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1,5-Hexadiene selective hydroformylation reaction catalyzed with $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ and $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$ complexes

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Abstract

Hydroformylation of 1,5-hexadiene, catalyzed by the system $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I), leads to the formation of mono- and dialdehydes, 4-heptenal, 2-Me-3-hexenal and octane-1,8-dial, 2,5-Me₂-hexanedial respectively. The yield of dialdehydes increases with temperature and pressure and reaches 100% at 80°C and 10 atm of $\text{CO}/\text{H}_2 = 1$. The reaction catalyzed by $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$ (II) system produces, besides dialdehydes, monoaldehydes with a terminal double bond, namely 6-heptenal and 2-Me-5-hexenal. The migration of the double bonds in monoaldehydes depends mainly on the donor properties of modifying ligands. Phosphine when used as a modifying ligand (II), because of its strong donor properties, restricts isomerization (double bond migration) and diminishes yield of 4-heptenal. In contrast, when less strongly donating ligands such as phosphites are used as modifying ligands (I), independently of its steric properties, 4-heptenal is the main reaction product.

Key words: Hydroformylation; Rhodium; Hexadiene; Catalysis

1. Introduction

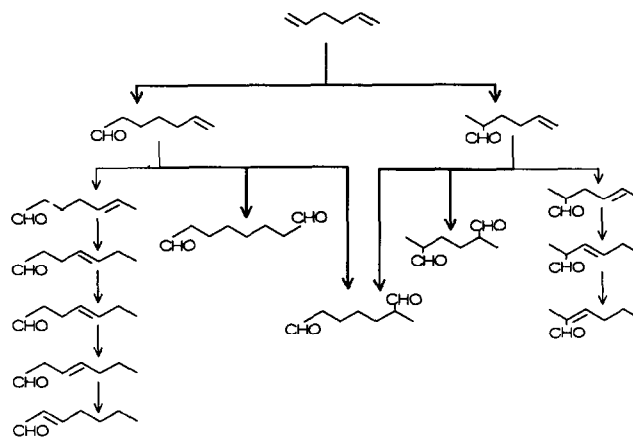
It is quite difficult to attain high selectivity hydroformylation of both linear and cyclic dienes because of the numerous reaction products that are possible. Mono- and dialdehydes, saturated and unsaturated, linear and branched, can all be formed [1]. The complexity of the problem of selectivity is demonstrated in Scheme 1 where most of the possible products of hydroformylation of 1,5-hexadiene are shown. In this paper the results of hydroformylation of 1,5-hexadiene with $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I) and $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$ (II) systems are presented.

It was expected that application of two different catalytic systems (I) and (II) at various reaction conditions would allow establishment of the reaction parameters which are crucial for selectivity.

2. Results and discussion

2.1. Hydroformylation of 1,5-hexadiene

Our previous studies on hex-1-ene hydroformylation with $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ system classified



Scheme 1.

this catalyst as being quite effective in isomerization reactions [2,3]. On the basis of spectroscopic studies it was found that $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$ (one of the catalytically active intermediates) is responsible for the hex-1-ene isomerization that is observed [4,5].

However, among the 1,5-hexadiene hydroformylation reaction products no iso-dienes have been found (*i.e.* 1,3- or 2,4-hexadienes). Under the reaction conditions applied (*ca.* 10 atm of $\text{CO}/\text{H}_2 = 1$) the rate of

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TABLE 1. Reaction products of isomerization of 1,5-hexadiene. Catalytic systems $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ $t = 40^\circ\text{C}$, $p = 1$ atm H_2/N_2

H_2 (%)	Products (% mol)			
	2,4-Hexadiene	Hex-1-ene	Hex-2-ene	Hexane
100	—	10	30	60
50	30	30	20	—
40	40	20	—	—

1,5-hexadiene hydroformylation is probably higher than that of the isomerization reaction.

Nevertheless, isomerization of 1,5-hexadiene to 2,4-hexadiene occurs easily at room temperature in H_2/N_2 atmosphere (1 atm). Increase of hydrogen concentration causes hydrogenation of 1,5-hexadiene to hexane (Table 1).

The catalytic system $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3/\text{H}_2/\text{CO}$ was found to be inactive in isomerization of 1,5-hexadiene, but active in migration of double bonds in the monoaldehydes formed in hydroformylation (Table 2). The typical fraction of monoaldehydes mainly composes 4-heptenal which is evidence of competition between two reactions: isomerization (reaction 1,1') and hydroformylation (2,2') (Scheme 2).

The 6-heptenal formed initially undergoes isomerization to 4-heptenal (1) or hydroformylation to octanedial (2). Similarly, 2-Me-5-hexenal isomerizes to 2-Me-3-hexenal (1') or undergoes hydroformylation to 2,5-Me₂-hexanedial (2') (Scheme 2). All reactions are highly selective as demonstrated by the lack of products other than those listed in Table 2, e.g. 5-heptanal or 2-Me-heptanedial have not been found.

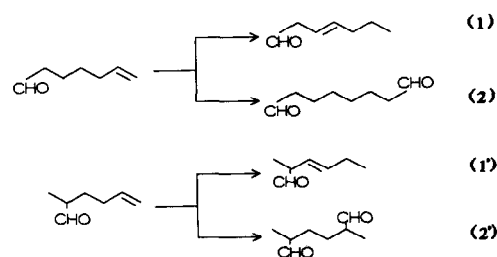
TABLE 2. The products of hydroformylation of 1,5-hexadiene catalyzed by $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I) and $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$ (II) at different temperatures at 10 atm after 2.5–3 h

Catalytic system	Temp. ($^\circ\text{C}$)	Products (% mol)		
		6-Heptenal ^a	4-Heptenal ^b	Octanedial ^c
I	30	70	16	—
I	40	38	32	30
II	40	48	—	52
I	50	3	25	70
II	50	25	—	75
I	50/6 atm	5	54	41
II	50/6 atm	80	—	20
I	60	—	17	83
II	60	—	—	100
I	60/6 atm	—	81	19
I	70	—	21	79
I	80	—	—	100
II	80	—	—	100

^a Total yield of 6-heptenal + 2-Me-5-hexenal.

^b Total yield of 4-heptenal + 2-Me-3-hexenal.

^c Total yield of octane-1,8-dial + 2,5-Me₂-hexanedial.



Scheme 2.

The effect of reaction conditions on the course of reaction can be estimated from the data presented in Table 2. The isomerization of 6-heptenal to 4-heptenal is retarded with temperature decrease or increase of CO/H_2 ratio. However, changes of both the above parameters lead to decreased 1,5-hexadiene conversion. The highest yield of 6-heptenal (ca. 70%) was obtained at 30°C and it decreased to only 38% at 40°C . Studies at different CO/H_2 ratios at 50° and 60°C led to the conclusion that increase of CO concentration in CO/H_2 mixture caused the increase of yield of 6-heptenal with simultaneous decrease of yield of 4-heptenal (Table 3). However, with changing CO/H_2 ratio, the yield of 6-heptenal may increase by no more than 10–20%. The increase of isomerization of 1,5-hexadiene with CO concentration decrease can be explained by the shift of equilibrium to the rhodium-hydride species $\text{HRh}\{\text{P}(\text{OPh})_3\}_4$, known to be the isomerization catalyst (eqn. (3)):



The decrease of $(\text{CO} + \text{H}_2)$ total pressure causes the drop in the rate of formation of dialdehydes and has no influence on the rate of isomerization of monoaldehydes. At 6 atm pressure, 4-heptenal is the

TABLE 3. The products of hydroformylation of 1,5-hexadiene catalyzed by $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I) with different H_2/CO ratios at 10 atm after 2–2.5 h

H_2/CO	Products (% mol)		
	6-Heptenal ^a	4-Heptenal ^b	Octanedial ^c
$t = 50^\circ\text{C}$			
1:1	3	25	70
4:6	13	17	70
3:7	15	—	59
2:8	22	—	33
$t = 60^\circ\text{C}$			
1:1	—	17	83
4:6	—	27	73
3:7	14	18	57
2:8	42	9	28

^{a,b,c} See Table 2.

main reaction product (81% at 60°C) (Table 2). Similar effects of total (CO + H₂) pressure are observed for the reaction catalyzed by the Rh(acacXCOXPPPh₃)/PPh₃ system. Also in this system, lower total (CO + H₂) pressure stops the hydroformylation reaction at the stage of monoaldehyde-6-heptenal (Table 2). With pressure changing from 10 to 6 atm the yield of 6-heptenal increases from 25 to 85%, but isomerization of 6-heptenal ~ 4-heptenal does not occur.

In contrast to 6-heptenal, which is an intermediate product and may undergo further hydroformylation, the 4-heptenal may be treated as the side product because in practical terms it is not reactive in hydroformylation. Applying the phosphine based catalytic system (II), which is not active in 4-heptenal formation, octanedials are obtained already at 100% yield at 60°C whereas the phosphite based system (I) requires higher temperature (80°C).

The selectivity factor, n/iso ratio, is practically independent of changes of reaction parameters (temperature, CO/H₂ ratio and total pressure). For phosphite based catalytic system (I) the n/iso factor is 2.5-3.2 whereas for the system (II) (phosphine based) it is lower (1.8-2.1) for both mono- and di-aldehydes.

Decrease of isomerization reaction yield, caused by reaction parameter changes, is not accompanied by n/iso increase. Similarly, in hex-1-ene hydroformylation [2,6], with increase of n/iso parameter some increase (not decrease) of hex-2-ene yield was observed.

Phosphite concentration increase causes decrease of reaction rate only, and not changes of the final reaction products. At seven-fold phosphite excess *versus* the rhodium complex (at 50°C and 10 atm) 23% of 4-heptenal and 77% of octanedial were obtained (a considerably higher percentage yield of dialdehydes was obtained with increase of phosphite concentration).

Undoubtedly, the catalytic activity of each system depends on the electronic and steric effects of the ligands coordinated to the metal. To judge which dominates in the phosphite system the content of the mono-aldehydes fraction in the reaction catalyzed by Rh(acac){P(OPh)₃}₂ + L (L -- PPh₃ or P(O-2,4,6-Me₃C₆H₃)₃) was determined. The data collected in Table 4 indicate the prevailing electronic effect of the ligands applied and only when the ligands have stronger donor properties (according to Tolman scale [7]) does some 6-heptenal appear in reaction products. This suggests that isomerization was partially limited only by stronger donor ligands. We failed to obtain the mixture of 4- and 6-heptenals in reaction catalyzed by Rh(acac)(CO)-(PPh₃)₃ modified with P(OPh)₃ or bulky P(O-2,4,6-Me₃C₆H₃)₃. Even at [L]:[Rh] = 1, 4-heptenal was the only monoaldehyde identified in both reaction mixtures. The results discussed above allow us to distin-

TABLE 4. Composition of the monoaldehyde fraction of the product of the hydroformylation reaction of 1,5-hexadiene catalyzed by Rh(acac){P(OPh)₃}₂ + L ([L]:[Rh] = 2) at 10 atm, 60°C, after 3 h

L =	4-Heptenal b	6-Heptenal a	v(CO)* (cm ⁻¹)	O (deg)
PEtPh ₂	30	70	2066.7	140
P(p-MeC ₆ H ₄) ₃	54	45	2066.7	145
PPh ₃	40	60	2068.9	145
P(OEt) ₃	100	0	2076.3	109
P(O-o,o-Me ₂ C ₆ H ₃) ₃	100	0	2083.2	190
P(O-o-MeC ₆ H ₄) ₃	100	0	2084.1	141
P(OPh) ₃	100	0	2085.3	130

* v(CO) (A 1) of Ni(CO)₃L in cn2c12.

a,b See Table 2.

guish some aspects of the behaviour of catalytic systems (I and II) revealed by studies using different phosphorus ligands (*e.g.* PPh₃ and P(OPh)₃) used for their modification. Two catalytic systems of practically identical content: Rh(acac){P(OPh)₃}₂/PPh₃ and Rh(acac)(COXPPPh₃)/P(OPh)₃ act differently as is demonstrated by the reaction products. In the first case, the presence of free phosphine causes retardation of isomerization whereas in the second system only 4-heptenal is obtained, similarly to the system with only the phosphite ligand.

To explain these experimental facts ³¹P-NMR studies were performed. The results of the measurements were the following:

a) For the system Rh(acac){P(OPh)₃}₂ + PPh₃ regardless of the PPh₃ concentration and reaction time, only the Rh(acac){P(OPh)₃}₂ complex was observed (8 123.1 ppm, J(Rh-P) 307 Hz);

b) in the system Rh(acac)(CO)(PPh₃)₃ + P(OPh)₃ ([P(OPh)₃]: [Rh] = 1) immediately after mixing, the bands typical for Rh(acacXCO)(PPh₃)₃ complex (8 48.6 ppm, J(Rh-P) 178 Hz) disappear and the bands, assigned for Rh(acac){P(OPh)₃}₂ appear. After a couple of hours an equilibrium is established and three complexes Rh(acac)(CO)(PPh₃)₃, Rh(acac){P(OPh)₃}₂ and Rh(acac)(CO){P(OPh)₃} (8 121 ppm, J(Rh-P) 293 Hz) are found in the solution;

c) in the system: Rh(acac)(CO)(PPh₃)₃ + P(O-o-MeC₆H₄)₃, ([P(O-o-MeC₆H₄)₃]: [Rh] = 2), in spite of the significant steric hindrance of this phosphite ligand (O = 141°) it substitutes immediately for both PPh₃ and CO and the only product identified is Rh(acac){P(O-o-MeC₆H₄)₃}₂ (8 123 ppm, J(Rh-P) = 305 Hz).

From the above experiments, one may conclude that any phosphite ligand used practically eliminates the phosphine ligand from the coordination sphere of the rhodium catalyst precursor at the very beginning of the reaction. The rhodium catalyst precursor with coordi-

nated phosphite ligand is, however, not changed under influence of excess of free phosphine. In the further stages of the reaction, when $\text{HRh}(\text{CO})\text{L}_3$, an active form of catalyst, is produced, its interaction with the modifying ligand may play an essential role. In our earlier studies [8] the $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)$ complex was identified as a product of reaction of $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ with a 3-fold excess of PPh_3 . Triphenylphosphine substitutes only one of the three coordinated phosphites. The reverse reaction, substitution of PPh_3 by $\text{P}(\text{OPh})_3$ was studied earlier with the ^1H -NMR method [4] and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)$ and $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ were identified in solution. These results are confirmed by ^{31}P -NMR studies of the solution containing $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and 3 $\text{P}(\text{OPh})_3$. The bands which originated from $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ (8 38.4 ppm, $J(\text{Rh-P})$ 158 Hz) disappear immediately after mixing and next, the lines characteristic for $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)$ (8 143.7 ppm, d of d, $J(\text{Rh-P})$ 250 Hz, 8 35.8 ppm, d of t, $J(\text{Rh-P})$ 150.4 Hz, $J(\text{P-P})$ 141.6 Hz) and for $\text{HRh}(\text{CO})\{\text{P}(\text{OPh})_3\}_3$ (8 138.6 ppm, $J(\text{Rh-P})$ 238 Hz) appear. Also the more bulky phosphite $\text{P}(\text{O}-o\text{-MeC}_6\text{H}_4)_3$, used in excess, substitutes two of the three phosphines coordinated in $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. The reaction product was identified by ^{31}P -NMR as $\text{HRh}(\text{CO})\{\text{P}(\text{O}-o\text{-MeC}_6\text{H}_4)_3\}_2(\text{PPh}_3)$ complex (8 135 ppm, d of d, $J(\text{Rh-P})$ 252 Hz, 8 38 ppm d of t $J(\text{Rh-P})$ 146 Hz). At higher excess of phosphite also $\text{HRh}(\text{CO})\{\text{P}(\text{O}-o\text{-MeC}_6\text{H}_4)_3\}_3$ is formed (8 132 ppm, $J(\text{Rh-P})$ 240 Hz).

These results allow the following conclusions:

- i) the phosphine ligand is always more easily substituted by any phosphite ligand than *vice versa*;
- ii) at any stage of catalytic reaction with the rhodium phosphine base catalyst precursor it may be modified with phosphite ligand and the catalytic properties of

such a system can ultimately be attributed to rhodium-phosphite species;

iii) a quite insignificant effect is observed when rhodium phosphite base catalyst precursor is modified with excess of free phosphine ligand. The final effect recorded represents an average impact of the two ligands.

2.2. Hydroformylation of 1,7-octadiene

To obtain more general information about hydroformylation of dienes we extended our studies to hydroformylation of 1,7-octadiene (Table 5). Similarly to 1,5-hexadiene, the rhodium phosphite system (I) applied in the case of 1,7-octadiene manifested higher activity in the isomerization reaction of mono-aldehydes. Among the reaction products, besides dialdehydes, only 6-nonenal was identified (Table 5). The isomerization reaction yield depends less on the (CO/H₂) pressure. The extremely high yield of 6-nonenal compared with that of 4-heptenal in the hydroformylation of 1,5-hexadiene must be noticed.

Small amounts of 6-nonenal appear even in the reaction catalyzed by $\text{Rh}(\text{acacXCO})(\text{PPh}_3)$ in which isomerization does not normally occur. This difference can only be caused by the reactivities of the substrates themselves differing.

3. Experimental section

Rhodium complexes were obtained according to methods described in the literature: $\text{Rh}(\text{acacXCO})(\text{PPh}_3)$ [9], $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2$ [10], $\text{HRh}(\text{COXPPH}_3)_3$ [11].

Toluene, 1,5-hexadiene and 1,7-octadiene were distilled before use. Hydroformylation was carried out in a thermostated autoclave of 40 ml volume with mag-

TABLE 5. The products of hydroformylation reaction of 1,7-octadiene catalyzed by $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I) and $\text{Rh}(\text{acacXCOXPPH}_3)/\text{PPh}_3$ (II)

Catalytic system	Temp. (°C)	Pressure (atm)	Time (h)	Products (% mol)		
				8-Nonenal a	6-Nonenal e	Decanediol f
I	50	6	2.5	-	37	63
II	50	6	2	28	7	65
I	50	10	3	-	27	73
II	50	10	3	-	-	100
I	60	6	2	-	48	52
II	60	6	5	-	6	94
I	60	10	3	-	53	47
II	60	10	3	-	-	100

d Total yield of 8-nonenal + 2-Me-7-octenal.

e Total yield of 6-nonenal + 2-Me-5-octenal.

f Total yield of decane-1,10-dial + 2,7-Me2-octane-1,7-dial.

netic stirrer. The reagents were introduced to the autoclave under a nitrogen atmosphere and it was filled with HE/CO mixture to the required pressure. After reaction the autoclave was cooled and samples collected for ^1H -NMR and GC-MS measurements. For each experiment $3.2 \cdot 10^{-5}$ mol of catalyst ($\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ or $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2$) and $9.4 \cdot 10^{-5}$ mol PPh_3 or $6.8 \cdot 10^{-5}$ mol $\text{P}(\text{OPh})_3$ were used. In both catalytic systems under study, $\text{Rh}(\text{acac})\{\text{P}(\text{OPh})_3\}_2/\text{P}(\text{OPh})_3$ (I) and $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)/\text{PPh}_3$ (II), the ratio $[\text{L}]:[\text{Rh}]$ was 4.

^1H -NMR and ^{31}P -NMR spectra were measured on Tesla BS 567A (100 MHz) and BS 587 A (32.35 MHz) spectrometers respectively. GC-MS analysis was made using a GC-MS Hewlett-Packard instrument.

3.1. Reaction product identification (^1H -NMR and MS data)

4-Heptenal: ^1H -NMR 6(CHO)9.3; 6(CH=CH)5.2 ppm; MS 112(M+ 1.7) 94(14) 84(6) 68(100) 67(48) 55(33) 41(19).

2-Me-3-hexenal: ^1H -NMR 6(CHO)9.2; 8(CH--CH)5.2 ppm; MS 112(M+ 14) 97(15) 94(9) 69(17) 55(100) 43(39) 41(36).

6-Heptenal: ^1H -NMR 8(CHO)9.2; $t^{\sim}(\text{=CHE})$ 4.8; 8(--CH) 5.5 ppm; MS 97(3) 94(6) 83(11) 79(31) 70(17) 68(100) 67(54) 57(34) 55(54) 41(76).

2-Me-5-hexenal: ^1H -NMR 6(CHO)9.2; 8(=CH2)4.8; 8(--CH) 5.5 ppm; MS 97(3) 94(7) 79(3) 68(4) 58(100) 55(41) 41(45).

Octane-1,8-dial: ^1H -NMR 6(CHO) 9.3 ppm; MS 124(11) 95(15) 81(100) 80(24) 69(17) 67(25) 57(85) 55(56) 54(32) 44(43) 41(51).

2,5-MeE-hexane-1,6-dial: ^1H -NMR 8(CHO)9.2 ppm; MS 124(3) 95(37) 81(22) 71(27) 69(41) 58(100) 57(65) 55(34) 43(55) 41(54).

6-Nonenal: ^1H -NMR 6(CHO)9.3; 6(CH--CH)5.2 ppm; MS 122(24) 98(29) 96(21) 93(29) 83(30) 81(41) 79(25) 70(27) 67(43) 55(100) 54(35) 41(51).

2-Me-5-octenal: ^1H -NMR 6(CHO)9.2; 6(CH=CH)5.2 ppm; MS 122(5) 112(25) 84(24) 83(27) 82(71) 71(24) 69(39) 68(78) 67(82) 58(26) 56(24) 55(100) 41(45).

8-Nonenal: ^1H -NMR 6(CHO)9.2; 8(--CH2) 4.8; 8(--CH) 5.5 ppm; MS 122(1) 111(8) 107(6) 98(17) 93(15) 81(37) 67(37) 55(100) 54(52) 41(65).

2-Me-7-octenal: ^1H -NMR 6(CHO)9.2; 6(=CH2)4.8; 8(=CH) 5.5 ppm; MS 125(3) 111(10) 98(11) 97(13) 82(23) 71(23) 69(42) 58(100) 55(65) 48(39).

Decane-1,10-dial: ^1H -NMR 8(CHO) 9.3 ppm; MS 152(2) 109(79) 98(28) 83(39) 82(44) 81(39) 68(31) 67(94) 57(100) 55(93) 41(58).

2,7-MeE-octane-1,7-dial: ^1H -NMR 8(CHO) 9.2 ppm; MS 152(2) 109(10) 95(22) 81(23) 67(22) 58(100) 55(42) 43(23) 41(26).

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