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The Selective *O*-Acylation of Enolates Providing a Simple Entry to *O*-Enesters

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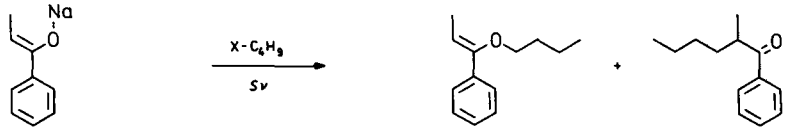
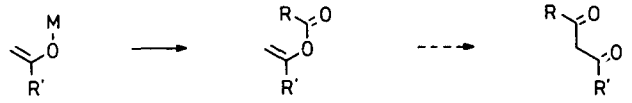
Abstract: In the presence of catalytic amounts of a fluoride source, *O*-trimethylsilyl enethers undergo condensation with acyl fluorides to afford *O*-enesters with high yields. The intermediates and final products are pure (*Z*) isomers if only one double bond is in conjugation with the oxygen atom whereas (*E*) isomers prevail if silyl dienethers or trienethers and *O*-dienesters or *O*-trienesters are formed.

Young students like experienced researchers consider enolate reactions [1] to be one of the most confusing chapters in chemistry. Of course, it is easily understood that the oxyallyl anion is a delocalized species and hence can react with an electrophile at either terminus. *A priori*, this positional ambiguity is no disadvantage. On the contrary, it can establish a very valuable option provided protocols can be elaborated that reliably promote one or the other substitution mode. The trouble with enolate reactions is their enormous mechanistic complexity which makes it so difficult to predict their outcome. The principal unknown is the role of the counterion, in general a metal. Depending on its nature, it is more or less tightly associated with the oxygen atom the nucleophilicity of which can be drastically altered in this way. Enolates are prone to cluster formation, either combining with each other to give homoaggregates or with other salt-like products to afford heteroaggregates (mixed aggregates) [2]. These oligomers may react as such or only after prior dissociation [3]. Moreover, both the aggregation state and the polarity of the metal-oxygen bond are subject to strong solvent effects. Finally, each kind of electrophile exhibits an individual sensitivity to the various factors that simultaneously influence the enolate structure. Thus, for example, the *O*/*C* ratios range from 1 : 99 to 78 : 22 when the sodium enolate of propiophenone is alkylated with either butyl iodide or tributyl phosphate as the electrophile in either diethyl ether (DEE) or dimethylsulfoxide (DMSO) as the solvent (*Sv*) [4].

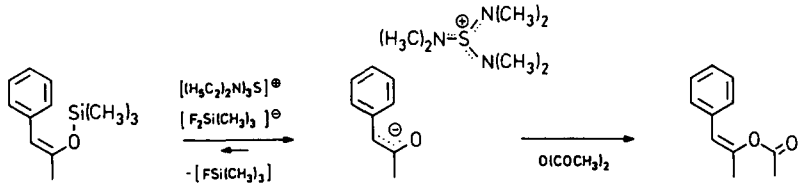


X = I ; *Sv* = DEE	1 : 99
X = I ; *Sv* = DMSO	10 : 90
X = $(H_9C_4O)_2P(O)O$; *Sv* = DEE	36 : 64
X = $(H_9C_4O)_2P(O)O$; *Sv* = DMSO	78 : 22

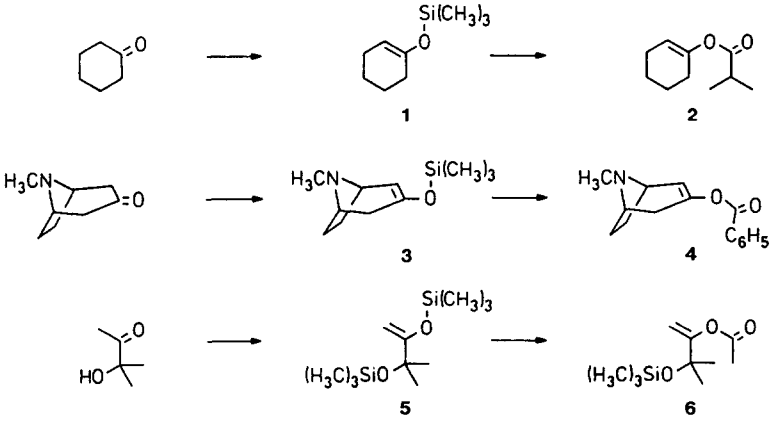
Enolates exhibit the same ambident character towards acylation reagents. Tightly binding, metals [5], unpolar solvents [6] and low temperatures [7] tend to promote substitution at carbon, while polar [6] or two-phase [8] media and the use of anhydrides [1] rather than acyl chlorides [5] or carboxylic esters [9] favor electrophilic attack at the oxygen atom. Furthermore, the *O*-enesters resulting from initial electrophilic attack at the enolate oxygen may subsequently undergo a base promoted *O*.→ *C* transacylation affording the thermodynamically more stable 1,3-diketones [6].



On the other side, methods for clean *O*-acylation of ketone derived enolates are lacking. The only exception is found in a report by Noyori *et al.* [10]. The Japanese authors have treated *O*-trimethylsilyl enethers with tris(dimethylamino)sulfonium difluorotrimethylsilicate ("TASF") and thus were able to generate for the first time "naked" enolates (*i.e.*, anions virtually unperturbed by the counterion). These species were shown to react with acetic anhydride exclusively under *O*-acetylation.



The only drawback of this reaction sequence is the necessity to use stoichiometric quantities of the expensive TASF compound. We reasoned that catalytic amounts of a desilylation reagent should suffice if the *in situ* generated enolate was intercepted with an acyl *fluoride*. This was found to be the case indeed. When the cyclohexanone derived 1-(trimethylsilyloxy)cyclohexene (**1**) was allowed to react in tetrahydrofuran 1 h at 25 °C with isobutyryl fluoride in the presence of a trace (0.05 equivalents) of tetrabutylammonium fluoride (in form of its trihydrate), an almost quantitative yield of 1-cyclohexenyl isobutanoate (**2**) was obtained. Similarly, tropinone and 3-hydroxy-3-methyl-2-butanone were converted *via* the corresponding *O*-silyl enethers (**3** and **5**) into the benzoate **4** and the acetate **6**.



Aldehyde derived lithium enolates can be readily set free from the corresponding *O*-trimethylsilyl enethers by simple treatment with methyllithium [1]. These species are known to favor *O*-acetylation with high selecti-vity irrespective of the reaction conditions. The yields of *O*-enesters **8a-e**, however, are notoriously poor or moderate at best, even when an excess of the acylation reagent and hexamethylphosphoric triamide as a cosolvent are employed. As a comparison reveals (see Table), the result is considerably improved if the *O*-trimethylsilyl enether **7** prepared from butanal is allowed to react with a variety of acyl fluorides (acetyl, propionyl, heptanoyl, hexadecanoyl and benzoyl fluoride) in the presence of catalytic amounts of tetrabutylammonium fluoride rather than if it is converted into the lithium enolate and the latter trapped with an anhydride or acyl chloride.

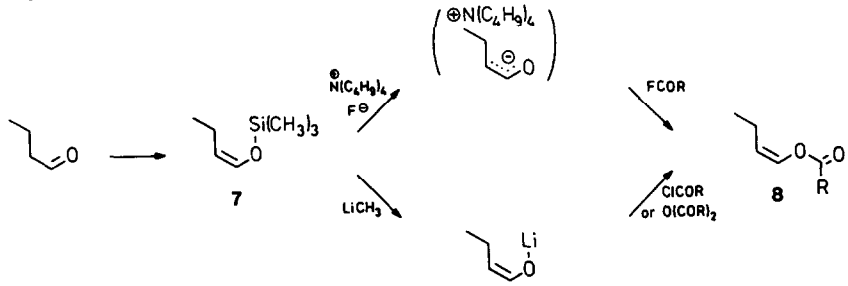
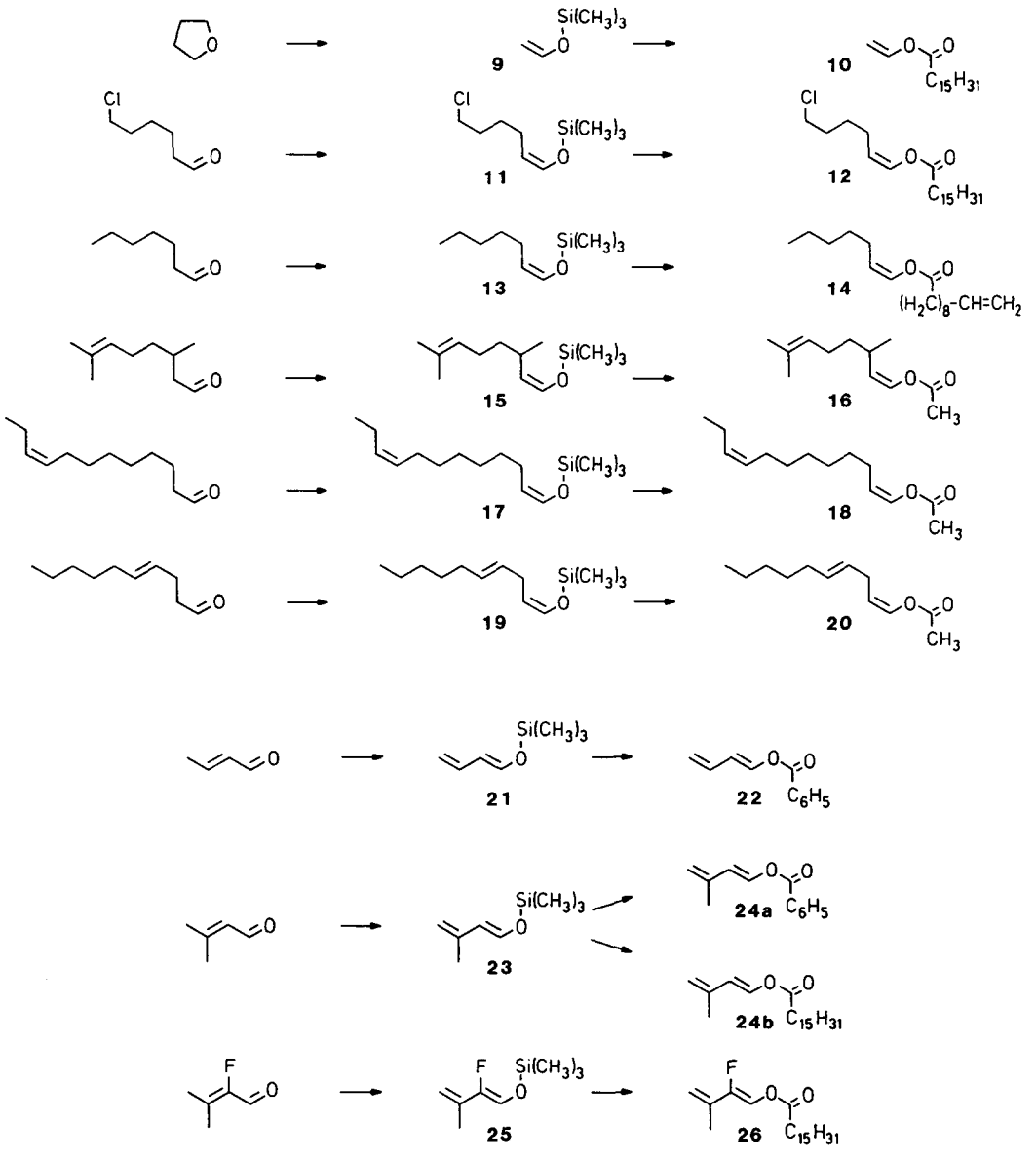


Table. Yields of *O*-enesters **8a-e** isolated after consecutive treatment of the *O*-trimethylsilyl enether **7** and an anhydride or acyl chloride and, in comparison, after reaction of the silylated intermediate **7** with acyl fluorides in the presence of fluoride ions.

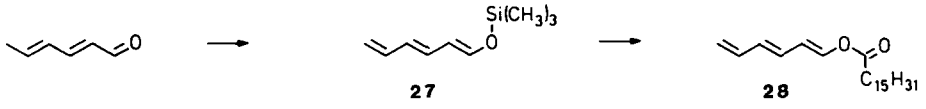
product cpd. nr.	acyl group R	lithium enolate + anhydride	+ acyl chloride	"naked enolate" + acyl fluoride
8a:	CH_3	57%	61%	82%
8b:	C_2H_5	46%	52%	77%
8c:	C_6H_{13}	32%	43%	82%
8d:	$C_{15}H_{31}$	-	42%	88%
8e:	C_6H_5	21%	31%	85%

A series of additional *O*-trimethylsilyl enethers (**9**, **11**, **13**, **15**, **17** and **19**) was submitted to the fluoride induced desilylation/acylation protocol in order to demonstrate the general applicability of the method. The expected *O*-enesters (**10**, **12**, **14**, **16**, **18** and **20**) were altogether formed with high yields and no contaminating by-products were observed.

Enolates appear to be thermodynamically more stable when adopting the (*Z*), or *endo*, configuration [11]. For this reason, the *O*-trimethylsilyl enethers preferentially emerge with this geometry when prepared from a saturated aldehyde in a deprotonation/silylation sequence. Virtually pure *(Z)* isomers can be obtained when the lithium enolates produced by the Wittig [1,4]-rearrangement of metalated allyl ethers are trapped with chloro-trimethylsilane [12]. These configurations are faithfully delivered into the final *O*-enesters. On the other hand, γ,δ-unsaturated enolates seem to favor the (*E*), or *exo*, configuration [13]. Therefore, one may expect a change in stereoselectivity when *O*-trimethylsilyl dienethers are produced from α,β- (or β,γ-) unsaturated aldehydes. Actually, both the *O*-trimethylsilyl dienethers **21**, **23** and **25** [14] as the *O*-(dien)esters **22**, **24** and **26**, into which they were converted, preferentially occupied the (*E*) structure although none of these compounds was isomerically pure.



Finally an α,β;γ,δ-unsaturated dienal was submitted to the base promoted *O*-silylation and to the subsequent fluoride mediated *O*-acylation. The resulting trimethylsilyl trienyl oxide **27** and the *O*-trienyl ester **28** were found to exist as a mixture of stereoisomers, again the ones having the (*E,E*)-configuration being the preponderant components.



EXPERIMENTAL

For generalities and laboratory routine see related articles [15]. - ^{1}H- and ^{19}F-nmr spectra were recorded of $CDCl_3$ solutions and at 250 and 188 MHz, respectively.

1. Acyl Fluorides

Acetyl and benzoyl fluoride have been purchased from Aldrich Co. Propionyl [16], isobutyryl [16], heptanoyl [16], undec-10-enoyl [17] and hexadecanoyl [17] fluoride were prepared according to literature references.

2. *O*-Trimethylsilyl Enethers

1-(Trimethylsilyloxy)cyclohexene (**1**) was purchased from Fluka AG. 1-(Trimethylsilyloxy)ethene (**9**) [18], 1-(trimethylsilyloxy)but-1-ene (**7**) [19], 1-(trimethylsilyloxy)hept-1-ene (**13**) [20], 3,7-dimethyl-1-(trimethylsilyloxy)octa-1,6-diene (**15**) [19], 1-(trimethylsilyloxy)buta-1,3-diene (**21**) [21], 3-methyl-1-(trimethylsilyloxy)buta-1,3-diene (**23**) [22] and 2-fluoro-3-methyl-1-(trimethylsilyloxy)buta-1,3-diene (**25**) [23] were prepared according to literature procedures. The labile 1-(trimethylsilyloxy)hexa-1,3,5-triene (**27**) was obtained in analogy to the *O*-trimethylsilyldienethers **21** and **23** but was immediately used after distillation (bp 90 - 100 °C/10 mmHg).

***N*-Methyl-3-trimethylsilyloxy-8-azabicyclo[3.2.1]oct-2-ene (3)** : *N*-Methyl-8-azabicyclo[3.2.1]octan-3-one (tropinone; 7.6 g, 50 mmol) was added, in the course of 15 min, to a solution of lithium diisopropylamide (50 mmol, generated by the instantaneous reaction between diisopropylamine and butyllithium) in a mixture of tetrahydrofuran (100 mL) and hexane (35 mL) at -15 °C. At 25 °C, chlorotrimethylsilane (9.3 mL, 8.0 g, 75 mmol) was added dropwise. After the evaporation of the solvents, the residue was distilled to afford a colorless oil; 9.9 g (87%), bp 100 - 102 °C/10 mmHg; n_D^{20} 1.4718. - ^{1}H-NMR : δ 4.88 (1 H, d, *J* 5.5), 3.23 (2 H, t, *J* 5.5), 2.5 (1 H, m), 2.33 (3 H, s), 2.1 (1 H, m), 1.96 (1 H, hept, *J* 5.6), 1.79 (1 H, td, *J* 10.1, 1.8), 1.5 (2 H, m), 0.16 (9 H, s). - Analysis : calc. for $C_{11}H_{21}NOSi$ (211.38) C 62.50, H 10.01; found C 63.06, H 9.84%.

3-Methyl-2,3-bis(trimethylsilyloxy)but-1-ene (5) [24] : It was prepared as described for compound **3** but using two equivalents of both lithium diisopropylamine and chlorotrimethylsilane; 79%; bp 51 - 52 °C/1 mmHg; n_D^{20} 1.4200. - ^{1}H-NMR : δ 4.45 (1 H, d, *J* 0.8), 4.02 (1 H, d, *J* 0.8), 1.33 (6 H, s), 0.24 (9 H, s), 0.15 (9 H, s).

6-Chloro-1-(trimethylsilyloxy)hex-1-ene (11) : A mixture of 6-chlorohexanal [25] (13 g, 0.10 mol), chlorotrimethylsilane (15 mL, 13 g, 0.12 mol), triethylamine (28 mL, 20 g, 0.20 mol) and *N,N*-dimethylformamide (40 mL) was heated 24 h under reflux. At 25 °C, it was diluted with pentane (0.5 L), washed with 5% hydrochloric acid (2 × 50 mL) and a 5% aqueous solution of sodium hydrogen carbonate (3 × 50 mL), dried, filtered and concentrated. Upon distillation under reduced pressure, a colorless liquid was collected; 16.1 g (75%); bp 93 - 94 °C/10 mmHg; n_D^{20} 1.4445. The (*Z*/*E*) ratio approximated 70 : 30. - ^{1}H-NMR : δ 6.23 (0.3 H, dt, *J* 12.0, 1.3), 6.19 (0.7 H, dt, *J* 6.8, 1.4), 4.98 (0.3 H, dt, *J* 12.0, 7.5), 4.48 (0.7 H, dt, *J* 6.8, 7.4), 3.56 (1.4 H, t, *J* 9.4), 3.54 (0.6 H, t, *J* 9.3), 2.11 (1.4 H, qd, *J* 7.4, 1.5), 1.94 (0.6 H, qd, *J* 7.3, 1.0), 1.8 (2 H, m), 1.5 (2 H, m), 0.19 (9 H, s.). - Analysis : calc. for $C_9H_{19}ClOSi$ (206.79) C 52.28, H 9.26; found C 52.34, H 9.32%.

1-(Trimethylsilyloxy)deca-1,4-diene (19) : In the course of 15 min, chlorotrimethylsilane (19 mL, 16 g, 0.15 mol) was added to a solution of sodium bromide (15 g, 0.15 mol) in anhydrous *N,N*-dimethylformamide (0.35 L). After 30 min at 25 °C, triethylamine (21 mL, 15 g, 0.15 mol) and *trans*-dec-4-enal (19 mL, 15 g, 0.10 mol) were added. The mixture was stirred 48 h at 25 °C before being diluted with pentane (0.5 L), extracted with a saturated aqueous solution of sodium hydrogen carbonate (2 × 0.2 L) and water (3 × 0.2 L), dried, filtered and concentrated. Distillation under reduced pressure gave a colorless liquid ; 19.0 g (70%); bp 80 - 83 °C/1 mmHg; n_D^{20} 1.4441. The (1*Z*,4*E*)/(1*E*,4*E*) ratio approximated 80 : 20 (by nmr). - ^{1}H-NMR : δ 6.22 (0.2 H, dt, *J* 12.0, 1.5), 6.19 (0.8 H, dt, *J* 5.8, 1.6), 5.4 (2 H, m), 5.01 (0.2 H, dt, *J* 12.0, 7.3), 4.53 (0.8 H, dt, *J* 6.0, 7.3), 2.8 (1 H, m), 2.0 (2 H, m, q-like, *J* 6.7), 1.3 (7 H, m), 0.89 (3 H, t, *J* 6.8), 0.21 (9 H, s). - Analysis : calc. for $C_{13}H_{26}OSi$ (226.44) C 68.96, H 11.57; found C 68.87, H 11.56%.

(1*Z*,9*Z*)-1-(Trimethylsilyloxy)dodeca-1,9-diene (17) was prepared from (*Z*)-dodec-9-enal [26] as described above for product **19**, but the crude, oily material was immediately used without isolation or purification.

3. *O*-Enesters

1-Butenyl [27] and 3,7-dimethylocta-1,6-dienyl [28] acetate (**8a** and **16**, 30% and 71%, respectively) as well as vinyl palmitate (**10**) [29] have already been described in the literature.

Vinyl palmitate (10) [29] : Tetrabutylammonium fluoride trihydrate (0.16 g, 0.50 mmol) was added to a solution of (trimethylsilyloxy)ethene [18] (3.7 mL, 2.9 g, 25 mmol) and palmitoyl fluoride (6.5 g, 25 mmol) in tetrahydrofuran (25 mL) at 0 °C. After 2 h, the solvents were evaporated and the residue was crystallized from ethanol to afford a softening white solid; 4.9 g (70%); mp 26 - 27 °C. - ^{1}H-NMR : δ 7.29 (1 H, dd, *J* 14.0, 6.5), 4.87 (1 H, dd, 14.3, 1.8), 4.56 (1 H, dd, *J* 6.5, 1.8), 2.41 (2 H, t, *J* 7.5), 1.66 (2 H, pent, *J* 7.4), 1.3 (24 H, m), 0.88 (3 H, t, *J* 6.4).

The other *O*-1-alkenyl carboxylates were prepared in the same manner.

1-Cyclohex-1-enyl isobutyrate (2) : From 1-(trimethylsilyloxy)cyclohexene (**1**) and isobutyryl fluoride; 81%; bp 83 - 85 °C/10 mmHg; n_D^{20} 1.4516. - ^{1}H-NMR : δ 5.3 (1 H, m), 2.59 (1 H, hept, *J* 7.1), 2.1 (4 H, m), 1.7 (2 H, m), 1.6 (2 H, m), 1.19 (6 H, d, *J* 7.1). - Analysis : calc. for $C_{10}H_{16}O_2$ (168.24) C 71.39, H 9.59; found C 71.12, H 9.64%.

***N*-Methyl-8-azabicyclo[3.2.1]oct-2-enyl benzoate (4)** : From *N*-methyl-3-trimethylsilyloxy-8-azabicyclo-[3.2.1]oct-2-ene (**3**) and benzoyl fluoride; by crystallization of the organic residue from 50% aqueous acetone; 66%; mp 77 - 78 °C. - ^{1}H-NMR : δ 8.06 (2 H, dm, *J* 7.3), 7.59 (1 H, tm, *J* 7.4), 7.44 (2 H, tm, *J* 7.6), 5.59 (1 H, dm, *J* 4.3), 3.4 (2 H, m), 2.79 (1 H, dd, *J* 17.0, 4.1), 2.51 (3 H, s), 2.2 (1 H, m), 2.09 (1 H, pent, *J* 5.6), 2.0 (1 H, m), 1.82 (1 H, d, *J* 16.5), 1.7 (1 H, m). - Analysis : calc. for $C_{15}H_{17}O_2$ (243.31) C 74.05, H 7.04; found C 74.39, H 7.06%.

1-(1-Methyl-1-[trimethylsilyloxy]ethyl)vinyl acetate (6) : From 3-methyl-2,3-bis(trimethylsilyloxy)but-1-ene (**5**) and acetyl fluoride; 57%; bp 41 - 43 °C/1 mmHg, n_D^{20} 1.4236. - ^{1}H-NMR : δ 5.14 (1 H, d, *J* 2.0), 4.76 (1 H, d, *J* 2.0), 2.16 (3 H, s), 1.32 (6 H, s), 0.15 (9 H, s). - Analysis : calc. for $C_{10}H_{20}O_3Si$ (216.35) C 54.52, H 9.32; found C 54.51, H 9.20%.

But-1-enyl propionate (8b) : From 1-(trimethylsilyloxy)but-1-ene [19] (*Z*/*E* = 80 : 20) and propionyl fluoride; 77%; bp 43 - 45 °C/10 mmHg; n_D^{20} 1.4195. - ^{1}H-NMR : δ 7.08 (0.2 H, dt, *J* 12.5, 1.5), 6.98 (0.8 H, dt, *J* 6.0, 1.5), 5.43 (0.2 H, dt, *J* 12.5, 7.0), 4.84 (0.8 H, q, *J* 7.0), 2.43 (2 H, q, *J* 7.5), 2.14 (1.6 H, qd, *J* 7.5, 1.4), 2.01 (0.4 H, qd, *J* 7.3, 1.5), 1.17 (3 H, t, *J* 7.5), 0.96 (3 H, t, *J* 7.5). - Analysis : calc. for $C_7H_{12}O_2$ (128.17) C 65.60, H 9.44; found C 65.49, H 9.38%.

But-1-enyl heptanoate (8c) : From 1-(trimethylsilyloxy)but-1-ene [19] (*Z*/*E* = 80 : 20) and heptanoyl fluoride; 82%; bp 67 - 68 °C/1 mmHg; n_D^{20} 1.4358. - ^{1}H-NMR : δ 7.08 (0.2 H, dt, *J* 12.5, 1.5), 6.99 (0.8 H, dt, *J* 6.0, 1.5), 5.44 (0.2 H, dt, *J* 12.5, 7.1), 4.85 (0.8 H, q, *J* 7.0), 2.40 (1.6 H, t, *J* 7.5), 2.34 (0.4 H, t, *J* 7.5), 2.15 (1.6 H, qd, *J* 7.4, 1.5), 2.03 (0.4 H, qd, *J* 7.3, 1.8), 1.7 (2 H, m), 1.3 (6 H, m), 1.03 (0.6 H, t, *J* 7.4), 0.99 (2.4 H, t, *J* 7.3), 0.88 (3 H, t, *J* 6.6). - Analysis : calc. for $C_{11}H_{20}O_2$ (184.28) C 71.70, H 10.94; found C 71.56, H 11.05%.

But-1-enyl palmitate (8d) : From 1-(trimethylsilyloxy)but-1-ene [19] (*Z*/*E* = 80 : 20) and palmitoyl fluoride; 88%; mp 10 - 12 °C (from ethanol). - ^{1}H-NMR : δ 7.09 (0.2 H, dt, *J* 12.5, 1.5), 7.00 (0.8 H, dt, *J* 6.4, 1.5), 5.44 (0.2 H, dt, *J* 12.4, 7.0), 4.86 (0.8 H, q, *J* 6.3), 2.41 (1.6 H, t, *J* 7.5), 2.35 (0.4 H, t, *J* 7.8), 2.16 (1.6 H, qd, *J* 7.5, 1.3), 2.03 (0.4 H, qd, *J* 7.3, 1.5), 1.7 (2 H, m), 1.2 (24 H, m), 1.03 (2.4 H, t, *J* 7.5), 1.00 (0.6 H, t, *J* 7.5), 0.88 (3 H, t, *J* 6.5). - Analysis : calc. for $C_{20}H_{38}O_2$ (310.52) C 77.36, H 12.33; found C 77.51, H 12.18%.

But-1-enyl benzoate (8e) : From 1-(trimethylsilyloxy)but-1-ene [19] (*Z*/*E* = 80 : 20) and benzoyl fluoride; 85%; bp 74 - 76 °C/1 mmHg; n_D^{20} 1.4046. - ^{1}H-NMR : δ 8.2 (2 H, m), 7.6 (1 H, m), 7.5 (2 H, m), 7.33 (0.2 H, dt, *J* 12.3, 1.6), 7.25 (0.8 H, dt, *J* 6.0, 1.5), 5.66 (0.2 H, dt, *J* 12.5, 7.1), 5.04 (0.8 H, q, *J* 7.0), 2.33 (1.6 H, qd, *J* 7.5, 1.5), 2.11 (0.4 H, dt, *J* 7.4, 1.5), 1.09 (3 H, t, *J* 7.4). - Analysis : calc. for $C_{11}H_{12}O_2$ (176.22) C 74.98, H 6.86; found C 75.10, H 6.97%.

6-Chlorohex-1-enyl palmitate (12) : From 6-chloro-1-(trimethylsilyloxy)hex-1-ene (**11**; *Z*/*E* = 70 : 30) and palmitoyl fluoride; by crystallization of the tetrahydrofuran soluble residue from ethanol; 84%; mp 27 - 28 °C. - ^{1}H-NMR : δ 7.11 (0.3 H, dt, *J* 12.5, 1.4), 7.06 (0.7 H, dt, *J* 6.5, 1.6), 5.39 (0.3 H, dt, *J* 12.5, 7.5), 4.85 (0.7 H, dt, *J* 6.5, 7.5), 3.54 (1 H, t, *J* 6.6), 3.53 (0.6 H, t, *J* 6.6), 2.41 (1.4 H, t, *J* 7.6), 2.36 (0.6 H, t, *J* 7.5), 2.19 (1.4 H, qd, *J* 7.3, 1.3), 2.05 (0.6 H, qd, *J* 7.4, 1.5), 1.8 (2 H, m), 1.7 (2 H, m), 1.6 (2 H, m), 1.3 (24 H, s, broad), 0.88 (3 H, t, *J* 6.5). - Analysis : calc. for $C_{22}H_{41}ClO_2$ (373.02) C 70.84, H 11.08; found C 71.07, H 10.91%.

Hept-1-enyl undec-10-enoate (14) : From 1-(trimethylsilyloxy)hept-1-ene [20] (*Z*/*E* = 80 : 20) and undec-10-enoyl fluoride [17]; isolated by chromatography on silica gel; 87%; mp -21 to -18 °C; n_D^{20} 1.4586. - ^{1}H-NMR :

δ 7.09 (0.2 H, dt, *J* 12.5, 1.4), 7.03 (0.8 H, dt, *J* 6.5, 1.5), 5.82 (1 H, ddt, *J* 12.0, 10.3, 6.8), 5.41 (0.2 H, dt, *J* 12.5, 7.5), 5.00 (1 H, dm, *J* 13.4), 4.93 (1 H, dm, *J* 11.0), 4.87 (0.8 H, dt, *J* 6.5, 7.5), 2.41 (1.6 H, t, *J* 7.5), 2.36 (0.4 H, t, *J* 7.5), 2.14 (2 H, qd, *J* 7.3, 1.3), 2.1 (2 H, m), 1.7 (2 H, m), 1.3 (16 H, m), 0.9 (3 H, m). - Analysis : calc. for $C_{18}H_{32}O_2$ (280.45) C 77.09, H 11.50; found C 77.55, H 11.63%.

(9*Z*)-Dodeca-1,9-dienyl acetate (18) : From (9*Z*)-1-(trimethylsilyloxy)dodeca-1,9-diene (**17**; 1*Z*,9*Z*/1*E*,9*Z* = 80 : 20) and acetyl fluoride; isolated by chromatography on silica gel; 88%; n_D^{20} 1.4557. - ^{1}H-NMR : δ 7.06 (0.2 H, dt, *J* 12.5, 1.5), 7.00 (0.8 H, dt, *J* 6.5, 1.5), 5.4 (2.2 H, m), 4.86 (0.8 H, dt, *J* 6.5, 7.5), 2.15 (2.4 H, s), 2.11 (0.6 H, s), 2.1 (2 H, m), 2.0 (4 H, m), 1.4 (8 H, m), 0.96 (3 H, t, *J* 7.4). - Analysis : calc. for $C_{14}H_{24}O_2$ (224.34) C 74.95, H 10.78; found C 74.85, H 10.76%.

(4*E*)-Deca-1,4-dienyl acetate (20) : From 1-(trimethylsilyloxy)deca-1,4-diene (**19**; 1*Z*,4*E*/1*E*,4*E* = 80 : 20) and acetyl fluoride; isolated by chromatography on silica gel; 78%; n_D^{20} 1.4604. - ^{1}H-NMR : δ 7.08 (0.2 H, dt, *J* 13.3, 1.6), 7.04 (0.8 H, dt, *J* 6.5, 1.8), 5.4 (2.2 H, m), 4.89 (0.8 H, dt, *J* 6.5, 6.3), 2.81 (1.6 H, tm, *J* 6.3), 2.69 (0.4 H, tm, *J* 6.2), 2.16 (2.4 H, s), 2.12 (0.6 H, s), 1.99 (2 H, q, *J* 6.5), 1.3 (6 H, m), 0.88 (3 H, t, *J* 6.6). - Analysis : calc. for $C_{12}H_{20}O_2$ (196.29) C 73.43, H 10.27; found C 73.26, H 10.67%.

Buta-1,3-dienyl benzoate (22) : From 1-(trimethylsilyloxy)buta-1,3-diene [21] (**21**; *Z*/*E* = 10 : 90) and benzoyl fluoride; isolated by distillation; 84%; mp -16 to -14 °C; bp 87 - 88 °C/1 mmHg; n_D^{20} 1.5661. - ^{1}H-NMR : δ 8.1 (2 H, m), 7.69 (0.9 H, d, *J* 12.0), 7.6 (1 H, m), 7.5 (2 H, m), 7.34 (0.1 H, dpent, *J* 6.3, 0.9), 6.90 (0.1 H, dtd, *J* 17.5, 10.1, 1.3), 6.3 (1.8 H, m), 5.66 (0.1 H, ddt, *J* 11.0, 6.5, 0.8), 5.33 (0.1 H, dm, *J* 17.5), 5.29 (0.9 H, dm, *J* 16.5), 5.20 (0.9 H, dm, *J* 10.0), 5.15 (0.1 H, dm, *J* 10.1). - Analysis : calc. for $C_{11}H_{10}O_2$ (174.20) C 75.84, H 5.79; found C 75.28, H 5.73%.

(*E*)-3-Methylbuta-1,3-dienyl benzoate (24a) : From (*E*)-3-methyl-1-(trimethylsilyloxy)buta-1,3-diene [22] (**23**) and benzoyl fluoride; isolated by distillation; 70%; mp -11 to -10 °C; bp 96 - 98 °C/1 mmHg; n_D^{20} 1.5612. - ^{1}H-NMR : δ 8.2 (2 H, m), 7.6 (2 H, m), 7.5 (2 H, m), 6.36 (1 H, d, *J* 12.5), 5.02 (2 H, dm, *J* 10.8), 1.94 (3 H, s). - Analysis : calc. for $C_{12}H_{12}O_2$ (188.23) C 76.57, H 6.43; found C 76.74, H 6.45%.

(*E*)-3-Methylbuta-1,3-dienyl palmitate (24b) : From (*E*)-3-methyl-1-(trimethylsilyloxy)buta-1,3-diene [22] (**23**) and palmitoyl fluoride; by crystallization of the organic residue from ethanol; 85%; mp 39 - 40 °C. - ^{1}H-NMR : δ 7.41 (1 H, d, *J* 18.0), 6.14 (1 H, d, *J* 13.0), 4.96 (2 H, d, *J* 6.5), 2.40 (2 H, t, *J* 7.5), 1.86 (3 H, s), 1.7 (2 H, m), 1.3 (24 H, m), 0.88 (3 H, t, *J* 6.4). - Analysis : calc. for $C_{21}H_{38}O_2$ (322.53) C 78.20, H 11.88; found C 78.41, H 11.76%.

2-Fluoro-3-methylbuta-1,3-dienyl palmitate (26) : From 2-fluoro-3-methyl-1-(trimethylsilyloxy)buta-1,3-diene (**25**; *Z*/*E* = 90 : 10) and palmitoyl fluoride; by crystallization of the organic residue from ethanol; 86%; mp 34 - 35 °C. - ^{1}H-NMR : δ 7.08 (1 H, d, *J* 22.5), 5.41 (1 H, s), 5.1 (1 H, m), 2.49 (2 H, t, *J* 7.5), 1.84 (3 H, s), 1.6 (2 H, m), 1.3 (24 H, s, broad), 0.89 (3 H, t, *J* 6.5). - ^{19}F-NMR : -72.6 (dm, *J* 22). - Analysis : calc. for $C_{21}H_{37}O_2$ (340.52) C 74.07, H 10.95; found C 73.72, H 10.82%.

Hexa-1,3,5-trienyl palmitate (28) : From 1-(trimethylsilyloxy)hexa-1,3,5-triene (**27**; see Chapter 2, first paragraph) and palmitoyl fluoride; by recrystallization of the organic residue from ethanol; 74%; mp 51 - 58 °C. - The product was not stable enough to be sent to an outdoor analytical service. - ^{1}H-NMR : δ 7,46 (1 H, d, *J* 12.0), 6.4 (1 H, m), 6.2 (2 H, m), 6.1 (1 H, m), 5.18 (1 H, dd, *J* 11.5, 2.0), 5.13 (1 H, dd, *J* 9.8, 2.0), 2.43 (2 H, t, *J* 7.3), 2.7 (2 H, m), 1.3 (24 H, s, broad), 0.88 (3 H, t, *J* 6.6).

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REFERENCES

1 H.O. House, *Modern Synthetic Reactions*, Benjamin, Menlo Park, 1972 (2nd edition), pp. 492 - 628 and 734 - 816.
2 L.M. Jackman, N.M. Szeverenyi, *J. Am. Chem. Soc.* **99** (1977), 4954; L.M. Jackman, B.C. Lange, *Tetrahedron* **33** (1977), 2737; D. Seebach, *Angew. Chem.* **100** (1988), 1685; *Angew. Chem. Int. Ed. Engl.* **27** (1988), 1624; G. Boche, *Angew. Chem.* **101** (1989), 286; *Angew. Chem. Int. Ed. Engl.* **28** (1989), 277; L.M. Jackman, T.S. Dunne, *J. Am. Chem. Soc.* **107** (1985), 2805.
3 H.D. Zook, W.L. Rellahan, *J. Am. Chem. Soc.* **79** (1957), 881; J.A. Miller, H.D. Zook, *J. Org. Chem.* **42** (1977), 2629; L.M. Jackman, B.C. Lange, *J. Am. Chem. Soc.* **103** (1981), 4494; J.S. DePue, D.B. Collum, *J. Am. Chem. Soc.* **110** (1988), 5524; J.C. Ellington, E.M. Arnett, *J. Am. Chem. Soc.* **110** (1988), 7778; J.A. Krom, A. Streitwieser, *J. Am. Chem. Soc.* **114** (1992), 8747.
4 R. Gompper, W. Schmidt, unpublished results; s.a. : W. Schmidt, diploma thesis, Universität München, 1966; R. Gompper, H.U. Wagner, *Angew. Chem.* **88** (1976), 389; *Angew. Chem. Int. Ed. Engl.* **15** (1976), 321; R. Gompper, H.H. Vogt, *Chem. Ber.* **114** (1981), 2866.
5 H.O. House, R.A. Auerbach, M. Gall, N.P. Peet, *J. Org. Chem.* **38** (1973), 514; E. Hirsch, S. Hünig, H.U. Reißig, *Chem. Ber.* **115** (1982), 3687.
6 W.J. LeNoble, H.F. Morris, *J. Org. Chem.* **34** (1969), 1969; H.D. Zook, J.A. Miller, *J. Org. Chem.* **36** (1971), 1112.
7 D. Seebach, T. Weller, G. Protschuk, A.K. Beck, M.S. Hoekstra, *Helv. Chim. Acta* **64** (1981), 716.
8 R.A. Jones, S. Nokkeo, S. Singh, *Synth. Commun.* **7** (1977), 195.
9 C.R. Hauser, F.W. Swamer, J.T. Adams, *Org. React.* **8** (1954), 59, spec. 70 - 96.
10 R. Noyori, I. Nishida, J. Sakata, *J. Am. Chem. Soc.* **105** (1983), 1598.
11 M. Schlosser, O. Desponds, R. Lehmann, E. Moret, G. Rauchschwalbe, *Tetrahedron* **49** (1993), 10175.
12 M. Schlosser, S. Strunk, *Tetrahedron* **45** (1989), 2649.
13 G.J. Heizwolf, H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas* **86** (1967), 807; H. Kloosterziel, J.A.A. van Drunen, *Recl. Trav. Chim. Pays-Bas* **89** (1970), 37.
14 G.-q. Shi, S. Cottens, S.A. Shiba, M. Schlosser, *Tetrahedron* **48** (1992), 10569; s.a.: G.-q. Shi, M. Schlosser, *Tetrahedron* **49** (1993), 1445.
15 *E.g.*, Y. Bessard, M. Schlosser, *Tetrahedron* **47** (1991), 1231; G.-q. Shi, S. Takagishi, M. Schlosser, *Tetrahedron* **50** (1994), 1129.
16 G.A. Olah, S. Kuhn, S. Beke, *Chem. Ber.* **89** (1956), 862.
17 F. Seel, J. Langer, *Chem. Ber.* **91** (1958), 2553.
18 M.E. Jung, R.B. Blum, *Tetrahedron Lett.* **18** (1977), 3791.
19 P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunoguès, *Tetrahedron* **43** (1987), 2075.
20 P. Duhamel, L. Hennequin, J.M. Poirier, G. Tavel, C. Vottero, *Tetrahedron* **42** (1986), 4777.
21 J. Iqbal, M.A. Khan, *Synth. Commun.* **19** (1989), 515.
22 K. Krohn, *Liebigs Ann. Chem.* **1981**, 2285.
23 G.-q. Shi, S. Cottens, S.A. Shiba, M. Schlosser, *Tetrahedron* **48** (1992), 10569.
24 J. P. Barnier, B. Garnier, C. Girard, J.M. Denis, J. Salaun, J.M. Conia, *Tetrahedron Lett.* **1973**, 1747.
25 H.H. Wasserman, R.J. Gambale, M.J. Pulwer, *Tetrahedron* **37** (1981), 4059.
26 H.J. Bestmann, W. Stransky, O. Vostrowsky, P. Range, *Chem. Ber.* **108** (1975), 3582.
27 H.J. Hagemeyer, D.C. Hull, *Ind. Eng. Chem.* **41** (1949), 2920.
28 D. Ladjama, J.J. Riehl, *Synthesis* **1979**, 504.
29 D. Swern, E.F. Jordan, *J. Am. Chem. Soc.* **70** (1948), 2334.

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