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Study of Photochemical Addition of Acyl Radical to Electron-Deficient Olefins

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Abstract: *The photochemical addition of acyl radical to electron-deficient olefins is studied. The scope of the reaction, the mechanism, the role that molecular oxygen plays, the influence of steric effects, and the side reaction that take place are discussed. The reaction was carried out using a range of electron-withdrawing substituents (ketones, amides, lactones, nitrile and esters) with good yields of the corresponding photoadduct in all cases.*

INTRODUCTION

Addition of aldehydes to electron-deficient double bonds in the presence of radical initiators is well known[1,2]. In a previous report, we found this reaction to be an efficient and mild process leading to 1,4-dicarbonyl compounds[3]. The best yields were obtained with substrates bearing an unsubstituted conjugated double bond, which can be converted to the corresponding methylketone in quantitative yield.

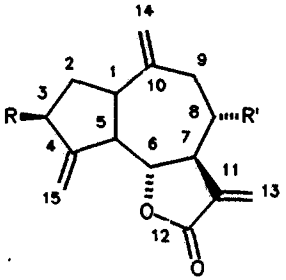
In the course of our studies towards the synthesis of sesquiterpene lactones bearing an oxetane ring, we found this reaction particularly useful for the synthesis of natural oxetane sesquiterpene lactones, starting with the corresponding α-methylene-γ-lactone[4,5].

In this paper we discuss the scope of the reaction, the mechanism, the role that molecular oxygen plays, the influence of steric effects, and the side reactions that take place. The ketones **6**, **9**, **12**, the esters **7**, **9**, **10**, **11**, **15**, the amide **8**, and nitrile **13**, illustrate the scope of the reaction.

RESULTS AND DISCUSSION

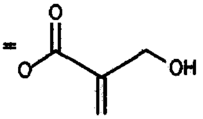
The reaction was initially carried out using a Hanovia reactor with a Pyrex filter and a medium pressure mercury lamp. Dehydrocostuslactone (**1**) gave two major compounds, **17** and **18** in a yield of 40 and 23% respectively. The structure of the methylketone **17** is confirmed by its EM [m/z 274 (M^+)] and ^{1}H-NMR [δ 2.60 (1H, ddd, $J_{7,11}=J_{11,13'}=J_{11,13'}=$ 6 Hz, C_{11}-H); 2.19 (3H, s, CO-C$\underline{H}_3$)]. The β-orientation of the chain was deduced from the $J_{7,11}$ value, which is clearly smaller than 10 Hz. It is noteworthy that we have obtained only one stereoisomer in all sesquiterpene lactones studied[4,5].

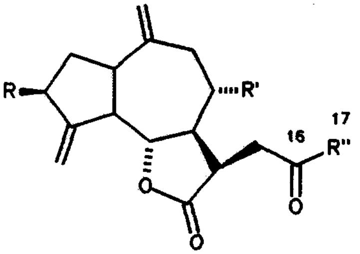
Compound **18** is the photoreduction product of **17**. This was confirmed when treatment of **17** with sodium borohydride yielded **18**. The ^{1}H NMR spectra of **18** showed a resonance assigned to H-6 which



1 R=R'=H
2 R=H; R'=OH
3 R=OH; R'=Metacr
4 R=O–TBDMS; R'=MetacrTBDMS
5 R=H; R'=MetacrTBDMS

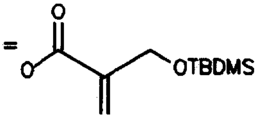
Metacr =

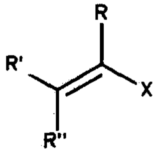




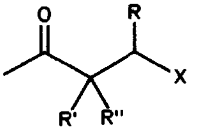
17 R=R'=H; R''= CH_3
19 R=R'=H ; R''= Phenyl
20 R=H; R'=OH ; R''= CH_3
22 R=O–TBDMS; R'=MetacrTBDMS ; R''= CH_3
23 R=H; R'=MetacrTBDMS; R''= CH_3

MetacrTBDMS =

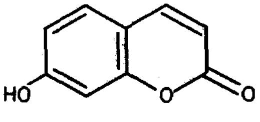




6 X=$COCH_2CH_3$; R=R'=R''=H
7 X=COOBu; R=R'=R''=H
8 X=$CONH_2$; R=R'=R''=H
9 X=$COCH_3$; R=R''=H; R'=CH_3
10 X=$COOCH_3$; R=CH_3; R'=R''=H
11 X=$COOCH_3$; R=R'=CH_3; R''=H
12 X=$COCH_3$; R=H; R'=R''=CH_3
13 X=CN; R=H; R'=R''=CH_3
15 X=$COOCH_3$; R=R''=H; R'=Phenyl



24 X=$COCH_2CH_3$; R=R'=R''=H
25 X=COOBu; R=R'=R''=H
26 X=$CONH_2$; R=R'=R''=H
27 X=$COCH_3$; R=R''=H; R'=CH_3
28 X=$COOCH_3$; R=R'=CH_3; R''=H
30 X=$COCH_3$; R=H; R'=R''=CH_3
31 X=CN; R=H; R'=R''=CH_3



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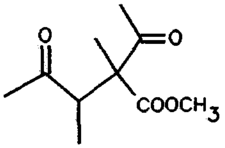

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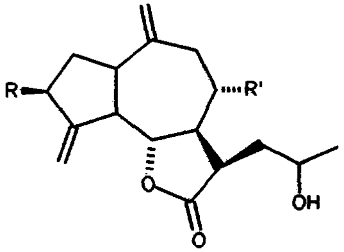


18

appeared doubled [δ3.98 and 4.03; $J_{5,6}=J_{6,7}=$ 10 Hz]. This is consistent with the presence of epimers at C-16. The photoaddition reaction with this particular class of substrates shows very high regioselectivity since no photoaddition to the unconjugated double bond was detected.

The use of a Ni(II) and Co(II) filter in solution restricts the radiation at about 3000 Å. This provides cleaner reactions without the formation of photoreduction products as well as fewer byproducts. Under these conditions the methylketone **17** was obtained in 70% yield.

The reaction was also carried out using double bond systems bearing different electron-withdrawing groups as substituent, such as: ketones, amides, lactones, nitrile and esters. We obtained the corresponding photoadduct in all cases. The introduction of one or two methyl groups as substituent at the β-position from the electron-withdrawing group resulted in a decrease of the yield. These results suggest that the steric effects play an important role in this reaction. In cases of double substitution at β position longer reactions and oxygen rich atmospheres were required in order to increase the yields of the photoaddition products.

Molecular oxygen is an important triplet quencher[6] that can interact with excited triplet states of other molecules, via either energy or single electron transfers. It is sometimes possible for molecular oxygen to assist in an intersystem crossing step going from a singlet to a triplet state[7]. When we reacted benzaldehyde, which has a higher intersystem crossing yield with dehydrocostuslactone (**1**) in the absence of oxygen it produced the corresponding phenylketone (**19**) at 13 position (Entry 4). We believe triplet oxygen acts to facilitate intersystem crossing. In accordance with this hypothesis, the photoaddition practically does not occur when α,β-unsaturated substrates are irradiated under N_2 atmosphere. The decreasing yields obtained at temperatures higher than 25°C are used may be related to a low solubility of the oxygen in the aldehyde.

It is worth noting that the photoaddition of a substrate bearing a methyl substituent at the position α to the electron-withdrawing group either did not give the corresponding 1,4-dicarbonyl compound or the yield was very low (Entry 15). This behaviour can be explained by assuming that the transition state structure has a charge distribution as shown in Scheme 1[8]. Thus, an alkyl substitution at the α-position may cause an raise in the activation energy of such a transition state.

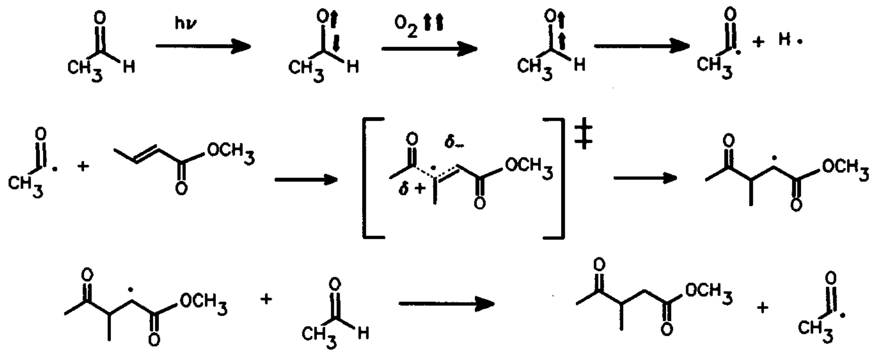
Substrates bearing a double bond conjugated to a benzene ring failed to give detectable amounts of the photoadduct, perhaps as a consequence of the loss of conjugation in the reaction product.

The reaction of methyl tiglate (**11**) gave product **28** as a diastereoisomeric mixture as shown by its ^{1}H-NMR spectrum (double signals in a 5:4 ratio). Furthermore, the double addition product **29** was isolated, in 15% yield. The mass spectrum [m/z 200 (M^+)] shows the addition of two acyl radicals. The ^{1}H-NMR spectrum shows double resonances in c.a. 2:1, indicating a diastereoisomeric mixture of photoadducts. In the region of acyl protons we observe two groups of singlets , δ2.23 and 2.21, for the most intense ones, and δ2.22 and 2.20. In a similar fashion, the signals assigned to the methyl group at the α-position to the ester moiety appear as two singlets δ1.50 and 1.56. The higher stability of the radical intermediate, with a methyl group in β position and the high concentration of acyl radicals allow to get this compound. This reaction is clearly competitive with the radical chain reaction mechanism.

Reaction of phoron (**14**) yields **32**, **33**, **34**, **35** and **36** (Scheme 2). Compound **34** (4%) was produced by an anomalous addition of the acyl radical at α position to the unsaturated carbonyl moiety. Its ^{1}H-NMR shows signals for the methyl groups on the double bond and the vinylic proton. It also shows

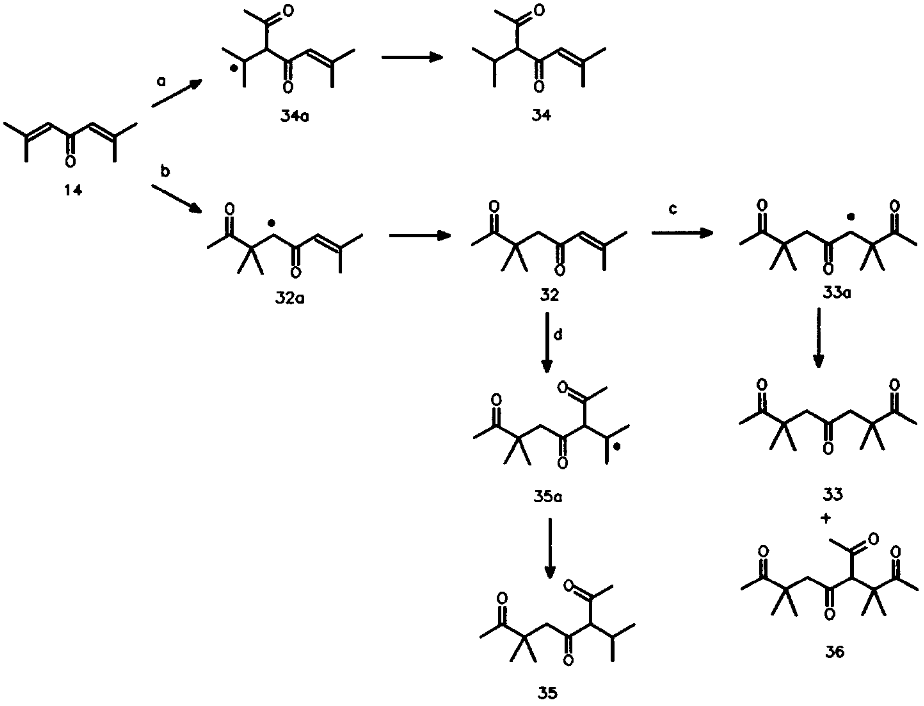
Table I

Substrate	Amount	Medium	t (h)	T (°C)	Products (% Yield)	Note
1	0.5 mmol	air	0.75	25	**17** (40), **18** (23)	without filter
1	1 mmol	air	1	25	**17** (70), **18** (8)	
1	1 mmol	N_2	1	25	**17** (<5)	
1	0.35 mmol	N_2	0.5	25	**19** (30)	10 mL Benzaldehyde
2	1 mmol	air	1	25	**20** (63), **21** (7)	
3	0.5 mmol	air	0.5	25	Complex mixture	Double addition
4	1.75 mmol	O_2	3	25	**22** (40)	
5	1.75 mmol	O_2	3	25	**23** (40)	
6	5 mmol	air	2.5	25	**24** (95)	
7	5 mmol	air	2.5	25	**25** (99)	
8	5 mmol	air	2.5	25	**26** (93)	
9	5 mmol	air	3	25	**27** (81)	
10	5 mmol	air	3	25	No reaction	
10	5 mmol	N_2	3	25	No reaction	
11	5 mmol	air	3	25	**28** (16)	
11	5 mmol	O_2	8	25	**28** (52), **29** (15)	
11	5 mmol	O_2	1	50	**28** (<5)	
11	5 mmol	O_2	2	0	**28** (<5)	
12	5 mmol	air	3	25	**30** (10)	
12	5 mmol	O_2	8	25	**30** (52)	
13	5 mmol	air	3	25	**31** (6)	
13	5 mmol	O_2	8	25	**31** (27)	
14	1 mmol	air	3	25	**32** (30), **33** (31)	
14	1 mmol	O_2	8	25	**32** (27), **33** (39), **34** (4), **35** (16), **36** (5)	
14	1 mmol	O_2	1	60	**32** (<1)	
15	1 mmol	air	2.5	25	No reaction	
15	1 mmol	N_2	2.5	25	No reaction	
16	1 mmol	air	2.5	25	No reaction	



Scheme 1

a singlet (δ2.17) assigned to the methylketone, and a doublet (δ1.07, J = 7.4 Hz) assigned to the isopropyl unit. The reaction is made possible due to the fact that the intermediate radical formed via this pathway is stabilized by the presence of two methyl groups. These results show that the presence of alkyl substituents at the double bond gives, in addition of the β-photoadduct (major), mixtures of compounds, in contrast to the non-substitued substrates.



Scheme 2

Compound **35** (16%) was produced by addition to both double bonds, one at the α position and the other at the β position. The ^{1}H NMR spectrum shows signals that integrate for 3H each as follows: two singlets (3H) δ2,15 and 2.18 assigned to the added acyl radicals; two doublets [3H, J=6.6 Hz] at δ0.89 and 0.88; and two more singlets δ1.18 and 1.19. In this case the ratio of products between the two coupling pathways, *c* and *d* (Scheme 2), is 2:5. It is higher in comparison with the ratio between the coupling pathways *a* and *b*, 1:10, because the difference in the stability of radicals **33a** and **35a** is less than the difference between the radicals **32a** and **34a**.

Compound **36** is a minor compound (5%) produced by a double addition to a double bond and a single addition to the other double bond at β position. All data and secondary products obtained are in agreement with the mechanism shown in Scheme 1.

Analogous secondary products were detected by gas chromatography in the reaction of mesityl oxide (**12**) and 3,3-dimethylacrylonitrile (**13**) in very small amount, but they could not be isolated. This suggests that α addition is possible on other systems where the β position is disubstituted. Otherwise the reaction has few number of side products in most cases, and they are always minor compounds. The only compound produced in significant amount was **35** (16%), a 1,3,6-triketone.

The synthetic potentiality of this route to obtain 1,4-difunctionalized compounds has been succesfuly used in the preparation of the natural oxetane lactones, subexpinnatine C[4], clementein and clementein B[5], showing a high degree of regio- and stereoselectivity in all cases.

EXPERIMENTAL SECTION

Materials and General Procedures: Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer in film. ^{1}H NMR and ^{13}C NMR spectra were made on Varian Gemini-200 and Varian FT-80 spectrometers, using $SiMe_4$ as internal standard. Mass spectra were recorded on a VG 12-250 spectrometer using 70 eV. The reaction were monitored by GC on a HP 589A chromatograph with a SUPELCO 2-5303 fused silica capillary column.

Chromatographic separations were made on silica gel (Merck), employing hexane, ethyl acetate mixtures as eluent. The photochemical reaction were performed in a modified Hanovia reactor with a Pyrex jacket as filter. The capacity of the reactor is 125 ml, and 100 ml of acetaldehyde were used. The reaction mixture was irradiated with a 125 W Hg/medium pressure lamp. The filter solution contained 46 g of $NiSO_4{\cdot}6H_2O$ and 14 g of $CoSO_4{\cdot}7H_2O$

Photochemical Reaction: 5 mmol of the substrate in freshly distilled acetaldehyde (100 ml) was placed in a Hanovia reactor and irradiated for 3-8 hours. Vigorous stirring was maintained. The reaction mixture was concentrated under reduced pressure with addition of small amounts of cyclohexane in order to remove the acetic acid produced. The residue was chromatographed on silica gel to give the corresponding 1,4-dicarbonyl compound.

For experimental details of compounds **17**, **18**, **25**, **28**,and **33** see ref 3; **20** and **21** see ref 4; and **22** and **23** see ref 5. For experimental details of reactions see Table I.

2,5 Heptadione (24): **IR** (film) cm^{-1}: 1707. **EM** m/z (rel. int.): 128 $[M]^+$ (1), 113 $[M\text{-}CH_3]^+$ (0.9), 99 $[M\text{-}CH_2CH_3]^+$ (96), 57 $[CH_3COCH_2]^+$ (66), 43 $[CH_3CO]^+$(100), etc. **^{1}H-NMR** (80 MHz, $DCCl_3$) δ:

2.67 (br s, 4H, CH_3CH_2, C_4-H_2), 2.5 (q, 2H, $J_{6,7}$ = 7 Hz, C_6-H_2), 2.18 (s, 3H, C_1-H_3), 1.05 (t, 3H, $J_{6,7}$ = 7 Hz, C_7-H_3).

Levulinamide (26): IR (KBr) cm^{-1} : 3342, 3211 (N-H), 1653 (broad, CO ketone, CO amide). **EM** m/z (rel. int.) 115 $[M]^+$ (2), 97 $[M-18]^+$ (46), 43 $[CH_3CO]$ (100), etc. ^{1}**H-NMR**, (80 MHz, py-d_6) δ: 8.13 (br s, 1H, N-H), 7.60 (br s, 1H, N-H^1), 2.84 (s br., 4 H, C_2-H_2, C_3-H_2), 2. 12 (s, 3H, C_5-H_3).

Methyl 3-methyl-levulinate (27): IR (film) cm^{-1} : 1770 sh (COOMe), 1705 (CO-Me). **EM** m/z (rel. int.) 144 $[M]^+$ (2), 129 $[M-CH_3]^+$ (5), 113 $[M-CH_3O]^+$ (35), 59 $[CO_2CH_3]^+$ (50), 43 $[CH_3CO]^+$ (100). ^{1}**H-NMR**, (80 MHz, $DCCl_3$) δ: 3.63 (s, 3H, O-CH_3), 2.90 (m, 1H, C_3-H), 2.62(d, 2H, $J_{2,3}$= 7Hz, C_2-H_2), 2.20 (s,3H, C_5-H_3), 1.15 (d, 3H, $J_{3,6}$= 7Hz, C_6-H_3).

Methyl 2-acetyl-2,3-dimethyllevulinate (29).: EM m/z (rel. int.): 200 $[M]^+$ (0.2), 169 $[M-CH_3O]^+$ (5), 168 $[M-CH_3OH]^+$ (8), 157 $[M-CH_3CO]^+$ (5), 143 $[M-CH_3CO-CH_3]^+$ (7), 125 $[M-CH_3CO-CH_3OH]^+$ (11). ^{1}**H-NMR**, (200 MHz, $DCCl_3$) δ : 3.73 and 3.70 (s, 3H, O-CH_3), 3.42 and 3.40 (c, 1H, $J_{3,9}$= 7.5 Hz, C_3-H), 2.23 and 2.22 (s,3H, C_7-H_3), 2.21 and 2.20 (s,3H, C_5-H_3), 1.56 and 1.50 (s,3H, C_2-CH_3), 1.16 (d,34, $J_{3,9}$= 7.5Hz, C_3-CH_3).

3,3-Dimethyl-2,5-hexadione (30).: IR (film) cm^{-1}: 1700 (CO-CH_3). **EM** m/z (rel. int.): 142 $[M]^+$ (4), 127 $[M-CH_3]^+$ (0.4), 100 $[M-C_2H_2O]^+$ (15), 85 $[M-C_3H_5O]^+$ (34), 43 $[CH_3CO]^+$ (100), etc. ^{1}**H-NMR** (80 MHz, $DCCl_3$) δ: 2.97 (s,2H, C_4-H_2), 2.37 (s,3H, C_1-H_3), 2.28 (s,3H, C_6-H_3), 1.32 (s,6H,C_7-H_3, C_8-H_3).

3,3-Dimethyl-4-oxo-pentanonitrile (31): IR (film) cm^{-1}: 2250 (CN), 1701 (CO-CH_3). **EM** m/z (rel. int.): 125 $[M]^+$ (4), 110 $[M-CH_3]^+$ (0.2), 82 $[M-CH_3CO]^+$ (3), 43 $[CH_3CO]^+$ (100), etc. ^{1}**H-NMR** (80 MHz, $DCCl_3$) δ: 2.48 (s,2H, C_2-H_2), 2.15 (s, 3H, C_5H_3), 1.32 (s,6H, C_6-H_3, C_7-H_3).

3,3,7-Trimethyl-6-octene-2,5-dione (32): IR (film) cm^{-1}: 1699 (CH_3CO), 1681 (CO), 1616 (C=C). **EM** m/z (rel. int.): 182 $[M]^+$ (1), 167 $[M-CH_3]^+$ (0.2), 140 $[M-C_2H_2O]^+$ (10), 83 $[M-C_6H_{11}O]^+$ (100), 43 $[CH_3CO]^+$ (17), etc. ^{1}**H-NMR** (80 MHz, $DCCl_3$) δ: 6.1 (s br, 1H, C_6-H), 2.82 (s, 2H, C_4-H_2), 2.23 (s, 3H, C_1-H_3), 2.13 (s,3H, C_7-CH_3), 1.90 (s, 3H, C_7-CH_3), 1.18 (s,6H,C_3-CH_3).

3-Isopropyl-6-methyl-5-heptene-2,4-dione (34): IR (film) cm^{-1} : 1727 ($COCH_3$), 1690 (CO α,β-unsaturated), 1610 (C=C). **EM** m/z (rel. int.): 182 $[M]^+$ (0.1), 167 $[M-CH_3]^+$ (0.1), 140 $[M-C_2H_2O]^+$ (0.5), 139 $[M-CH_3CO]^+$ (0.3), 125 $[M-C_2H_2O-CH_3]^+$ (2), 99 $[C_6H_{11}O]^+$ (5), 83 $[C_5H_7O]^+$ (100), 43 $[CH_3$-$CO]^+$ (14). ^{1}**H-NMR** (200 MHz, $DCCl_3$) δ: 6.05 (br s, 1H, C_5-H, 3.61 (m, 1H, C_3-H), 2.17 (s,3H, C_1-H_3), 2.12 (s, 3H, C_6-CH_3), 1.88 (s, 3H, C_6-CH_3), 1.07 (d, 3H, $J_{1',2'}$= 7.4, $C_{2'}$-H_3, $C_{3'}$-H_3).

3-Isopropyl-6,6-dimethyl-2,4,7-octatrione (35): IR (film) cm^{-1} : 1690 (CO). **EM** m/z (rel. int.): 208 $[M-H_2O]^+$ (3), 184 $[M-C_2H_2O]^+$ (3), 183 $[M-CH_3CO]^+$ (1), 169 $[M-C_2H_2O-CH_3]^+$ (23), 127 $[M-C_6H_{11}O]^+$ (100), 99 $[C_6H_{11}O]^+$ (31), 43.4 $[CH_3$-$CO]$ (97), 43 $[C_3H_7]^+$ (67), etc. ^{1}**H-NMR**, (200 MHz, $DCCl_3$) δ: 3.354 (d,1H, J= 10Hz,C_3-H), 2.77 (s, 2H, C_5-H_2), 2.18 (s, 3H, C_1-H_3), 2.15 (s, 3H, C_8-H_3), 1.19 (s, 3H, C_6-CH_3), 1.18 (s, 3H, C_6-CH_3), 0.89 (d, 3H, J= 6.6 Hz, C_{11}-CH_3), 0.89 (d, 3H, J= 6.6Hz, $C_{1'}$-CH_3).

4-Acetyl-3,3,7,7-tetramethyl-2,5,8-nonatrione (36).: IR (film) cm^{-1}: 1696 (CO). **EM** m/z (rel. int.): 226 $[M-C_2H_2O]^+$ (0.3), 225 $[M-CH_3CO]^+$ (1), 211 $[M-C_2H_2O-CH_3]^+$ (0.2), 210 $[M-CH_3CO-CH_3]^+$ (0.5), 183 $[M-C_5H_9O]^+$ (7), 127 $[C_7H_{11}O_2]^+$ (100), 99 $[C_6H_{11}O]^+$ (45), 43 $[CH_3CO]^+$ (78). ^{1}**H-NMR** (80 MHz, $DCCl_3$) δ: 4.20 (s,1H, C_4-H), 2.86 (s, 2H, C_6-H_2), 2.12 (br s, 9H, CO-CH_3), 1.22 (s, 6H, C_3-CH_3), 1.15 (s, 6H, C_7-CH_3).

13-Benzoylcostuslactone (19): IR (film) cm^{-1}: 1960, 1980 (aromatic ring), 1770-1690 (γ-lactone, arylketone), etc. **EM** m/z (rel. int.): 336 $[M]^+$ (1), 105 $[C_6H_5CO]^+$ (100). ^{1}**H-NMR** (200 MHz, $DCCl_3$)

δ: 7.91 (dd, 2H, $J_{2',4'}$= 1.5Hz, $J_{2',3'}$= 7Hz, $C_{2'}$-H, $C_{6'}$-H), 7.5 (br dd, 1H, $J_{2',4'}$= 1.5Hz, $J_{3',4'}$= $J_{4',5'}$= 7Hz, $C_{4'}$-H), 7.41 (ddd, 2H, $J_{2',3'}$= $J_{3',4'}$= 7 Hz, $J_{3',5'}$= 1.5Hz, $C_{3'}$-H, $C_{5'}$-H), 5.17 (d, 1H, $J_{3,15}$= 1.5Hz, C_{15}-H), 5.00 (dd, 1H, $J_{3,15'}$= 1.5 Hz, C_{15}-H'), 4.79 (br s, 1H, C_{14}-H), 4.71 (br s, C_{14}-H'), 3.96 (dd, 1H, $J_{5,6}$= $J_{6,7}$= 9 Hz, C_6-H), 3.51 (dd, 1H, $J_{11,13}$= 4Hz, $J_{13,13'}$= 18Hz, C_{13}-H), 3.19 (dd, 1H, $J_{11,13'}$= 6 Hz, $J_{13,13'}$= 18Hz, C_{13}-H'), 2.90-2.71 (m, 2H, C_1-H, C_5-H), 2.54-2.13 (m,5H, C_3-H_2, C_9-H_2,C_{11}-H), 2.03-1.75 (m, 4H, C_2-H_2, C_7-H, C_8-H). **^{13}C-NMR** (20 MHz, $DCCl_3$) δ: 195.7 (C-16), 176.7 (C-12), 15O.6 (C-4), 148,8 (C-10), 135,5 (C-1'), 127.8 (C-2', C-4'), 127.2 (C-3', C-5'), 132.5 (C-6'), 111.0 (C-15), 108.4 (C-14), 84.5 (C-6), 51.0 (C-5), 47.0 (C-15), 108.4 (C-14), 84.5 (C-6), 51.0 (C-5), 47.0 (C-1), 46.3 (C-7), 41.7 (C-13)*, 36.6 (C-11)*, 36.4 (C-9), 31.6 (C-2), 29.3 (C-8), 29.1 (C-3). * These signals may be interchanged.

Reduction of 17: 60 g of 17 were dissolved in 6 ml of methanol. Sodium borohydride (12 mg) was added in portions at 25°C with continuous stirring over a period of 4 minutes. After 1 min. the reaction mixture was then quenched with water. The solution was extracted with ethyl acetate, obtaining, after prep. TLC (Hexane:Ethyl acetate, 7:3), 40 mg of 18.

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