INVESTIGATION OF THE SYNTHESIS OF VERBENYL COMPOUNDS, EFFECTIVE ATTRACTANTS OF COCKROACH SPECIES, BY ACYLOXYLATION OF α-PINENE*

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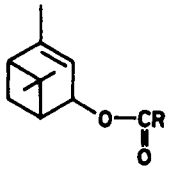
The synthesis of verbenyl acetate (*Ia*) and propionate (*Ib*) was investigated by acyloxylation of α-pinene with lead(IV) acetate (LTA), lead(IV) propionate (LTP), mercury(II) acetate (MA) and iodosobenzene diacetate (IBDA) in neutral and acidic medium. The neutral medium is better for the formation of *Ia* and *Ib*, because the acidic medium helps the opening of cyclobutane ring of α-pinene. These methods can be used for large scale preparation of insect attractants to cockroach species (*Blatella germanica*, *Blatella orientalis* and *Periplaneta americana*).

Verbenyl compounds are potent synthetic attractants to cockroach species (*Blatella germanica*, *Blatella orientalis*, and *Periplaneta americana*). The most potent representatives of them are the acetic and propionic acid esters of verbenol (*Ia* and *Ib*, respectively)[2].



Ia, R = CH_3
Ib, R = C_2H_5

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Verbenyl acetate (*Ia*) has been prepared by acyloxylation[2-4] of α-pinene (*II*; Scheme 1) by lead(IV) acetate[5]. The corresponding propionate (*Ib*) was formed from *Ia* by hydrolysis followed by acylation. Recently, we developed a new method for the preparation of *Ib* using lead(IV) propionate[6,7,11] for the oxidation of α-pinene[7]. This reaction was similar to the one previously used for the formation of *Ia* and gave excellent yield.

In connection with the synthesis of these insect attractants we have systematically studied the acyloxylation of α-pinene[8-10]; there are large differences among the results in this topic in the literature. Namely, how the yield of the reaction depends on the acyloxylating reagents and the pH of the reaction mixture. The reagents used were lead(IV) acetate (LTA), lead(IV) propionate[6,11-13] (LTP), mercury(II) acetate[14-17] (MA) and iodosobenzene diacetate[18-21] (IBDA).

RESULTS AND DISCUSSION

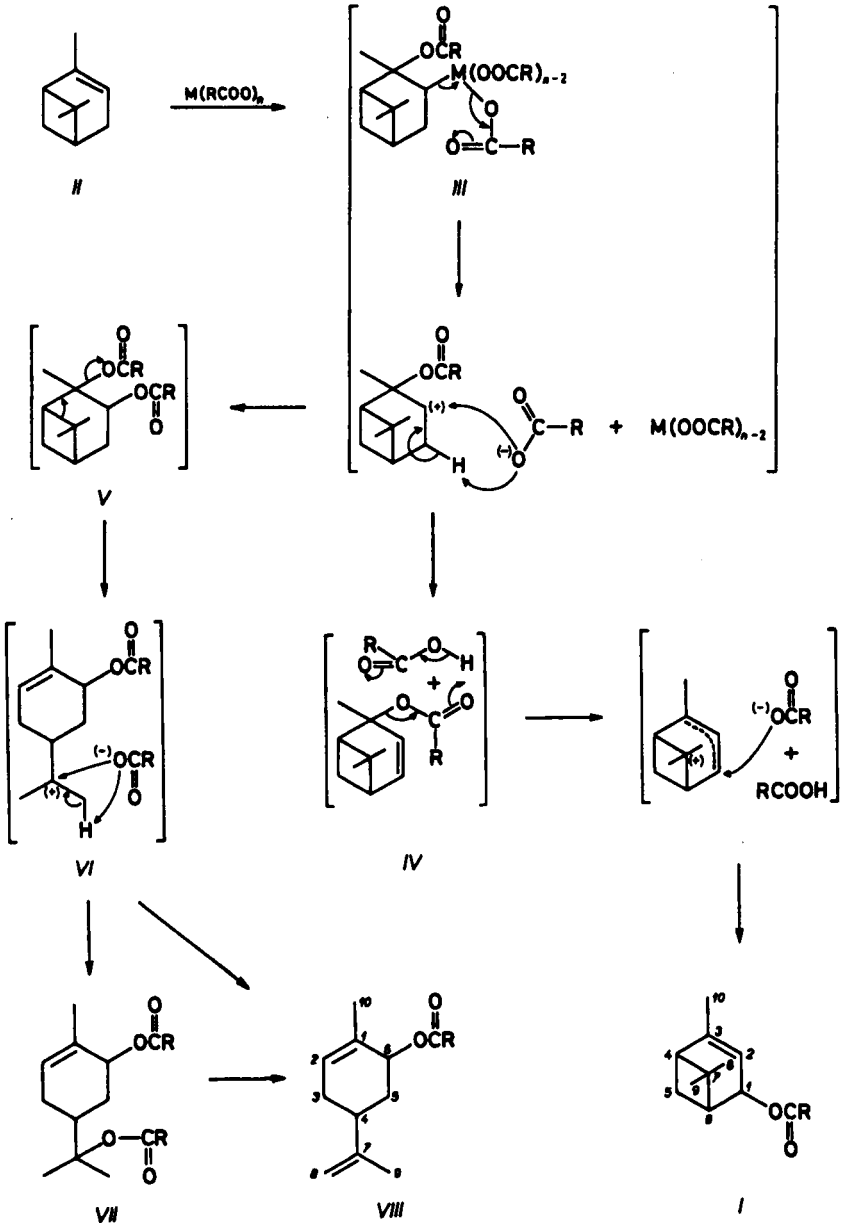
The reaction between α-pinene and LTA was carried out under a variety of reaction conditions (Tables I and II), in each case by the addition of the reagent to a stirred solution of the substrate. The reaction mixture was analysed by GC and ^{1}H, ^{13}C NMR (ref.[22]) and GC-MS spectroscopy. In every case the reaction afforded a mixture of two or more products (cf. Scheme 1).

In neutral medium, the main product was the desired verbenyl derivative (*Ia*) besides small amounts of carvyl (*VIIIa*), sobreryl (*VIIa*), and terpinyl (*XVa*) derivatives (Table I, entries 1 – 3). The relative amounts of these compounds were the function of the reaction time. After a shorter time, only compounds *VIIa* and *XVa* were detected as side products. After 24 h reflux compounds *VIIa* disappeared and small amount of *VIIIa* was observed.

TABLE I
Acyloxylation of α-pinene (*II*) in neutral medium

Entry	Reagent	Conditions	Conversion %	Product composition, %			
				I	*VII*	*VIII*	*XV*
1	LTA	1 h, reflux	90	60[a]	5	–	2
2	LTA	24 h, reflux	92	60[a]	–	3	3
3	LTA + HOAc	1 h, 65 °C 20 min, 20 °C	70	40[a]	10	–	–
4	LTP	1 h, reflux	92	90[b]	–	–	–
5	MA	24 h, reflux	30	2	6	–	–
6	IBDA	24 h, reflux	10	–	–	3	–

[a] Ratio of *cis*- and *trans-Ia*: 2/8; [b] ratio of *cis*- and *trans-Ib*: 1/9.



In formulae *I*, *III*–*VIII*: *a*, R = CH_3 *b*, R = C_2H_5

SCHEME 1

In the frame of this work we did not investigate thoroughly how depends on the *cis/trans* ratio of compounds *I*, *VII*, and *VIII* from the reaction conditions. It was claimed on the literature, LTA formed *trans*-verbenyl acetate (*Ia*) from α-pinene[2 - 4]. Analysing thoroughly the isolated *Ia* by GC and NMR, a mixture of *cis* and *trans* isomers of *Ia* was found. The ratio was 2/8 (*cis/trans*). The situation was the same in case of the formation of *Ib* but here, the ratio was 1/9.

In acidic medium, the desired verbenyl acetate (*Ia*) was obtained in poor yield (Table II, entries 1 – 3). When the reaction was affected at room temperature (entry 1) sobreryl acetate (*VIIa*) was the major product (38%), besides substantial amounts of *Ia* and *XVa* (26% and 10%, respectively). At higher temperature (entries 2 and 3) only trace amounts of *Ia* were obtained (5%), with the major product *VIIa* or *VIIIa*. The verbenyl propionate (*Ib*) was formed in higher yield than *Ia* in acidic medium, but in lower yield comparing to the results obtained in neutral medium. Rationalization of the above results can be based on earlier work by Wigberg et al.[9] and Whitham[4] (Scheme 1).

In neutral medium, initial electrophilic attack of LTA on the double bond of α-pinene (*II*) leads to intermediate *IIIa*, which decomposes with the loss of lead(II) acetate and acetic acid. The product *IVa* undergoes a fast acidmediated allylic rearrangement to afford the desired product *Ia*. Although intermediate *IVa* was isolated by Whitham[4], no trace of it was detected in our experiments. The rapid conversion to the product *Ia* due to higher temperature used may account for this observation.

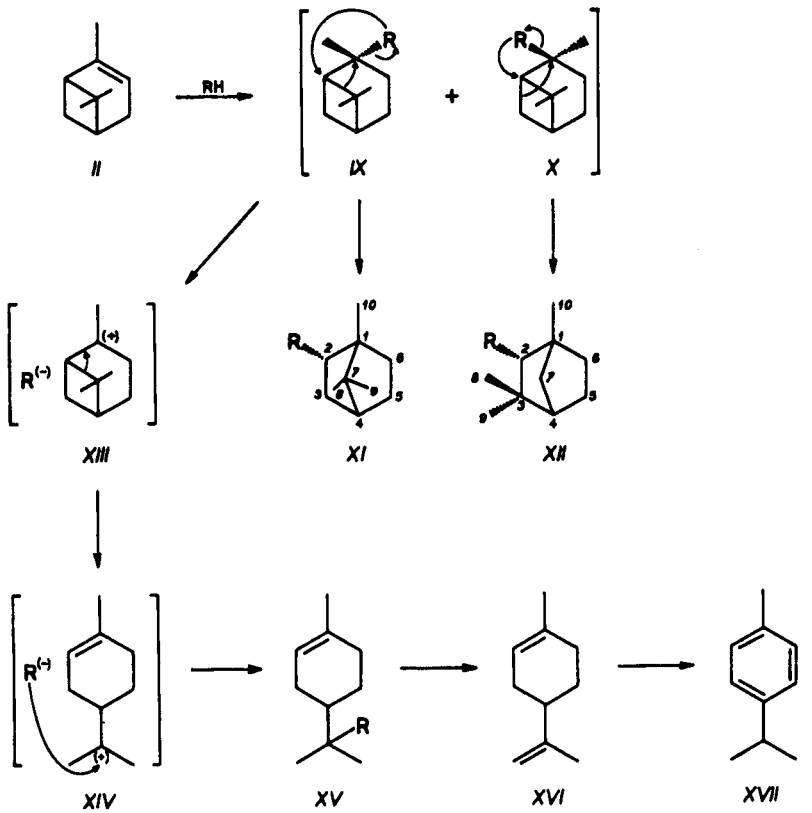
On the other hand, intermediate *IIIa* may decompose to diacetate *Va*, which then undergoes ring-opening reaction to produce intermediate *VIa*. The latter can either lose a proton or react with acetate ion to give two of observed products (*VIIIa* and *VIIa*, respectively).

TABLE II
Acyloxylation of α-pinene (*II*) in acidic medium

Entry	Reagent	Conditions	Conversion %	Product composition, %				
				I	*VII*	*VIII*	*XV*	*XVI*
1	LTA	24 h, 25 °C	80	26[a]	38[c]	3	10	–
2	LTA	1 h, reflux	85	5	41[c]	15[d]	16	–
3	LTA	24 h, reflux	90	5	8	40[d]	20	–
4	LTP	24 h, 25 °C	95	60[b]	20[e]	2	–	–
5	LTP	1 h, reflux	95	20[b]	25[e]	30[f]	10	–
6	MA	24 h, reflux	93	11	14[c]	31[d]	7	–
7	IBDA	24 h, reflux	100	–	8	41[d]	–	26

Ratio of *cis*- and *trans* isomers: [a] *Ia* 2/8; [b] *Ib* 1/9: [c] *VIIa* 2/8; [d] *VIIIa* 3/7; [e] *VIIb* 1/9; [f] *VIIIb* 1/9.

Under acidic condition, the only moderate yield of *Ia* is due to competing acid-accelerated reactions which probably occur as depicted in Scheme 2 (cf. refs[23 - 28]). Electrophilic addition of acetic acid to the double bond of α-pinene produces intermediate *XIIIa*. Then ring-opening of the latter takes place to afford cation *XIVa*, which is trapped by the acetate ion to yield compound *XVa*. A trace amounts of *XVa* were also detected in the acyloxylation reactions in neutral medium (Table I, entries 1 and 2), which is believed to result from this process initiated by acetic acid formed in the second step (*III* → *IV*).



In formulae *IX*–*XV*: *a*, R = OOCCH$_3$ *b*, R = OOCC$_2$H$_5$

SCHEME 2

With lead(IV) propionate[6 - 7] we observed the exclusive formation of the desired verbenyl propionate[7] (*Ib*) (Table I, entry 4) and the yield was excellent (82%). In acidic medium, the result was strongly dependent on the reaction temperature. At room temperature, the formation of *Ib* slightly dropped and substantial amounts of *VIIb* were

detected (Table II, entry 4). Heating at reflux in propionic acid, the reaction afforded mainly the sideproducts (*VIIb*, *VIIIb*, and *XVb*; Table II, entry 5).

In view of the similarity of the two oxidizing agents (LTA and LTP) the better result obtained with LTP in neutral medium may due to the higher stability of this reagent. The ring opening effect of propionic acid as solvent was smaller than acetic acid (Table III).

The suggested mechanism is supported by the products formed in the reaction of α-pinene with carboxylic acids (Table III)[23 - 28]. Although, the main product was *XVI*, but substantial amounts of *XV* were also detected. Here, three new products were also formed. Compounds *XI* and *XII* are the result of Wagner–Meerwein rearrangements[29 - 34] of intermediates *IX* and *X*, respectively. Furthermore, it should be no surprise that *XVII* was also formed during the long reflux period (several hours).

With MA and IBDA the oxidation of *II* was very slow and the conversion was very low in neutral medium and proceeded without significant formation of *Ia* (Table I, entries 5 and 6). In refluxing acetic acid, these reactions also gave a mixture of sideproducts in which compound *VIIIa* was the main product (Table II, entries 6 and 7).

The preliminary biological tests showed that the side products (*VII*, *VIII*, *XI*, *XII*, *XV* – *XVII*) exhibited significant synergetic effect to the verbenyl compounds. Full biological data will be published in due course.

Our results demonstrate that large scale preparation of verbenyl compounds can be achieved by acyloxylation of α-pinene in neutral medium. LTP and LTA introduce the acyloxy group into α-pinene without opening the cyclobutane ring in neutral medium. MA and IBDA do not react in such conditions. Acidic medium helps the migration of acyloxy group and the opening of cyclobutane ring. The monocyclic terpenoids formed can be acyloxylated easily by LTA, LTP, MA, and IBDA.

TABLE III
Reaction of α-pinene (*II*) with acids

Entry	Acid	Conditions	Conversion %	Product composition[a], %				
				XI	*XII*	*XV*	*XVI*	*XVII*
1	acetic	4 h, reflux	93	9	3	13	36	11
2	acetic	24 h, reflux	93	9	14	15	37	3
3	propionic	24 h, reflux	87	16	10	3	35	3

[a] The products contain more unidentified products, too. The amount of these compounds was icreased if the time of heating was longer.

EXPERIMENTAL

^{1}H NMR (100 and 400 MHz) and ^{13}C NMR (25.2 and 100.8 MHz) spectra were determined on a Varian XL-100 and XL-400 instrument using deuteriochloroform as solvent (Tables IV, V and VI). All signals are expressed by the ppm (δ-scale) downfield from tetramethylsilane used as an internal standard. The GC analysis were made by Perkin Elmer F22 instrument with CPSIL 5CB capillary column (50 m × 0.22 mm i.d.) and FID detector. Temperature of column: 100 °C for 4 min then 4 °C/min to 200 °C. Temperature of detector and injector: 200 °C. Carrier: N_2; 2.7 ml/min, split: 1 : 100 (Table VII). The mass spectra were measured on Hewlett–Packard 5985A instrument at 70 eV (Table VIII).

TABLE IV
^{1}H NMR data of compounds *I*, *VII*, *VIII*, *XI*, *XII*, *XV*, *XVI*, and *XVII*; chemical shifts in ppm (δ-scale), coupling constants (*J*) in Hz

Compound	Data
trans-Ia	5.37 brs, 2 H (H-1, H-2); 1.9 – 2.4 m, 3 H (H_B-5, H-4, H-6); 2.00 s, 3 H (CH_3C=O); 1.75 s, 3 H (H-10); 1.48 d, 1 H (H_A-5, *J* = 8); 1.35 s, 3 H (H-8 or H-9); 0.92 s, 3 H (H-8 or H-9)
cis-Ib	5.50 m, 1 H (H-1); 5.33 m, 1 H (H-2); 2.48 m, 1 H (H_B-5); 2.32 m, 1 H (H-6); 2.31 m, 2 H (H-2'); 2.00 m, 1 H (H-4); 1.74 m, 3 H (H-10); 1.01 s, 3 H (H-8); 1.40 m, 1 H (H_A-5); 1.13 m, 3 H (H-3'); 1.63 s, 3 H (H-9)
trans-Ib	5.34 dddq, 1 H (H-2, *J*(2,6) = 1.8; *J*(2,1) = 3.0; *J*(2,4) = 1.5; *J*(2,10) = 1.5); 5.355 ddq, 1 H (H-1, *J*(1,2) = 3.0; *J*(1,6) = 3.2; *J*(1,10) = 1.5); 2.31 q, 2 H (H-2', *J* = 7.5); 2.29 d, 1 H (H_B-5, *J* = 8.8); 2.23 dddd, 1 H (H-6, *J*(6,1) = 3.2; *J*(6,4) = 5.5; *J*(6,5A) = 4.8; *J*(6,2) = 1.8); 2.05 ddd, 1 H (H-4, *J*(4,2) = 1.5; *J*(4,5A) = 5.7; *J*(4,6) = 5.5); 1.74 dd, 3 H (H-10, *J*(10,1) = 1.5; *J*(10,2) ≈ 1.8); 1.45 ddd, 1 H (H_A-5, *J*(A,B) ≈ 8.8; *J*(5A,4) = 5.7; J(5A,6) = 4.8); 1.34 s, 3 H (H-9); 1.127 t, 3 H (H-3', *J* = 7.5); 0.92 s, 3 H (H-8)
trans-VIIa	5.74 m, 1 H (H-6); 5.25 m, 1 H (H-2); 2.06 s, 3 H (H-2'(C(6))); 1.95 s, 3 H (H-2''(C(7))); 1.70 brs, 3 H (H-10); 1.44 s, 6 H (H-8, H-9)
cis-VIIa	5.58 m, 1 H (H-6); 5.25 m, 1 H (H-2); 2.07 s, 3 H (H-2'(C(6))); 1.97 s, 3 H (H-2''(C(7))); 1.70 bs, 3 H (H-10); 1.44 s, 6 H (H-8, H-9)
trans-VIIIa	5.75 m, 1 H (H-6); 5.28 m, 1 H (H-2); 4.74 m, 2 H (H-8); 2.06 s, 3 H (CH_3C=O); 1.60 – 1.75 m, 6 H (H-9, H-10)
cis-VIIIa	5.60 m, 1 H (H-6); 5.28 m, 1 H (H-2); 4.74 m, 2 H (H-8); 2.06 s, 3 H (CH_3C=O); 1.60 – 1.75 m, 6 H (H-9, H-10)
XIa	4.92 ddd, 1 H (H-2, *J* = 10.0; 3.5; 2.0); 2.04 s, 3 H (H-2'); 0.83 s, 3 H (CH_3); 0.88 s, 3 H (CH_3); 0.91 s, 3 H (CH_3)
XIb	4.92 ddd, 1 H (H-2, *J* = 10.0; 3.5; 2.0); 2.32 q, 2 H (H-2', *J* = 7.5); 1.14 t, 3 H (H-3', *J* = 7.5); 0.83 s, 3 H (CH_3); 0.88 s, 3 H (CH_3); 0.91 s, 3 H (CH_3)
XIIa	4.39 d, 1 H (H-2, *J* = 1.8); 2.06 s, 3 H (H-2'); 1.10 s, 3 H (CH_3); 1.04 s, 3 H (CH_3); 0.79 s, 3 H (CH_3)
XIIb	4.38 d, 1 H (H-2, *J* = 1.8); 2.34 q, 2 H (H-2', *J* = 7.5); 1.15 t, 3 H (H-3', *J* = 7.5); 1.10 s, 3 H (CH_3); 1.04 s, 3 H (CH_3); 0.78 s, 3 H (CH_3)

TABLE IV
(*Continued*)

Compound	Data
XVa	5.38 m, 1 H (H-2); 1.95 s, 3 H (CH_3C=O); 1.64 brs, 3 H (H-10); 1.42 s, 3 H (CH_3); 1.44 s, 3 H (CH_3)
XVI	5.40 m, 1 H (H-2); 4.71 m, 2 H (H-8); 1.72 t, 3 H (H-9, J = 1.0); 1.64 m, 3 H (H-10)
XVII	7.11 m, 4 H (aromatic protons); 2.86 m, 1 H (H-7); 2.86 m, 1 H (H-7); 2.28 s, 3 H (H-10); 1.23 d, 6 H (H-8, H-9, J = 6.6)

Acyloxylation of α-Pinene (*II*) in Neutral Medium

Method A: To a stirred solution of α-pinene (*II*, 1.0 equiv.) in dry benzene (20 ml/ml α-pinene) was added lead(IV) acetate (LTA) or propionate (LTP; 1.0 equiv.) and the resulting mixture was stirred under conditions given in Table I. The cooled mixture was diluted with benzene (40 ml/ml α-pinene) and washed successively with water (10 ×), 5% $NaHCO_3$ (3 ×) and brine (2 ×). After drying ($MgSO_4$) the solution was concentrated in vacuo and the residue was purified by column chromatography (eluent: cyclohexane/acetone 10 : 2) (see Table I).

Using the toluene as solvent, the results were the same as above.

Method B: To a stirred solution of α-pinene (*II*, 1.0 equiv.) in dry benzene (or toluene; 5 ml/ml α-pinene) was added mercury(II) acetate (MA; 1.0 equiv.) and the resulting mixture was heated at reflux for 24 h.

TABLE V
^{13}C NMR data of compounds *I*, *VII*, *VIII*, *XI*, *XII*, *XV*, *XVI*, and *VII* (the skeleton), chemical shifts in ppm (δ-scale)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
trans-Ia	73.6	115.4	150.2	47.6	29.4	44.4	46.1	20.6	26.5	22.7
cis-Ib	75.2	115.7	149.5	47.6	35.5	45.5	41.5	22.6	26.7	22.7
trans-Ib	73.6	115.2	150.6	47.6	29.4	44.4	46.2	20.6	26.5	22.7
cis-VIIa	133.2	125.4	26.4	41.9	30.2	73.3	83.7	23.0	23.3	18.6
trans-VIIa	131.8	127.6	26.6	37.6	29.7	70.8	83.8	23.5	23.3	20.6
cis-VIIIa	132.9	125.9	30.8	40.3	34.0	73.2	148.2	109.4	20.5	18.6
trans-VIIIa	130.9	127.8	30.9	35.8	33.7	70.6	148.6	109.3	20.8	20.6
XIa	48.7	79.9	36.8	44.9	28.1	27.1	47.8	18.8	19.7	13.5
XIb	48.7	79.5	36.9	45.0	28.1	27.1	47.7	18.9	19.8	13.5
XIIa	48.2	86.2	39.4	48.4	25.8	26.6	41.4	29.7	20.0	19.4
XIIb	48.3	85.9	39.4	48.5	25.9	26.7	41.4	29.7	20.0	19.4
XVa	133.9	120.4	26.4	42.7	23.9	30.9	84.8	23.4	23.4	23.1
XVI	133.6	120.8	30.7	41.2	28.0	30.9	150.1	108.5	20.8	23.5
XVII	135.2	129.0	126.3	146.1	126.3	129.0	34.0	24.1	24.1	21.0

The cooled mixture was diluted with hexane (40 ml/ml α-pinene) and after filtration the filtrate was washed with 1M HCl (6 – 8 ×), 5% $NaHCO_3$ (2 – 3 ×, to neutral) and brine (2 ×). After drying ($MgSO_4$) the solution was concentrated in vacuo and the residue was purified by column chromatography (eluent: cyclohexane/acetone 10 : 2) (see Table I).

TABLE VI
^{13}C NMR data of compounds *I*, *VII*, *VIII*, *XI*, *XII*, and *XV* (the chain), chemical shifts in ppm (δ-scale)

Compound	C-1'	C-2'	C-3'	C-1''	C-2''
trans-Ia	170.5	21.3	–	–	–
cis-Ib	174.4	28.1	9.2	–	–
trans-Ib	174.4	28.0	9.2	–	–
cis-VIIa	170.9	21.1	–	170.2	22.4
trans-VIIa	170.9	21.3	–	170.2	22.3
cis-VIIIa	170.8	21.1	–	–	–
trans-VIIIa	170.8	21.3	–	–	–
XIa	171.2	21.2	–	–	–
XIb	174.5	27.9	9.3	–	–
XIIa	171.3	21.2	–	–	–
XIIb	174.6	27.8	9.4	–	–
XVa	170.4	23.3	–	–	–

TABLE VII
GC retention times (min) of compounds *I*, *II*, *VII*, *VIII*, *XI*, *XII*, *XV*, *XVI*, and *XVII*. For other conditions see Experimental

Compound	*t*	Compound	*t*
trans-Ia	12.7	*trans-Ib*	14.5
cis-Ia	12.4	*cis-Ib*	14.2
trans-VIIa	23.3	*trans-VIIb*	26.4
cis-VIIa	24.5	*cis-VIIb*	28.0
trans-VIIIa	14.3	*trans-VIIIb*	16.4
cis-VIIIa	15.1	*cis-VIIIb*	17.3
XIa	10.7	*XIb*	13.5
XIIa	9.9	*XIIb*	11.5
XVa	13.0	*XVb*	15.2
XVI	7.3	*XVII*	6.9
II	5.7		

Method C: To a stirred solution of α-pinene (*II*, 1.0 equiv.) in dry benzene (or toluene; 5 ml/ml α-pinene) iodosobenzene diacetate (IBDA; 1.0 equiv.) was added and the resulting mixture was heated at reflux for 24 h. The cooled mixture was diluted with hexane (100 ml/ml α-pinene) and water (50 ml/ml α-pinene). The precipitate formed was filtered off and the aqueous layer was extracted with hexane. The combined organic layers was washed with 10% NaOH, 1M HCl and brine. After drying ($MgSO_4$) the solution was concentrated in vacuo and the residue was purified by column chromatography (eluent: cyclohexane/acetone 10 : 2) (see Table I).

TABLE VIII
Mass spectra of compounds *I*, *VII*, *VIII*, *XI*, *XV*, *XVI*, and *XVII*, *m/e* (%)

Compound	Data
Ia	57 (32), 77 (8), 91 (24), 109 (18), 119 (100), 134 (14), 152 (0.2), 194 (0.2)
Ib	39 (22), 41 (28), 43 (34), 53 (13), 57 (49), 65 (14), 77 (37), 79 (20), 82 (16), 91 (61), 92 (11), 93 (38), 94 (12), 95 (11), 105 (19), 109 (24), 119 (100), 134 (11), 152 (19), 208 (0.2)
cis-VIIa	43 (21), 93 (15), 109 (31), 119 (100), 134 (39), 152 (22), 194 (1)
cis-VIIb	40 (18), 43 (17), 57 (58), 91 (20), 92 (17), 105 (10), 107 (22), 109 (14), 117 (26), 119 (11), 121 (12), 132 (71), 133 (27), 135 (64), 150 (100), 163 (10), 191 (37), 206 (17)
trans-VIIa	43 (17), 59 (4), 79 (4), 92 (4), 93 (14), 94 (5), 108 (4), 109 (19), 119 (100), 134 (48), 135 (9), 137 (4), 151 (11), 194 (0.3)
trans-VIIb	41 (11), 43 (19), 57 (100), 67 (9), 77 (12), 79 (15), 83 (10), 91 (19), 93 (33), 94 (28), 95 (17), 96 (10), 107 (12), 108 (32), 109 (32), 119 (70), 134 (24), 135 (23), 137 (13), 152 (32), 209 (12), 211 (1)
cis-VIIIa	39 (21), 41 (28), 43 (100), 55 (20), 77 (17), 79 (18), 84 (91), 91 (35), 92 (22), 93 (20), 109 (51), 119 (50), 134 (25), 152 (27)
cis-VIIIb	39 (11), 41 (13), 57 (40), 65 (9), 77 (19), 79 (17), 91 (100), 92 (36), 93 (23), 105 (27), 108 (14), 109 (33), 117 (10), 119 (65), 133 (33), 134 (23), 135 (15), 152 (29), 206 (4)
trans-VIIIa	43 (100), 55 (22), 77 (23), 79 (21), 84 (88), 91 (50), 92 (28), 93 (30), 109 (78), 119 (66), 134 (20), 152 (49), 194 (0.5)
trans-VIIIb	41 (12), 57 (35), 77 (14), 79 (10), 91 (30), 92 (12), 93 (20), 109 (17), 119 (100), 134 (19), 152 (2), 208 (1)
XIa	41 (18), 43 (43), 55 (13), 67 (15), 69 (11), 77 (10), 79 (12), 80 (11), 81 (9), 91 (11), 92 (11), 93 (45), 95 (100), 108 (19), 109 (13), 110 (9), 121 (42), 136 (31), 154 (8), 196 (2)
XVa	43 (16), 67 (9), 77 (9), 79 (12), 91 (16), 92 (11), 93 (51), 107 (12), 121 (100), 136 (78), 137 (13), 139 (9), 181 (2)
XVI	53 (18), 67 (72), 68 (100), 77 (18), 79 (31), 80 (13), 81 (11), 91 (21), 92 (22), 93 (72), 94 (25), 107 (21), 121 (22), 136 (19)
XVII	51 (4), 63 (7), 65 (14), 89 (7), 91 (63), 119 (100), 134 (27)

Acyloxylation of α-Pinene (*II*) in Acidic Medium

To a stirred solution of α-pinene (*II*, 1.0 equiv.) in acetic or propionic acid (10 ml/ml α-pinene) the proper acyloxylation reagent (LTA, LTP, MA or IBDA; 1.0 equiv.) was added and the resulting mixture was stirred under conditions which are given in Table II. The cooled mixture was diluted with hexane (50 ml/ml α-pinene) and water (50 ml/ml α-pinene). The aqueous layer was extracted with hexane and the combined organic extracts were neutralized by washing with 10% NaOH, water and brine. After drying ($MgSO_4$) the solution was concentrated in vacuo and the products were separated by column chromatography (eluent: cyclohexane/acetone 10 : 2) (see Table II).

Reaction of α-Pinene (*II*) with Acids

α-Pinene (*II*) was dissolved in the proper acid (10 ml/ml α-pinene, Table III) and the resulting solution was heated at reflux for 4 – 24 h. The cooled mixture was diluted with hexane (100 ml/ml α-pinene) and neutralized by washing with water, 10% NaOH and brine. After drying ($MgSO_4$) the solution was concentrated in vacuo and the products were separated by column chromatography (eluent: cyclohexane/acetone 10 : 2) (see Table III).

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