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REACTION OF α,β-UNSATURATED ALDEHYDES WITH HYDROGEN PEROXIDE CATALYSED BY BENZENESELENINIC ACIDS AND THEIR PRECURSORS

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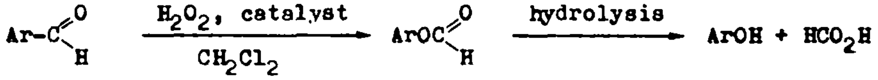
Abstract: Oxidation of α,β-unsaturated aldehydes with hydrogen peroxide catalysed by benzeneseleninic acids and their precursors has been investigated. Bis 2-nitrophenyl diselenide has proved to be the most effective catalyst. The major products resulting from the oxidation are vinyl formates (a) which on hydrolysis give saturated aldehydes or ketones (g) having the carbon chain shortened by one carbon atom, compared with the starting aldehydes. The minor products are formyloxyoxiranes (b), α-hydroxycarbonyl (e) and α-formyloxycarbonyl (f) compounds with the carbon chain shortened by one carbon atom. Carbonyl compounds d, formally derived from an oxidative fission of the carbon-carbon double bond, have been also isolated. Diformyloxy (4c) and formyloxyacetoxy phenylmethane (5c) have been isolated when cinnamaldehyde (4) or 1-phenyl-2-formyloxypropane (5a) were oxidized, respectively. Possible mechanisms of formation of these products are discussed. Similar products resulted when α,β-unsaturated aldehydes were oxidized with organic peroxy acids.

The usefulness of organoselenium compounds as reagents and catalysts for organic synthesis is a current interest of many laboratories[1-4]. Among dozens reports concerned in this problem, several ones[5-10] pointed out that hydrogen peroxide in the presence of organoseleninic acids or their precursors reacts similarly to organic peroxy acids. It led us to synthetically valuable oxidative transformation of aromatic aldehydes 1 into phenols 3 via formates 2[11,12], as schown in Scheme 1.



$$\underset{1}{\text{Ar-CHO}} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{H}_2\text{O}_2\text{, catalyst}} \underset{2}{\text{ArOCHO}} \xrightarrow{\text{hydrolysis}} \underset{3}{\text{ArOH}} + \text{HCO}_2\text{H}$$

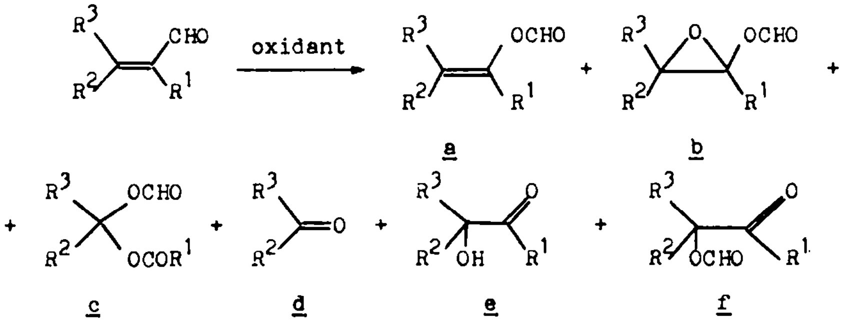
1 2 3

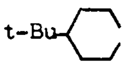
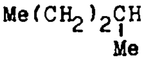
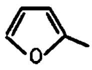
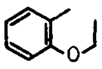
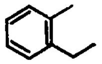
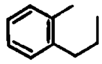
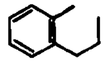
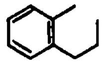
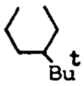
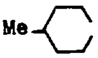
Scheme 1

The similar reaction of several α,β-unsaturated ketones with organic peroxy acids, resulting in esters of corresponding enols, was also reported[13]. Only two cases of the Baeyer-Villiger oxidation of α,β-unsaturated aldehydes were mentioned in the literature[14,15]. Citral[14] and 2-ethyl-2-hexenal[15], when treated with carbonylperoxy acids, underwent transformation to corresponding vinyl formates which were then epoxidized.

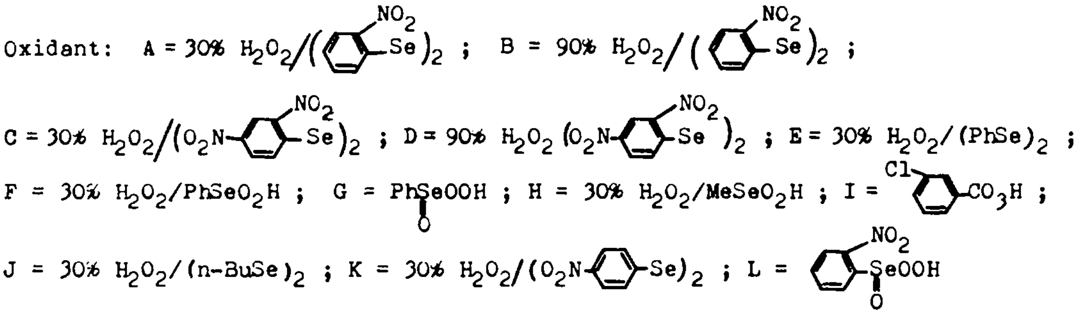
The behaviour of α,β-unsaturated aldehydes towards organic peroxy acids and catalytically activated hydrogen peroxide remains generally unknown. α,β-Unsaturated aldehydes are an important class of organic compounds and they are available by a variety of methods. That is why we considered that their behaviour under conditions of the Baeyer-Villiger reaction deserves more detailed investigation. The results would be valuable for organic synthesis and might offer a better understanding of the oxidative properties of hydrogen peroxide activated by organoseleninic acids.

Our initial experiments involved oxidation of nine selected α,β-unsaturated aldehydes, 4-12, with various oxidants (A-L) shown in Scheme 2.



	R^1	R^2	R^3
4	H	Ph	H
5	Me	Ph	H
6	H	Ph	Ph
7	H	$n-C_7H_{15}$	H
8	H	n-Pr	n-Pr
9	H	Ph	Me
10	H		
11	H	1-Naphtkyl	H
12	H		
13	H	Me	Ph
14	Me	Ph	Ph
15	H	 $\mathrm{Me(CH_2)_2}\underset{\mathrm{Me}}{\mathrm{CH}}$	H
16	H	$n-C_6H_{13}$	Me
17	Me		
18	H		H
19			H
20			H
21			H
22			Me
23			Ph
24		$(-CH_2-)_3$	Ph
25		$(-CH_2-)_4$	Ph
26		$(-CH_2-)_5$	Ph
27			Ph
28	Me	1-Naphthyl	H
29	H	2-Naphthyl	H
30	H	$(-CH_2-)_5$	
31	H	$(-CH_2-)_6$	
32	H		

Scheme 2



The reaction was carried out in CH_2Cl_2 at room temperature and controlled by TLC. Depending on the substrate, reaction time, concentration of H_2O_2 and the method of working up the reaction mixture, various products were isolated. In most cases products were separated by column chromatography on silica gel. The results are given in Table 1.

Table 1. Results of the oxidation of α,β-unsaturated aldehydes with various oxidants

Aldehyde	Oxidant	Reaction time h	Products, Yield % a	b	d	e	other
4	A	32	a	-	-	-	4g, 63
	A	165	22	-	26	-	4c, 7
	B	24	28	-	19	-	4c, 12
	C	28	a	-	-	-	4g, 53
	D	18	32	-	23	-	-
	E	54	68[b]	-	-	-	-
	F	48	63[b]	-	-	-	-
	G	53	68[b]	-	-	-	-
	H	173[c]	42[d]	-	-	-	-
5	A	128	85	-	-	-	-
	C	96	78	-	-	-	-
	D	18	79	-	-	-	-
	I	125	25	-	21	-	5, 45
	I[e]	125	41	-	24	-	5, 21
6	A	63	66	-	16	13	-
	D	15	67	-	14	18	-
	D	50	57	-	17	25	-
	E	123	42	-	29	25	-
	G	48	26	-	-	-	6, 68
	I	80	29	-	-	5	6, 62
	J	144[c]	73	-	15	10	-
	K	250	17	-	-	-	6, 81
	L	13	92	-	-	5	-
7	A	190	52	-	-	-	7, 11
	B	17	23	23	-	-	-
	L	33	34	-	-	-	7, 11
8	A	33	64	17	-	-	-
	I[e]	39	29	-	-	31	8, 7
9	A	15	73	-	<1	12	9, 7
	A	20	69	-	10	-	-
	C	20	67	-	8	17	9, 5
10	A	14	60	-	21	-	10, 7
	C	9	26	-	50	16	-
11	A	25	72	-	-	-	11, 8
	I[e]	31	54	-	-	-	11, 33
12	A	19	39	25	-	-	-
	C	16	<1	2	19	-	-

[a] reaction mixture was hydrolysed to d,

[b] product was isolated by distillation,

[c] reaction did not proceede to completion,

[d] product was isolated by distillation and purified by column chromatography,

[e] two-fold excess of the oxidant was used.

Vinyl formates a were formed as the major products in fairly good yields. The data obtained shown that oxidation of α,β-unsaturated aldehydes with hydrogen peroxide actiwated with bis(2-nitrophenyl) diselenide (oxidant A and B) afforded vinyl formates a in the best yields. Organic peroxy acids and hydrogen peroxide activated by other diselenides and organoseleninic acids were less effective xidants. When oxidants other than A and B were used, the reaction stopped frequently, the unreacted aldehydes were isolated and the yields of the main products were lower.

The subsequent experiments, involving oxidation of twenty different α,β-unsaturated aldehydes, 13-32 were performed with hydrogen peroxide in the presence of catalytic amount of bis(2-nitrophenyl) diselenide. The results are summarized in Table 2.

Table 2. Results of the oxidation of α,β-unsaturated aldehydes with 30% H_2O_2 (A) and 90% H_2O_2(B) activated with bis(2-nitrophenyl) diselenide

Aldehyde	Oxidant	Reaction time h	Products, Yield %				
			a	b	d	f	other
13	A	22	60	-	7	-	13,5
14	A	192	87	-	-	-	14,9
	B	18	92	-	-	-	-
	B	41	90	-	8	-	-
15	A	174	45	-	-	-	15,12
	B	19	20	20	-	-	-
16	A	22	52	10	-	-	-
17	A	123	71	17	-	-	-
	B	24	70	20	-	-	-
18	A	27	53[a]	-	-	-	-
19	A	24	59	-	-	-	-
20	A	22	70	-	-	-	-
21	A	97	40	-	-	20	21,5

Aldehyde	Oxidant	Reaction time h	Products, Yield %				
			a	b	d	f	other
22	A	168	17	-	-	69	-
	B	9	4	-	10[b]	75	-
	B	33	-	-	17[b]	78	-
23	A	170	66	-	-	25	-
	B	23	18	-	15[b]	62	-
24	A	34	<1	-	-	60	-
	B	22	-	-	26[b]	46	-
25	A	105	67	13	-	-	-
26	A	124	69	-	-	-	26,12
27	B	11	74	7	-	-	-
	B	34	60	8	12[b]	-	27e,11
28	A	79	94	-	-	-	-
	B	28	83	-	-	-	-
29	A	33	62	-	-	-	-
30	A	23	61	6	-	-	30,8
31	A	23	38	-	13	-	-
32	A	32	52	11	-	-	-

[a] Isolated by distillation

[b] Keto acid d/h

Again the major products of the oxidation are vinyl formates (a), except aldehydes 22 and 24 which afforded upon oxidation corresponding α-formyloxyketones 22f and 24f, respectively, in good yield.

The minor products (see Table 1 and 2) were formyloxyoxiranes b, aldehydes or ketones d, α-hydroxyaldehydes or α-hydroxyketones e or their formates f. When cinnamaldehyde was oxidized, rather unexpected product was isolated i.e. diformyloxyfenylmethane 4c. The same product was isolated when 2-phenyl-1-formyloxyethylene 4a was oxidized with oxidant B. Similar product, i.e. formyloxyacetoxyphenylmethane 5c was isolated in the case of oxidation of 1-phenyl-2-formyloxypropene 5a with oxidant B (see Table 3).

The oxidation did not stop on the step of vinyl formate as a rule, but some following steps took place only under more severe conditions (90% H_2O_2, prolonged reaction time). To get better insight in the overall process of oxidation, we treated several vinyl formates with 90% H_2O_2 in the presence of bis(2-nitrophenyl) diselenide. The results of these experiments are summarized in Table 3.

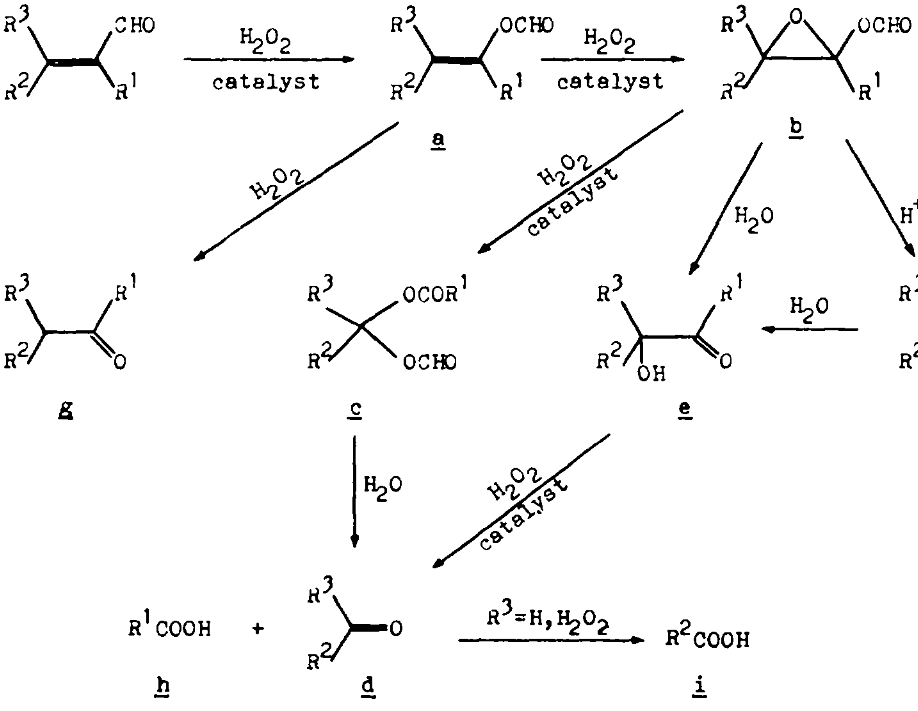
Table 3. Results of the oxidation of vinyl formates with 90% H_2O_2 activated with bis(2-nitrophenyl) diselenide

Vinyl formate	Reaction time h	Products, Yield % b	c	d	e	f	other	Vinyl formate	Reaction time h	Products, Yield % b	c	d	e	f	other
4a	18	-	18	-	-	-	4a,5 [a]	17a	42	36	-	38	-	-	17a,23
5a	72	-	8	-	-	20	5a,43 [a]	25a	46	16	-	34[b]	-	-	-
6a	26	-	-	70	24	-	-	27a	47	66	-	20[b]	-	-	-
9a	47	-	-	60	9	-	9a,12	30a	2	16	-	-	-	-	30a,14

[a] Small amount of benzoic acid was isolated

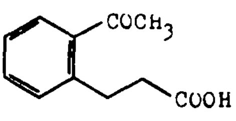
[b] Keto acid d/h

On the basis of experimental results (Table 1-3) we were able to sketch an overall scheme of transformations taking place during oxidation of α,β-unsaturated aldehydes with activated hydrogen peroxide (Scheme)3 .

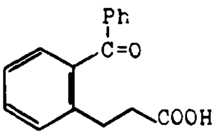


Scheme 3

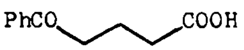
Recently[16], we have proved that aromatic diselenides are oxidized with hydrogen peroxide to seleninic acids which are subsequently transformed into peroxyseleninic acids resposible for the observed oxidative transformations. The mechanism of formation of vinyl formates from α, β-unsaturated aldehydes under action of peroxcarboxylic acids and peroxyseleninic acids schould be similar to the mechanism of the Baeyer-Villiger oxidation of aromatic aldehydes, aromatic ketones and alicyclic ketones[17-20] with peroxycarboxylic acids. The final oxidation products depend on the pattern of substitution of the parent unsaturated aldehyde. Oxidation of the β-disubstituted α,β-unsaturated aldehydes (R^1=H, R^2,R^3≠H) terminates in ketones d. One cannot exclude further oxidation of ketones d but we did not isolate any product of such oxidation. Mono-β-substituted aldehydes (R^1=R^3=H, R^2≠H) are oxidized as far as to carboxylic acids i, but formation of these acids is a very slow process. The final products of oxidation of trisubstituted aldehydes (R^1,R^2,R^3≠H) are ketones d and acids h. This is clearly exemplified by oxidstion of aldehydes 22, 23, 24, 25 and 27 where corresponding keto acids 22d/h, 23d/h, 24d/h, 25d/h and 27d/h were isolated.



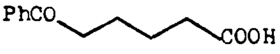
22d/h



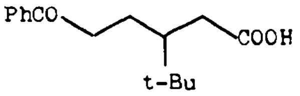
23d/h



24d/h

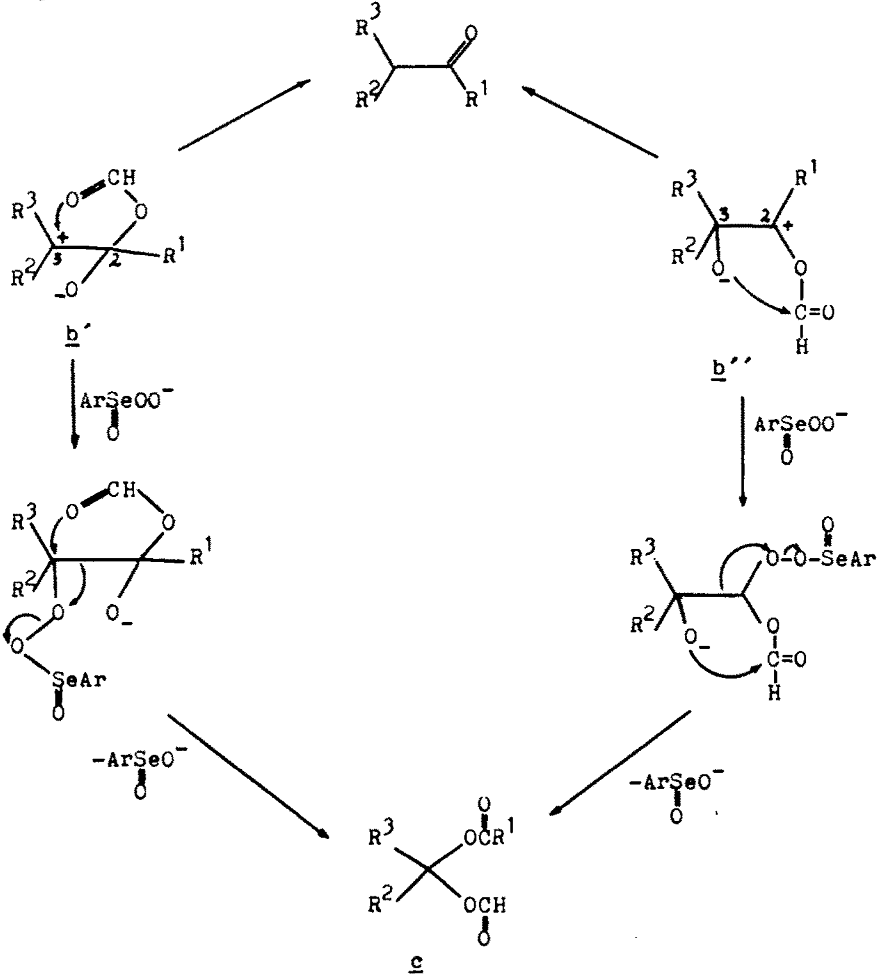


25d/h



27d/h

Ketones d and acids h (or keto acids d/h) could be formed by two possible routes. First of them involves hydrolysis of 2-formyloxyoxiranes b to α-hydroxycarbonyl compounds e which would be oxidized to d and h. α-Hydroxycarbonyl compounds d could also result from hydrolysis of α-formyloxycarbonyl compounds f. Independent experiments showed that α-hydroxyaldehydes e underwent oxidation with oxidant A to ketones d. For example 6e and 9e were oxidized to benzophenone (6d) and acetphenone (9d), respectively, though their reactivities were very different. Thus, 6d was obtained quantitatively after 20 h whereas 9d only in moderate yield after 60 h of reaction with oxidant A. Other experiments have shown that α-formyloxyketones f are resistant towards oxidation conditions applied, therefore the possibility of their transformation into ketones d via compounds c can be neglected. On the low reactivity of α-formyloxyketones f indicates the fact that ketones 22f and 24f were the major products when aldehydes 22 and 24 were oxidized. The second possible route to ketones d and acids h involves hydrolysis of diacyloxymethanes c. These compounds were isolated in two cases (4c and 5c) and it was found that they undergo hydrolysis very easily. Diacyloxymethanes c were probably formed in other cases but due to their hydrolytic instability they could not be isolated. They could be the major precursors of frequently isolated aldehydes and ketones d. α-Formyloxyketones f result from a rearrangement of 2-formyloxyoxiranes b. Such rearrangement is wel known in the case of 2-acetoxyoxiranes[21-25]. It is catalysed by acids or can be rought about by elevated temperature only. This rearrangement consists in opening of the oxirane ring and migration of the formyloxy group. There are two possible modes of the oxirane ring opening indicated by formula b′ and b′′ in Scheme 4. When the mode b′′ operates, a positive charge on the carbon atom 2 is stabilized by the formyloxy group, and as a consequence this mode is favoured against the mode b′. In the of 2-acetoxyoxiranes having aliphatic substituents only, it has been proved that the mode b′′ operates[22]. On the other hand, when R^2 either R^3 or both are the aromatic groups, the mode b′ would be favoured. In this case a positive charge on the carbon atom 3 is stabilized due to the interaction with the aromatic ring. Now the oxygen atom of the carbonyl group acts as nucleophile towards the positively charged carbon atom 3. We isolated α-formyloxyketones d having aromatic substituents only (R^2=Ar), sometimes in quite good yields. That means that they are formed earlier than α-formyloxyketones having aliphatic substituents (R^2,R^3= aliphatic or H) only, and this fact implies that the mode b′ operates in the cases under discussion.



Scheme 4

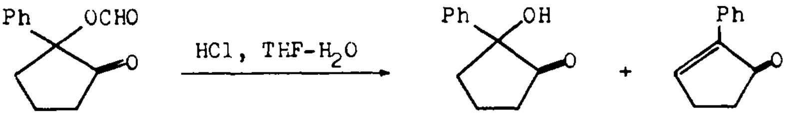
Diacyloxymethanes c are formed as a result of two rearrangements. One of them is migration of the formyloxy group, discussed above, and the second one is the rearrangement pertinent to the Baeyer-Villiger oxidation. For the whole process we propose the mechanism as shown in Scheme 4. Arylperoxyseleninic acid or its anion acts as a nucleophile towards 2-formyloxyoxirane b. Again, two modes of the oxirane ring opening are possible, b′ and b′′. The attachment of the arylperoxyseleninic anion and detachment of arylseleninic anion leaves the positively charged oxygen atom and the negatively charged formerly oxirane oxygen atom and that would result in the observed bond reorganization. Another route to diacyloxymethanes c consist in the oxidation of α-formyloxyketones f ($R^1 \neq H$) and α-formyloxyaldehydes f ($R^1 = H$). However due to resistance of α-formyloxyketones against oxidation, this route should be ruled out for the 5c formation, but it must not be true for the 4c formation. We had no α-formyloxyaldehyde to check its reactivity under applied conditions but α-hydroxyaldehydes e are oxidized rather slowly to the carbonyl compounds d. There is no reason to suppose that α-formyloxyaldehydes are more reactive than α-hydroxyaldehydes.

Vinyl formates a are reasonably stable compounds, they do not hydrolyse during the reaction and isolation. Upon acidic or basic hydrolysis under mild conditions, they gave corresponding saturated aldehydes or ketones g (Table 4).

Table 4. Results of the hydrolysis of vinyl formates a to aldehydes or ketones g

Vinyl Formate	Reaction medium	Reaction time h	Product yield %	Vinyl Formate	Reaction medium	Reaction time h	Product yield %
4a	$Et_2O/H_2O/NaHCO_3$	31	87	20a	$THF/H_2O/HCl$	7	98
5a	$THF/H_2O/HCl$	7	88	21a	- " -	30	76
6a	- " -	15	62	25a	- " -	31	96
7a	- " -	23	94	26a	- " -	30	58
8a	- " -	24	65	27a	- " -	49	72
10a	- " -	10	84	28a	$EtOH/H_2O/HCl$	22	92
11a	$EtOH/H_2O/HCl$	22	90	30a	$THF/H_2O/HCl$	23	61
14a	$THF/H_2O/HCl$	48	94	31a	- " -	26	74
15a	- " -	26	57	35a	- " -	22	57
16a	- " -	26	86				

Thus, oxidation of α,β-unsaturated aldehydes with H_2O activated by bis(2-nitrophenyl) diselenide and hydrolysis of resulting vinyl formates can be utilized for synthesis of some saturated aldehydes or ketones. α-Formyloxyketones f and 2-formyloxyoxiranes b gave upon hydrolysis with HCl in the EtOH-H_2O or THF-H_2O mixture α-hydroxycarbonyl compounds e. 2-Formyloxy-2-phenylcyclopentanone 24f gave upon acidic hydrolysis a mixture of two compounds: α-hydroxyketone 24e and 2-phenyl-2-cyclopentenon 33.



24f 24e, 40% 33, 26%

EXPERIMENTAL

Capillary m.ps and b.ps are uncorrected. ^{1}H-NMR spectra were recorded on a Tesla 100 MHz apparatus. IR spectra were obtained on a Perkin-Elmer 621 spectrophotometer.

Bis(2-nitrophenyl), bis(4-nitrophenyl) and bis(2,4-dinitrophenyl) diselenides were obtained by reacting lithium diselenide in THF with 2-nitrochlorobenzene, 4-nitrochlorobenzene and 2,4-dinitrochlorobenzene, respectively. The preparation of phenylperoxyseleninic and 2-nitroperoxybenzeneseleninic acids and other organoselenium compounds was described previously[16,26,27]. α,β-Unsaturated aldehydes not commercially avaiable were prepared according to established synthetic procedures. The formulas, physicochemical and spectral data of all compounds obtained are listed in Table 5.

Oxidation of cinnamaldehyde 4 with H_2O_2 in the presence of various activators. To a vigorously stirred solution of 4 (13.2 g, 0.1 mol) in dichloromethane (100 ml), bis(2-nitrophenyl) diselenide (1.5 g, 3.7 mmol) and 30% H_2O_2 (25 ml, 0.22 mol) were added. The mixture was stirred at room temperature untill all aldehyde was consumed (TLC). The solid was filtered off, washed with dichloromethane and water. The filtrate was transferred to a separatory funel and the layers separated. The organic layer was washed with water, 5% aq. $NaHCO_3$, 10% aq. $NaHSO_3$, again with water and dried over Na_2SO_4. The solvent was evaporated in vacuo, the residue was dissolved in ethyl ether (100 ml), water (100 ml) and $NaHCO_3$ (10 g, 0.12 mol) were added and the mixture was vigorously stirred at room temperature for 31 h. The organic layer was separated, washed with water and dried over Na_2SO_4. Ether was evaporated and phenylacetic aldehyde 4g was distilled at reduced pressure, b.p. 92°C/20 mm, yield 7.5 g (63%).

In another experiment, a solution of 4 (4.0 g, 30 mmol) in dichloromethane (30 ml), bis(2-nitrophenyl) diselenide (0.45 g, 1.1 mmol) and 90% H_2O_2 (2.7 ml, 90 mmol) were vigorously stirred at room temperature. When cinnamaldehyde disappeared (TLC), the mixture was filtered off, the solid was washed with water and dichloromethane and the layers were separated.

The organic layer was washed three times with water and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel using light petroleum (40-60°C) - dichloromethane mixture (7:3 v/v) as an eluent. 2-Phenylvinyl formate 4a (1.22 g, 28%), diformyloxyphenylmethane 4c (0.60 g, 19%) were obtained.

Oxidation of 4 (13.2 g, 0.1 mol) in dichloromethane (100 ml) with 30% H_2O_2 (25 ml, 0.22 mol) in the presence of other diselenides (3.5 mmol) or seleninic acids (7.0 mmol) was carried out in similar manner. The crude product was purified by distillation (106°C/15 mm) giving pure 4a in yields indicated in Table 1. The pure 2-phenylvinyl formate solidified in the refrigerator and remained solid at about 5°C.

Oxidation of α,β-unsaturated aldehydes. General procedure. The mixture of aldehyde (15 mmol), dichloromethane (20 ml), bis(2-nitrophenyl) diselenide (0.2 g, 0.5 mmol) and 30% H_2O_2 (5 ml, 43 mmol) or 90% H_2O_2 (1.5 ml, 50 mmol) was vigorously stirred at room temperature for appropriate time (Table 1 and 2). The reaction mixture was filtered off, the solid was washed with water and dichloromethane and the layers were separated. The organic layer was washed three times with water and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel using a mixture of light petroleum (40-60°C) with ethyl ether as an eluent. The same procedure was applied when peroxy acids (18 mmol) were used as oxidants, in this case the reaction was carried out in dry dichloromethane (30 ml). The above procedure was applied for oxidation of vinyl formates (Table 4) and other substrates with H_2O_2 in the presence of bis(2-nitrophenyl) diselenide.

Hydrolysis of vinyl formates b. To the solution of vinyl formate b (10 mmol) in THF (30 ml) or ethanol (25 ml), water (5 ml) and concentrated HCl (0.5 ml) were added. When the mixture was not homogenous, an additional amount of organic solvent was added and the homogenous solution was allowed to stand at room temperature till all vinyl formate disappeared (TLC). Water was added and product was extracted with ethyl ether. The extract was washed with 5% aq. $NaHCO_3$, then with saturated aq. NaCl, and dried over Na_2SO_4. The solvent was evaporated and crystalline products were purified by recrystallization, and liquid ones by column chromatography on silica gel using light petroleum (40-60°C) - ethyl ether as an eluent. Other hydrolysable compounds were hydrolysed in the similar manner.

Table 5. Physicochemical and spectroscopic data of the oxidation product of α,β-unsaturated aldehydes

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm) TMS	Molecular formula^a or other data
4a	b.p. 106/15	1723	6.55 (d, 1H, J=12Hz, ArCH=); 7.38 (s, 5H, ArH); 8.01 (d, 1H, J=12Hz); 8.11 (s, 1H, OCHO)^b	$C_9H_8O_2$ (148.2)
4c	b.p. 139/20^c	1740	7.32-7.58 (m, 5H, ArH); 7.82 (s, 1H, $-\underline{\mathrm{CH}}\begin{smallmatrix}\diagup \mathrm{O}-\\ \diagdown \mathrm{O}-\end{smallmatrix}$); 8.02 (s, 2H, CHO)	$C_9H_8O_4$ (180.2)
4d=5d	b.p. 179-180	-	-	lit.[28] b.p. 178-185°C
4g	b.p. 92/20	-	-	DNPH^d m.p. 121°C lit.[29] m.p. 121°C
5a	b.p. 101/13	1752 1730	2.02 (s, 3H, CH_3); 6.20 (s, 1H, ArCH=); 7.20 (m, 5H, ArH); 8.02 (s, 1H, OCHO);	$C_{10}H_{10}O_2$ (162.2)
5c	oil^{c,e}	1753 1734	2.00 (s, 3H, CH_3); 7.35 (m, 5H, ArH); 7.73 (s, 1H, $-\underline{\mathrm{CH}}\begin{smallmatrix}\diagup \mathrm{O}-\\ \diagdown \mathrm{O}-\end{smallmatrix}$); 8.00 (s, 1H, OCHO)	$C_{10}H_{10}O_4$ (194.2)
5f	oil	1737 1719	2.05 (s, 3H, CH_3); 6.10 (s, 1H, $\mathrm{ArCH}{<}$); 7.33 (m, 5H, ArH); 8.11 (s, 1H, OCHO)	$C_9H_{10}O_3$ (166.2)

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm TMS)	Molecular formula^a or other data
5g	b.p. 101/15	-	-	Lit.[30] b.p. 98°C/13 DNPH m.p. 156°C Lit.[31] m.p. 154-155°C
6a	b.p. 120/0.3	1728	6.70-6.75 (m, 10H, ArH); 7.94 (s, 1H, =$\underline{\text{CH}}$OCHO); 8.06 (s, 1H, CHO$\underline{\text{CH}}$O)	$C_{15}H_{12}O_2$ (224.3)
6d=14d	m.p. 50 (hexane)	-	-	Lit.[28] m.p. 49-51°C
6e	m.p. 56 (hexane)	-	-	Lit.[32] m.p. 52-53°C SC^t m.p. 242°C Lit.[33] m.p. 243°C
6g	oil	-	-	DNPH m.p. 148°C Lit.[34] m.p. 147°C
7a	b.p. 101/13	1728	0.85 (t, 3H, J=6Hz, CH_3); 1.28 (broad s, 10H, -CH_2-); 1.90-2.10 (m, 2H, -$\underline{CH_2}$-CH=); 5.36-5.64 (m, 1H, -CH=); 7.13 (d, 1H, J=12Hz, $\underline{\text{CH}}$OCHO); 7.98 (s, 1H, OCHO)	$C_{10}H_{18}O_2$ (170.3)
7b	m.p. 47 (hexane)	1730^g 1708	0.86 (t, 3H, J=6Hz, CH_3); 1.20-1.60 (m, 12H, -CH_2-); 3.04-3.14 (m, 1H, -$CH_2\underline{\text{CH}}$<); 5.40 (s, 1H, $\underline{\text{CH}}$OCHO)	$C_{10}H_{18}O_3$ (186.3)
7g	b.p. 88/20	-	-	Lit.[28] b.p. 93°C/23 DNPH m.p. 106°C Lit.[35] m.p. 106.5°C
8a	b.p. 81/14	1728	0.89 (t, 6H, J=6Hz, CH_3); 1.25-1.62 (m, 4H, $\underline{CH_2}CH_3$); 1.85-2.20 (m, 4H, $\underline{CH_2}$-C=); 7.00 (s, 1H, $\underline{\text{CH}}$OCHO); 8.04 (s, 1H, OCHO)	$C_9H_{16}O_2$ (156.2)
8b	oil	1742	0.82-1.02 (m, 6H, CH_3); 1.26-1.70 (m, 8H, -CH_2-); 5.42 (s, 1H, $\underline{\text{CH}}$OCHO); 8.12 (s, 1H, OCHO)	$C_9H_{16}O_3$ (172.2)

Compound	m.p. (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR (CDCl$_3$) δ (ppm) TMS	Molecular formula[a] or other data
8e	oil	1725 3470(ν_{OH})	0.80-1.00 (m, 6H, CH$_3$); 1.06-1.74 (m, 8H, -CH$_2$-); 4.37 (broad s, 1H, OH); 9.50 (s, 1H, CHO)	$C_8H_{16}O_2$ (144.2)
8g	oil	1720	0.88 (t, 6H, J=7Hz, CH$_3$); 1.10-1.70 (m, 8H, -CH$_2$-); 2.38 (t, 1H, J=6Hz, >CH-); 9.82 (s, 1H, CHO)	$C_8H_{16}O$ (128.2)
9a	b.p. 110/14	1723	1.21 (d, 3H, J=1Hz, CH$_3$); 7.30-7.50 (m, 5H, ArH); 7.70 (d, 1H, J=1Hz, CHOCHO); 8.18 (s, 1H, OCHO)	$C_{10}H_{10}O_2$ (162.2)
9d≡13d	b.p. 200	-	-	Lit.[28] b.p. 202°C DNPH m.p.249°C Lit.[31] m.p. 274-248°C
9e	oil	1725 3456(ν_{OH})	1.70 (s, 3H, CH$_3$); 4.06 (broad s, 1H, OH); 7.36-7.68 (m, 5H, ArH); 9.64 (s, 1H, CHO)	SC m.p.184°C Lit.[36] m.p. 182-183°C
10a	m.p. 117 (i-Pr$_2$O/AcOEt)	1735[g]	7.12-7.34 (m, 4H, ArH); 7.44-7.68 (m, 3H, ArH); 7.90-8.00 (m, 1H, ArH); 8.06 (s, 1H, CHOCHO); 8.24 (s, 1H, OCHO)	$C_{15}H_{10}$ (222.2)
10d≡17d	m.p. 83	-	-	Lit.[28] m.p. 82-83°C
10e	m.p. 104 (i-Pr$_2$O)	1697[g] 3482(ν_{OH})	4.54 (s, 1H, OH); 7.18-7.48 (m, 6H, ArH); 7.60-7.66 (m, 2H, ArH); 8.70 (m, 1H, CHO)	$C_{14}H_{10}O_2$ (210.2)
10g	oil	-	-	PH[h] m.p.125°C Lit.[37] m.p. 126°C DNPH m.p. 236°C
11a	m.p. 50 (hexane)	1725[g] 1730	7.02-7.84 (m, 9H, ArH, ArCH=, CHOCHO); 7.99 (s, 1H, OCHO)	$C_{13}H_{10}O_2$ (198.2)
11g	oil	1725	3.95 (d, 2H, J=2Hz, -CH$_2$-); 7.24-7.52 (m, 4H, ArH); 7.75-7.86 (m, 3H, ArH); 9.66 (t, 1H, J=2Hz, CHO)	DNPH m.p. 182°C Lit.[38] m.p. 184°C

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^1H-NMR ($CDCl_3$) δ (ppm) TMS	Molecular formula[a] or other data
12a	oil	1728	0.82 (s, 9H, CH_3); 0.84-1.40 (m, 4H, $-CH_2-$); 1.60-2.38 (m, 8H, $-CH_2-$); 2.70-3.00 (m, 1H, >CH-); 6.93 (s, 1H, $=\underline{CH}OCHO$); 8.03 (s, 1H, OCHO)	$C_{12}H_{20}O_2$ (196.3)
12b	oil	1736	0.83 (s, 9H, CH_3); 1.08-1.95 (m, 9H, $-CH_2-$, >CH-); 5.40 and 5.44 (ds, 1H, $\underline{CH}OCHO$); 8.11 and 8.13 (ds, 1H, OCHO)	$C_{12}H_{20}O_3$ (212.3)
12g	m.p. 49 (hexane)	-	-	Lit.[28] m.p. -50°C
13a	b.p. 112/14	1720	2.07 (s, 3H, CH_3); 7.34-7.62 (m, 6H, ArH, =CHOCHO); 8.05 (s, 1H, OCHO)	$C_{10}H_{10}O_2$ (162.2)
14a	b.p. 124/0.3	1729 1755	0.99 (s, 3H, CH_3); 7.16 (s, 5H, ArH); 7.21 (s, 5H, ArH); 7.75 (s, 1H, OCHO)	$C_{16}H_{14}O_2$ (214.3)
14g	m.p. 63	-	-	Lit.[39] m.p. 62-63°C DNPH m.p. 145°C Lit.[40] m.p. 143-144°C
15a	b.p. 63/13	1728	0.72-1.02 (m, 6H, CH_3); 1.43-1.37 (m, 4H, $-CH_2-$); 1,96-2.31 (m, 1H, >CH-); 5.38 (dd, 1H, J=14Hz and 8Hz, -CH=); 7.22 (d, 1H, J=14Hz, $=\underline{CH}OCHO$); 7.95 (s, 1H, OCHO)	$C_8H_{14}O_2$ (142.2)
15b	oil	1728	0.88-1.00 (m, 6H, CH_3); 1.20-1.54 (m, 5H, $-CH_2-$, >CH-); 2.94 (dd, 1H, J=6Hz and 3Hz, >CHO); 5.42 (d, 1H, J=3Hz, $\underline{CH}OCHO$); 8.08 (s, 1H, OCHO)	$C_8H_{14}O_3$ (154.2)
15g	oil	1710	0.78-0.98 (m, 6H, CH_3); 1.18-1.40 (m, 4H, $-CH_2-$); 1.92-2.44 (m, 3H, $-\underline{CH_2}-CHO$, >CH-); 9.71 (t, 1H, J=2Hz, CHO)	SC m.p. 108°C Lit.[41] m.p. 108-109°C
16a	b.p. 102/14	1723	0.86 (t, 3H, J=6Hz, $CH_2\underline{CH_3}$); 1.27 (m, 8H, $-CH_2-$); 1.65 (s, 3H, $=\underset{\mid}{C}-CH_3$); 1.96, (t, 2H, J=7Hz, $-CH_2-C=$); 6.96 (s, 1H, $=\underline{CH}OCHO$); 8.05 (s, 1H, OCHO)	$C_{10}H_{18}O_2$ (170.3)

Compound	m.p.°C (solvent) or b.p./Torr	IR(film) $\nu_{C=O}$, cm^{-1}	^1H-NMR ($CDCl_3$) δ(ppm) TMS	Molecular formula[a] or other data
16b	oil	1708	0.83 (t, 3H, J=6Hz, $CH_2\underline{CH_3}$); 1.24 (m, 9H, $-CH_2-$, $>CH-$); 1.44 (s, 3H, $CH_3-\overset{\mid}{\underset{\mid}{C}}-$); 1.68 (t, 2H, J=7.5 Hz, $-CH_2-\overset{\mid}{\underset{\mid}{C}}-$); 5.40 (s, 1H, $\underline{CH}OCHO$); 8.06 (s, 1H, OCHO)	$C_{10}H_{18}O_3$ (186.3)
16g	b.p. 95/5	1702 1720	0.86 (t, 3H, J=6Hz, $CH_2-\underline{CH_3}$); 1.49-1.74 (m, 13H, $-CH_2-$, $>\underline{CH}-CH_3$); 9.64 (s, 1H, OCHO)	Lit.[42] b.p. 90°C/4 SC m.p. 46°C
17a	m.p. 64 ($i-Pr_2O$/heksane)	1720	2.52 (s, 3H, CH_3); 7.12-7.34 (m, 4H, ArH); 7.26-7.70 (m, 3H, ArH); 7.77-7.92 (m, 1H, ArH); 8.21 (1H, OCHO)[b]	$C_{16}H_{12}O_2$ (236.3)
17b	oil	1718	1.72 (s, 3H, CH_3); 7.16 (m, 8H, ArH); 8.08 (s, 1H, OCHO)	$C_{16}H_{12}O_3$ (252.3)
18a	b.p. 79/20	1735	6.65-6.89 (m, 3H, ArH, ArCH=); 7.41 (m, 1H, ArH); 7.98 (d, 1H, J=13Hz, $\underline{CH}OCHO$); 8.09 (s, 1H, OCHO)	$C_7H_6O_3$ (138.1)
19a	b.p. 97/0.5	1735	2.70 (s, 2H, $-CH_2-$); 6.27 (s, 1H, -CH=); 6.72-7.20 (m, 4H, ArH); 8.01 (s, 1H, OCHO)	$C_{10}H_8O_3$ (176.2)
20a	m.p. 33 (hexane)	1730 1760	3.45 (s, 2H, $-CH_2-$); 6.53 (s, 1H, -CH=); 7.03-7.30 (m, 4H, ArH); 8.08 (s, 1H, OCHO)	$C_{10}H_8O_2$ 160.2)
20g	m.p. 58 (hexane)	-	-	Lit.[43] m.p. 57-58°C DNPH m.p. 204°C Lit.[44] m.p. 202°C
21a	b.p. 94/0.5	1730 1755	2.45 (t, 2H, J=7Hz, $-CH_2-$); 2.83 (t, 2H, J=7Hz, $-CH_2-$); 6.20 (s, 1H, -CH=); 6.88-7.20 (m, 4H, ArH); 8.07 (s, 1H, OCHO)	$C_{11}H_{10}O_2$ (174.2)
21f	oil	1705 1745	2.20-2.70 (m, 2H, $-CH_2-$); 3.00-3.20 (m, 2H, $-CH_2-$); 6.30 (s, 1H, $\underline{CH}OCHO$); 7.19-7.33 (m, 4H, ArH); 8.31 (s, 1H, OCHO)	$C_{11}H_{10}O_3$ (178.2)
21g	oil	-	-	SC m.p. 196°C Lit.[45] m.p. 194-195°C

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^1H-NMR ($CDCl_3$) δ (ppm) TMS	Molecular formula[a] or other data
22a	m.p. 53 (hexane)	1720^g	1.87 (s, 3H, CH_3); 2.40 (t, 2H, J=7Hz, $-CH_2-$); 2.86 (t, 2H, J=7Hz, $-CH_2-$); 7.05-7.17 (m, 4H, ArH); 8.03 (s, 1H, OCHO)	$C_{12}H_{12}O_2$ (188.2)
22f	m.p. 82 ($i-Pr_2O$)	1705^g 1720	1.59 (s, 3H, CH_3); 2.74(t, 2H, J=7Hz, $-CH_2-$); 3.06 (t, 2H, J=7Hz, $-CH_2-$); 7.13-7.32 (m, 4H, ArH); 7.80 (s, 1H, OCHO)	$C_{12}H_{12}O_3$ (204.2)
22d/h	m.p. 70 (hexane)	1680^g 1700 2600-3200(ν_{OH})	2.57 (s, 3H, CH_3); 2.70 (t, 2H, J=7Hz, $-CH_2-$); 3.07 (t, 2H, J=7Hz, $-CH_2-$); 7.20-7.45 (m, 3H, ArH); 7.66-7.78 (m 1H, ArH); 11.58 (s, 1H, COOH)	$C_{11}H_{12}O_3$ (192.03)
23a	m.p. 84 (hexane)	1717^g	2.62 (t, 2H, J=8Hz, $-CH_2-$); 3.07 (t, 2H, J=8Hz, $-CH_2-$); 6.67-6.77 (m, 1H, ArH); 6.93-7.44 (m, 8H, ArH); 7.82 (s, 1H, OCHO)	$C_{17}H_{14}O_2$ (250.3)
23f	m.p. 104 ($i-Pr_2O$/hexane)	1703^g 1728	2.58-2.81 (m, 2H, $-CH_2-$); 3.01-3.30 (m, 2H, $-CH_2-$); 7.12-7.31 (m, 9H, ArH); 7.99 (s, 1H, OCHO)	$C_{17}H_{14}O_3$ (266,3)
23d/h	m.p. 84	1656^g 1695 2600-3200(ν_{OH})	2.66 (dt, 2H, J=7Hz and 2Hz,$-CH_2-$); 3.01 (dt, 2H, J=7Hz and 2Hz,$-CH_2-$); 7.23-7.60 (m, 7H, ArH); 7.80 (dd, 2H, J=8Hz and 2Hz, ArH); 11.24 (s, 1H, COOH)	$C_{16}H_{14}O_3$ (254.3)
24f	oil	1713 1748	1.68-2.84 (m, 6H, $-CH_2-$); 7.26-7.55 (m, 5H, ArH); 7.99 (s, 1H, OCHO)	$C_{11}H_{12}O_3$ (192.2)
24e	m.p. 67 (hexane)	1740^g 3420(ν_{OH})	1.60-2.40 (m, 6H, $-CH_2-$); 3.85 (broad s, 1H, OH); 6.98-7.42 (m, 5H, ArH)	$C_{10}H_{12}O_2$ (164.2)
33	oil	1692	2.40-2.62 (m, 4H, $-CH_2-$); 7.20-7.36 (m, 3H, Ar-C=CH); 7.85-7.22 (m, 3H, ArH)	$C_{10}H_{10}O$ (146.2)
24d/h	m.p. 126 ($i-Pr_2O$/AcOEt)	-	-	Lit.[46] m.p. 127°C
25a	b.p.95/0.25	1717	1.64-1.84 (m, 4H, $-CH_2-$); 2.17-2.26 (m, 4H, $-CH_2-$); 7.21 (m, 5H, ArH); 7.72 (s, 1H, OCHO)	$C_{13}H_{14}O_2$ (202.3)

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR (CDCl$_3$) δ (ppm) TMS	Molecular formula^a or other data
25b	b.p. 110/0.25	1728	1.50-1.70 (m, 4H, -CH$_2$-); 2.07-2.42 (m, 4H, -CH$_2$-); 7.21-7.43 (m, 5H, ArH); 7.50 (s, 1H, OCHO)	$C_{13}H_{14}O_3$ (218.3)
25g	m.p. 59 (hexane)	-	-	Lit.[47] m.p. 59.5-60°C
25d/h	m.p. 77 (hexane)	-	-	Lit.[46] m.p. 77-78°C
26a	b.p. 108/0.4	1725	1.73 (m, 6H, -CH$_2$-); 2.35-2.52 (m, 4H, -CH$_2$-); 7.02-7.32 (m, 5H, ArH); 7.68 (s, 1H, OCHO)	$C_{14}H_{16}O_2$ (216.3)
26g	oil	1675	1.20-1.58 (m, 2H, -CH$_2$-); 1.72-2.12 (m, 6H, -CH$_2$-); 2.19-2.80 (m, 2H, -CH$_2$-); 3.67 (dd, 1H, J=10Hz and 5Hz, $>$CH-); 7.22 (m, 5H, ArH)	$C_{13}H_{16}O$ (172.3)
27a	m.p. 44 (hexane)	1720^g	0.90 (s, 9H, CH$_3$); 2.24-3.54 (m, 1H, $>$CH-); 7.23 (m, 5H, ArH); 7.78 (s, 1H, OCHO)	$C_{17}H_{22}O_2$ (258.4)
27b	m.p. 60 (hexane)	1731^g	0.86 (s, 9H, CH$_3$); 1.10-1.66 (m, 3H, -CH$_2$-, $>$CH-); 2.10-2.19 (m, 4H, -CH$_2$-); 7.22-7.40 (m, 5H, ArH); 7.50 (s, 1H, OCHO)	$C_{17}H_{22}O_3$ (274.4)
27e	m.p. 174 (i-Pr$_2$O)	1695^g 3382 (ν_{OH})	0.88 (s, 9H, CH$_3$); 1.52-1.80 (m, 3H, -CH$_2$-, $>$CH-); 2.14-2.20 (m, 2H, -<u>CH$_2$</u>-C-OH); 2.50-2.66 (m, 2H, CH$_2$CO); 7.32 (m, 5H, ArH)	$C_{16}H_{22}O_2$ (246.4)
27g	m.p. 95 (hexane)	1698^g	0.88 (s, 9H, CH$_3$); 2.43-3.68 (m, 7H, $>$<u>CH</u>-Bu^t, -CH$_2$-); 3.48 (dd, 1H, J=10Hz and 6Hz, $>$<u>CH</u>-Ph); 7.01-7.30 (m, 5H, ArH)	$C_{16}H_{22}O$ (230.4)
27d/h	m.p. 88 (hexane)	1673^g 1695 2550-3150 (ν_{OH})	0.90 (s, 9H, CH$_3$); 1.32-2.66 (m, 5H, -CH$_2$-, $>$CH-); 3.00 (t, 2H, J=8Hz, -CH$_2$-CO); 7.26 7.60 (m, 3H, ArH); 7.93 (dd, 2H, J=8Hz and 2Hz, ArH); 11.36 (s, 1H, COOH)	$C_{16}H_{22}O_3$ (262.4)

Compound	m.p. °C (solvent) or b.p./Torr	IR (film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm) TMS	Molecular formula[a] or other data
28a	b.p. 125/0.5	1732 1761	1.89 (s, 3H, CH_3); 6.63 (s, 1H, -CH=); 7.28-7.84 (m, 4H, ArH); 7.65-7.99 (m, 3H, ArH); 8.06 (s, 1H, OCHO)	$C_{14}H_{22}O_2$ (212.3)
28g	oil	-	-	SC m.p.193°C Lit.[48] m.p. 190.5-191.5°C DNP m.p.172°C Lit.[49] m.p. 174-176°C
30a	b.p. 80/13	1725	1.52 (m, 6H, $-CH_2-$); 2.04-2.24 (m, 4H, $-CH_2-$); 6.92 (s, 1H, =C$\underline{H}$OCHO); 8.02 (s, 1H, OCHO)	$C_8H_{12}O_2$ (140.2)
30b	oil	1730	1.56 (m, 9H, $-CH_2-$); 2.14-2.40 (m, 1H, $-CH_2-$); 5.40 (s, 1H, OC$\underline{H}$OCHO); 8.14 (s, 1H, OCHO)	$C_8H_{12}O_3$ (156.2)
30g	b.p.162-164	-	-	Lit.[28] b.p. 161-163°C SC m.p.173°C Lit.[50] m.p. 171°C DNPH m.p.172°C Lit.[50] m.p.172°C
31a	oil	1728	1.53 (m, 8H, $-CH_2-$); 2.13-2.21 (m, 4H, $-CH_2-$); 6.98 (s, 1H, =C$\underline{H}$OCHO); 8.04 (s, 1H, OCHO)	$C_9H_{14}O_2$ (154.2)
31d	b.p. 179	-	-	Lit.[28] b.p. 179°C
32a	oil	1726	0.86 (d, 3H, J=2Hz, CH_3); 0.94-2.30 (m, 8H, $-CH_2-$); 2.64-2.86 (m, 1H, >CH-); 6.92 (s, 1H, =C$\underline{H}$OCHO); 8.01 (s, 1H, OCHO)	$C_7H_{10}O_2$ (162.2)
32b[j]	oil	1735	0.90 and 0.96 (dd, 1H, J=2Hz, CH_3); 1.12-1.85 (m, 9H, $-CH_2-$, >CH-); 5.40 and 5.43 (ds, 1H, C$\underline{H}$OCHO); 8.13 and 8.14 (ds, 1H, OCHO)	$C_7H_{10}O_3$ (142.2)

Compound	m.p.°C(solvent) or b.p./Torr	IR(film) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ(ppm) TMS	Molecular formula[a] or other data
32g	oil	-	-	DNPH m.p. 180°C Lit.[52] m.p. 180-182°C

[a] Satisfactory microanalyses abtained: C ± 0.4%, H ± 0.3%

[b] HMDSO was used as an external standardt

[c] Hydrolysed to benzaldehyde

[d] DNPH - 2,4-Dinitrophenylhydrazone

[e] If b.p. is not given, the compound was purified by column chromatography only

[f] SC - Semicarbazone

[g] IR spectrum measured in KBr

[h] PH - Phenylhydrazone

[j] Mixture of diastereoisomers.

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