81, 41.57, 22.53, 20.27, 12.11, and 10.56; MS m/z 274 (M^+) and 215. Found: C, 74.44; H, 8.15%. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39%.

***cis*-2,2,3-Trimethyl-6-methoxycarbonyl-4-phenyl-3,4-dihydro-2*H*-pyran (*cis*-2d):** Colorless oil; IR (neat) 1740 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.1—7.4 (5H, m), 6.20 (1H, dd, J=2.3 and 1.6 Hz), 3.95 (1H, dd, J=6.0 and 2.3 Hz), 3.84 (3H, s), 1.43 (6H, s), 1.7—1.8 (1H, m), and 0.54 (3H, d, J=7.0 Hz); ^{13}C NMR ($CDCl_3$) δ=163.43, 143.11, 141.73, 128.32, 128.27, 126.40, 110.17, 78.75, 52.02, 40.29, 39.18, 26.83, 25.28, and 9.82; MS m/z 260 (M^+), 245, and 242. Found: C, 73.90; H, 7.80%. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%.

***trans*-2,2,3-Trimethyl-6-methoxycarbonyl-4-phenyl-3,4-dihydro-2*H*-pyran (*trans*-2d):** Colorless oil; IR (neat) 1740 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.1—7.4 (5H, m), 5.99 (1H, d, J=2.3 Hz), 3.78 (3H, s), 3.01 (1H, q, J=10.8 and 2.4 Hz), 1.44 (6H, s), 1.3—1.5 (1H, m), and 0.80 (3H, d, J=10.8 Hz); ^{13}C NMR ($CDCl_3$) δ=163.73, 142.62, 142.00, 128.46, 128.40, 126.83, 113.86, 79.75, 51.94, 44.46, 43.30, 27.69, 18.05, and 14.18; MS m/z 260 (M^+), 245, and 242. Found: C, 73.90; H, 7.80%. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%.

2,2,3,3-Tetramethyl-6-methoxycarbonyl-4-phenyl-3,4-dihydro-2*H*-pyran (2e): Colorless oil; IR (neat) 1740 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.0—7.4 (5H, s), 6.15 (1H, d, J=3.3 Hz), 3.80 (3H, s), 3.48 (1H, d, J=3.3 Hz), 1.46 (3H, s), 1.39 (3H, s), 0.91 (3H, s), and 0.68 (3H, s); ^{13}C NMR ($CDCl_3$) δ=163.64, 142.49, 140.38, 130.54, 127.89, 127.70, 126.81, 113.75, 82.54, 52.07, 47.56, 36.44, 23.82, 22.98, 21.08, and 17.62; MS m/z 274 (M^+), 243, 217, and 215. Found: C, 74.57; H, 8.12%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H 8.08%.

3-Methoxycarbonyl-5-phenyl-2-oxabicyclo[4.4.0]-dec-3-ene (2f): Yellow oil; IR (neat) 1738 and 1648 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.1—7.5 (5H, m), 6.09 (1H, d, J=4.8 Hz), 4.06 (1H, q, J=2.3 Hz), 3.89 (3H, s), 3.26 (1H, q, J=4.8 and 2.6 Hz), and 1.2—2.2 (9H, m); ^{13}C NMR ($CDCl_3$) δ=163.39, 144.55, 143.78, 128.60, 127.99, 126.68, 110.22, 71.12, 52.37, 42.96, 41.38, 29.78, 27.69, 24.86, and 20.96; MS m/z 272 (M^+), 254 and 241. Found: C, 74.93; H, 7.28%. Calcd for $C_{17}H_{20}O_3$; C, 74.97; H, 7.40%.

Methyl 4-(2-Chlorocyclohexyl)-2-oxo-4-phenylbutanoate (3): Colorless oil; IR (neat) 1760 and 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.28 (5H, s), 4.0—4.3 (1H, m), 3.35 (3H, s), 2.9—3.2 (3H, m), and 0.6—2.4 (9H, m); ^{13}C NMR ($CDCl_3$) δ=192.55, 161.56, 138.83, 129.08, 128.11, 126.91, 63.29, 52.83, 49.77, 42.40, 39.80, 37.64, 26.50, 26.01, and 25.17; MS m/z 309, 308 (M^+), 290, and 205. Found: C, 66.05; H, 6.79%. Calcd for $C_{17}H_{21}O_3Cl$; C, 66.12; H, 6.85%.

4-Methoxalyl-1-methyl-5-phenyl-1-cyclohexene

(4): Colorless oil; IR (neat) 1730 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.20 (5H, s), 5.49 (1H, br s), 3.5—4.0 (1H, m), 3.60 (3H, s), 2.9—3.4 (1H, m), 2.0—2.5 (4H, m), and 1.69 (3H, s); ^{13}C NMR ($CDCl_3$) δ=197.29, 161.70, 143.09, 133.77, 128.52, 127.68, 126.73, 118.63, 52.46, 47.69, 42.98, 38.46, 28.30, and 23.04; MS *m/z* 258 (M^+) and 240. Found: C, 74.60; H, 7.17%. Calcd for $C_{16}H_{18}O_3$; C, 74.40; H, 7.02%.

***trans*-2-Butyl-6-methoxycarbonyl-4-methyl-3,4-dihydro-2*H*-pyran (2g):** Yellow oil; IR (neat) 2950, 1740, and 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.01 (1H, d, *J*=4.3 Hz), 3.8—4.0 (1H, m), 3.77 (3H, s), 2.3—2.5 (1H, m), 1.2—2.0 (8H, m), 1.06 (3H, d, *J*=7.1 Hz), and 0.92 (3H, t, *J*=6.8 Hz); ^{13}C NMR ($CDCl_3$) δ=163.75, 143.14, 116.24, 73.36, 51.91, 34.01, 33.87, 27.61, 24.98, 22.66, 21.82, and 13.99; MS *m/z* 212 (M^+) and 153. Found: C, 67.85; H, 9.46%. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50%.

2,2,4-Trimethyl-6-methoxycarbonyl-3,4-dihydro-2*H*-pyran (2h): Colorless oil; IR (neat) 2980, 1715, and 1640 cm^{-1}; ^1H NMR (CCl_4) δ=5.7—5.9 (1H, m), 2.1—2.6 (2H, m), 1.5—1.8 (1H, m), 1.35 (3H, s), 1.25 (3H, s), and 1.10 (3H, d, *J*=7 Hz); ^{13}C NMR ($CDCl_3$) δ=163.33, 141.55, 114.35, 75.27, 51.35, 41.19, 29.11, 24.53, 23.15, and 19.85; MS *m/z* 184 (M^+), 168 and 140. Found: C, 65.10; H, 8.67%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

2-Butyl-3,4-dihydro-6-methoxycarbonyl-4,4-dimethyl-2*H*-pyran (2i): Yellow oil; IR (neat) 2975, 1730, and 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.87 (1H, d, *J*=1.6 Hz), 3.7—4.0 (1H, m), 3.78 (3H, s), 1.0—1.9 (8H, m), 1.10 (3H, s), 1.08 (3H, s), and 0.93 (3H, t, *J*=6.9 Hz); ^{13}C NMR ($CDCl_3$) δ=163.79, 142.39, 120.94, 74.18, 51.86, 42.06, 34.88, 30.11 30.03, 29.73, 27.35, 22.61, and 13.89; MS *m/z* 226 (M^+), 211 and 167. Found: C, 68.91; H, 9.59%. Calcd for $C_{13}H_{23}O_3$: C, 68.69; H, 10.20%.

2,2,4,4-Tetramethyl-6-methoxycarbonyl-3,4-dihydro-2*H*-pyran (2j): Yellow oil; IR (neat) 3000, 1730, and 1640 cm^{-1}; ^1H NMR (CCl_4) δ=5.72 (1H, s), 3.65 (3H, s), 1.59 (2H, s), 1.28 (6H, s), and 1.08 (6H, s); ^{13}C NMR ($CDCl_3$) δ=162.97, 139.67, 119.09, 74.74, 50.85, 46.82, 29.89, 28.80, and 26.80; MS *m/z* 198 (M^+), 183, and 142. Found: C, 66.86; H, 9.20%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

2,2-Dimethyl-4-methoxy-6-methoxycarbonyl-3,4-dihydro-2*H*-pyran (2k): Yellow oil; IR (neat) 1742 and 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.14 (1H, dd, *J*=3.2 and 0.7 Hz), 3.95 (1H, m), 3.82 (3H, s), 3.40 (3H, s), 1.94 (1H, dd, *J*=13.7 and 6.2 Hz), 1.79 (1H, dd, *J*=13.7 and 7.1 Hz), 1.43 (3H, s), and 1.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ=163.40, 143.52, 107.71, 76.42, 69.95, 55.67, 52.02, 38.15, 27.10, 25.85, and 25.66; MS *m/z* 200 (M^+), 185 and 179. Found: C, 59.88; H, 7.81%. Calcd for $C_{10}H_{16}O_3$: C, 60.00; H, 8.00%.

2-Butyl-6-methoxycarbonyl-5-phenyl-3,4-dihydro-2*H*-pyran (2l): Yellow oil; IR (neat) 2950, 1730, and 1640 cm^{-1}; ^1H NMR (CCl_4) δ=6.8—7.4 (5H, m), 3.5—4.1 (1H, m), 3.45 (3H, s), and 0.7—2.6 (13H, m); ^{13}C NMR ($CDCl_3$) δ=164.32, 140.86, 140.57, 127.97, 127.70, 126.83, 122.55, 75.66, 51.56, 34.33, 28.67, 27.48, 27.29, 22.68, and 13.99; MS *m/z* 274 (M^+), 243, and 171. Found: C, 74.51; H, 8.02%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%.

2-Methoxalyl-6-methoxycarbonyl-2,5-diphenyl-3,4-dihydro-2*H*-pyran (5): Colorless crystals; mp 92—95 °C; IR (Nujol) 1740 and 1645 cm^{-1}; ^1H NMR (CCl_4) δ=6.7—7.6 (10H, m), 3.83 (3H, s), 3.47 (3H, s), 2.1—2.5 (4H, q, *J*=7 Hz); ^{13}C NMR ($CDCl_3$) δ=195.8, 163.6, 163.2, 139.1, 136.9, 128.7, 128.5, 128.0, 127.6, 127.3, 125.2, 124.8, 85.2, 52.6, 51.8, 30.1, and 26.8; MS *m/z* 380 (M^+), 293, and 233. Found: C, 69.52; H, 5.43%. Calcd for $C_{22}H_{20}O_6$: C, 69.46; H, 5.30%.

2,2-Dimethyl-6-methoxycarbonyl-5-phenyl-3,4-dihydro-2*H*-pyran (2m): Colorless oil; IR (neat) 1735 and 1642 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.0—7.4 (5H, m), 3.50 (3H, s), 2.41 (2H, t, *J*=6.0 Hz), 1.78 (2H, t, *J*=6.0 Hz), and 1.38 (6H, s); ^{13}C NMR ($CDCl_3$) δ=164.54, 140.48, 139.48, 127.86, 127.51, 126.62, 120.25, 74.12, 51.37, 32.71, 26.50, and 25.96; MS *m/z* 246 (M^+), 211, and 162. Found: C, 73.30; H, 7.11%. Calcd for $C_{15}O_{18}O_3$: C, 73.15; H, 7.37%.

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