UV-LIGHT- AND RADIATION-INITIATED ADDITION OF ACETALDEHYDE TO ALLYL ALKANOATES

František Liška[a], Miroslav Valenta[a], Jiří Fikar[a], Martina Jandová[a], Miroslav Pešek[b] and Petr Trška[a]

[a] *Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6 and*
[b] *Institute for Research, Production and Application of Radioisotopes, 102 27 Prague 10*

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UV-light- and γ-^{60}Co-initiated addition of acetaldehyde to allyl formate (*I*) and allyl acetate(*II*) yielded the 1 : 1 adducts — 4-oxopentyl formate (*III*) and 4-oxopentyl acetate (*IV*), respectively, together with the 1 : 2 telomers — 7-formyloxy-4-formyloxymethyl-2-heptanone (*V*) and 7--acetoxy-4-acetoxymethyl-2-heptanone (*VI*). The initial radiation yields are: $G(III) = 200{\cdot}8$, $G(IV) = 211{\cdot}3$, $G(V) = 39{\cdot}5$, $G(VI) = 37{\cdot}9$. Base-catalyzed transesterification of oxopentyl alkanoates *III* and *IV* afforded 5-hydroxy-2-pentanone (*XIV*), the same reaction of dialkylalkanoates *VI* and *VII* gave 5-hydroxy-4-hydroxymethyl-2-heptanone (*XV*).

5-Hydroxy-2-pentanone (*XIV*) represents a useful intermediate in organic synthesis. It is used e.g. in the preparation of cyclopropyl methyl ketone[1], pheromones[2] or an azo-initiator in the synthesis of telechelic elastomers[3,4]. Usually, it is prepared by reactions based on hydroxyethylation of ethyl acetoacetate[5,6], acetylation of 4-butanolide[7], partial hydrogenation of 2-methylfuran[8,9], radical addition of acetaldehyde to allyl alcohol[10] or hydrolysis of 4-oxopentyl acetate (*IV*)[11]. Oxopentyl acetate *IV* is obtained by radical addition of acetaldehyde to allyl acetate (*II*), initiated with dibenzoyl peroxide[12] or oxygen or air in the presence of manganese or cobalt acetates[13,14].

Our present study investigates the UV-light- or radiation-initiated addition of acetaldehyde to allyl formate (*I*) and allyl acetate (*II*) with the aim to elaborate a preparative method leading to 4-oxopentyl formate (*III*) and 4-oxopentyl acetate (*IV*) which can be hydrolyzed to the hydroxypentanone *XIV*.

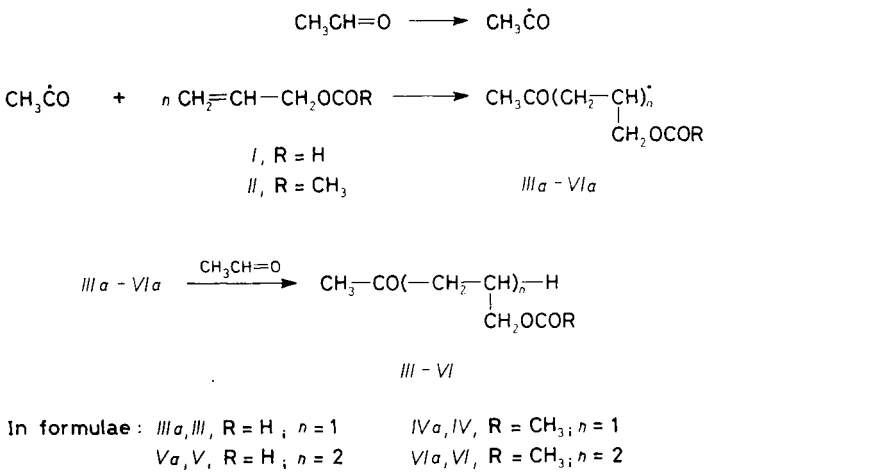
The radical reactions were carried out by irradiation with ultraviolet light or γ-^{60}Co radiation of the formate *I* or acetate *II* in an excess of acetaldehyde. Both methods of initiation afforded 1 : 1 adducts — oxopentyl formate *III* and oxopentyl acetate *IV* — and 1 : 2 telomers — 7-formyloxy-4-formyloxymethyl-2-heptanone (*V*) and 7-acetoxy-4-acetoxymethyl-2-heptanone (*VI*) — as the principal products. The reaction conditions and results are given in Table I.

TABLE I

Reaction conditions and results of radiation-induced addition of acetaldehyde (AcH) to allyl formate (*I*) and allyl acetate (*II*)

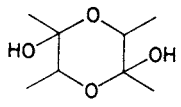
Molecular ratio AcH/*I*, *II*	Allyl alkanoate g/mol (conversion, %)	Acetaldehyde g/mol	Radiation dose kGy	Yield, g (%)		Distillation residue, g
				1 : 1 adduct	1 : 2 telomer	
10 : 1	*I* 52·0/0·60 (96·2)	266·4/6·05	100	*III* 45·50 (58·0)	*V* 13·22 (20·0)	9·40
20 : 1	*I* 26·8/0·31 (87·9)	274·2/6·22	100	*III* 27·26 (67·7)	*V* 4·40 (13·1)	1·70
20 : 1	*I* 280·0/3·22 (74·0)	2 865·0/65·4	42	*III* 213·55 (50·15)	*V* 58·3 (16·6)	19·40
10 : 1	*II* 58·8/0·59 (90·0)	258·5/5·86	100	*IV* 48·05 (56·0)	*VI* 15·3 (21·3)	7·0
20 : 1	*II* 31·2/0·31 (86·0)	274·2/6·2	100	*IV* 30·43 (67·7)	*VI* 5·72 (12·4)	2·3
20 : 1	*II* 326·0/3·26 (73·7)	2 869·0/65·3	42	*IV* 236·53 (50·4)	*VI* 72·83 (18·3)	16·2

We assume that the products *III*–*VI* are formed according to the mechanism suggested for the radical addition of acetaldehyde to unsaturated compounds[15]. Irradiation of the reaction mixture gives rise to acetyl radicals which add highly regioselectively to the double bond in alkanoates *I* and *II* to give the respective 1 : 1 adduct – radicals *IIIa* and *IVa* which are then converted into the 1 : 2 telomer radicals *Va* and *VIa* (generally 1 : *n* telomer radicals). Chain transfer to the solvent from the radicals *IIIa*–*VIa* affords the corresponding 1 : 1 adducts *III* and *IV* and the 1 : 2 telomers *V* and *VI*, together with acetyl radical. No isolation and identification of higher telomers has been attempted.

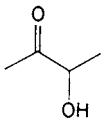


Gas-liquid chromatography has shown that low-boiling fractions, obtained in the addition of acetaldehyde to the acetate *II*, contain several side products of shorter elution time than has the 1 : 1 adduct *IV*. From these fractions we isolated and identified by ^1H, ^{13}C NMR, IR and mass spectra 2,5-dihydroxy-2,3,5,6-tetramethyl-1,4-dioxane (*VII*), 3-hydroxy-2-butanone (*VIII*) and 3-hydroxy-3-methyl-2,4-pentanedione (*IX*). Structure of other compounds was derived on the basis of gas-liquid chromatography – mass spectrometry measurements: we have proven the presence of 2,3-butanedione (*X*), 2,3-butanediol (*XI*), 3-acetoxy-2-butanone (*XII*) and 3,4-dihydroxy-3,4-dimethyl-2,5-hexanedione (*XIII*), the latter being separated by gas-liquid chromatography into the diastereoisomeric racemates.

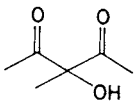
The formation of compounds *VII*–*XIII* can be explained by photochemical transformations of acetaldehyde and biacetyl, arising in photolysis of acetaldehyde[16,17].



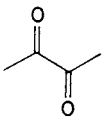
VII



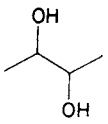
VIII



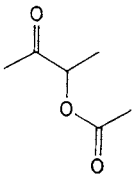
IX



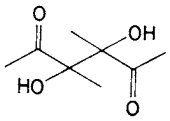
X



XI



XII



XIII

As concerns the radiation-initiated addition of acetaldehyde to esters *I* and *II*, we studied the dependence of the chemical yield of adducts *III* and *IV* and of telomers *V* and *VI* on the radiation dose (molar ratio acetaldehyde: allyl ester 20 : 1) and on the ratio of the reactants. From the radiation dependence results (Table II) we calculated the initial radiation yields[18] *G* (molecules/100 eV) for the 1 : 1 adducts *III* and *IV* and for the 1 : 2 telomers *V* and *VI*: $G(III) = 200{\cdot}8$, $G(IV) = 211{\cdot}3$, $G(IV) = 211{\cdot}3$, $G(V) = 39{\cdot}5$, $G(VI) = 37{\cdot}9$.

The dependence of chemical yields of *IV* and *V* on the molar ratio of the reactants was followed only for the addition of acetaldehyde to acetate *II*. As seen from the results in Table III, with increasing excess of acetaldehyde the 1 : 1 adduct *IV* is preferred at the expenses of the 1 : 2 (*VI*) and higher telomers (whose amount is indicated by the weight of the distillation residue). With the molar ratio acetaldehyde: *II* 40 : 1 the chain transfer in the 1 : 1 radical *IVa* is so preferred to the telomerization that the addition becomes a suitable method of obtaining the oxopentyl acetate *IV*.

The acetate *IV* had been converted to the hydroxypentanone *XIV* by acid-catalyzed alcoholysis[11]. In the present study we prepared *XIV* by transesterification of the formate *III* and acetate *IV* with methanolic sodium methoxide at room temperature[19]. The obtained crude hydroxypentanone *XIV* was obtained in yields over 90% and was sufficiently pure according to thin-layer chromatography and ^{1}H NMR spectra. On distillation in vacuo or prolonged standing at room temperature, the

TABLE II

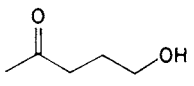
Radiation-initiated addition of acetaldehyde to allyl formate[a] (*I*) and allyl acetate[b] (*II*): dependence of chemical yields of adducts *III* and *IV* and telomers *V* and *VI* on the radiation dose

Radiation dose kGy	Conversion of ester *I* (*II*)	Chemical yield, g (%)		Distillation residue in the addition to *I* (*II*), g
		1 : 1 adducts	1 : 2 telomers	
10	36·8 (37·5)	*III* 3·55 (24·5) *IV* 3·75 (24·4)	*V* 0·98 (8·1) *VI* 0·99 (7·6)	0·40 (0·59)
20	47·6 (53·1)	*III* 4·60 (31·7) *IV* 5·48 (35·6)	*V* 1·22 (10·1) *VI* 1·60 (12·3)	0·56 (0·56)
30	79·8 (83·7)	*III* 8·57 (58·9) *IV* 9·58 (62·2)	*V* 1·53 (12·7) *VI* 1·96 (15·0)	0·79 (0·70)
50	82·0 (90·2)	*III* 8·86 (61·0) *IV* 10·54 (68·4)	*V* 1·77 (14·7) *VI* 1·88 (14·4)	0·60 (0·79)
100	87·0 (93·7)	*III* 9·13 (62·9) *IV* 10·87 (70·6)	*V* 1·74 (14·5) *VI* 2·02 (15·5)	0·93 (0·82)

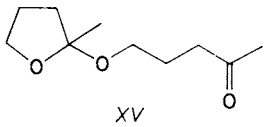
[a] The ampoule contained 9·6 g (0·11 mol) of formate *I* and 98·0 g (2·22 mol) of acetaldehyde; [b] the ampoule contained 10·7 g (0·107 mol) of acetate *II* and 94·0 g (2·13 mol) of acetaldehyde.

ketone *XIV* slowly turned into another compound which was separated by extraction with pentane and shown by IR and NMR spectra to be tetrahydro-2-(4-oxopentyloxy)-2-methylfuran[20] (*XV*).

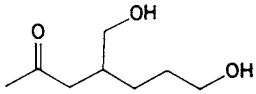
Analogous deacylation of the 1 : 2 telomers *V* and *VI* afforded 7-hydroxy-4-hydroxymethyl-2-heptanone (*XVI*).



XIV

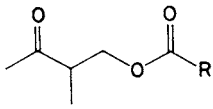


XV



XVI

The structures *III*–*VI* and *XIV*–*XVI* were confirmed by elemental analysis and ^1H and ^{13}C NMR spectra. The ^1H NMR spectra of the acetate *III* and formate *IV* exhibit signals at 1·2 ppm (doublet) and at 2·25 ppm (singlet). We cannot exclude that these signals belong to the isomeric 1 : 1 adducts, i.e. 2-methyl-3-oxobutyl formate (*XVII*) and 2-methyl-3-oxobutyl acetate (*XVIII*), which we did not isolate so far.



XVII, R = H
XVIII, R = CH_3

TABLE III

Radiation-induced addition of acetaldehyde (AcH) to allyl acetate (*II*): dependence of chemical yields of *IV* and *VI* on the molar ratio of reactants

Molar ratio *II* : AcH	*II* g (mol)	Acetaldehyde g (mol)	*IV* g (%)	*VI* g (%)	Distillation residue mg/g *II*
1 : 40	6·4 (0·064)	112·6 (2·56)	7·67 (83·2)	0·45 (5·8)	46
1 : 20[a]	10·87 (0·107)	94·0 (2·13)	10·87 (70·6)	2·02 (15·5)	75
1 : 10	6·4 (0·064)	28·2 (0·64)	5·56 (60·3)	1·58 (20·3)	109
1 : 5	6·4 (0·064)	14·1 (0·32)	2·92 (31·7)	1·85 (23·7)	248

[a] Taken from Table II.

Acetoin *VIII* dimerizes on standing to give the dioxane *VII* whose structure could be confirmed by ^1H and ^{13}C NMR spectra only in pyridine solution. When dissolved in chloroform, *VII* was converted into the monomeric form *VIII*.

EXPERIMENTAL

Boiling points are uncorrected. Proton NMR spectra were measured on a Varian XL-100-15 (100 MHz) and a Bruker AM 400 (400·13 MHz) instruments, ^{13}C NMR spectra on an AM R400 (100·62 MHz) Bruker spectrometer, all in deuteriochloroform (unless stated otherwise) with tetramethylsilane as internal standard. Chemical shifts are given in ppm, coupling constants J in Hz, digital resolution 0·18 Hz and 0·75 Hz for the ^1H and ^{13}C spectra, respectively. Mass spectra were obtained with a JEOL DX 303 or Finigan Ltd. spectrometers, IR spectra were recorded on a Perkin–Elmer 325 instrument in tetrachloromethane, wavenumbers are given in cm^{-1}. The photochemically initiated additions were performed in a submersible, water-cooled, photochemical reactor using a high-pressure mercury lamp RVK (400 W) and a quartz filter[21].

Allyl Formate (*I*)

A mixture of allyl alcohol (697·0 g; 12 mol), formic acid (533·0 g; 12 mol) and calcium chloride (160·0 g; 1·4 mol) was heated in a flask attached to a fractionation column, filled with Raschig rings and equipped with a distillation head. Fraction boiling at 72–80°C was collected, washed with a solution of sodium carbonate and dried over magnesium sulfate. Fractionation afforded 451·0 g (43·7%) of allyl formate (*I*), b.p. 80–82°C.

Allyl Acetate (*II*)

Acetic anhydride (510·0 g; 5 mol) was added during 90 min at 90°C to a stirred mixture of allyl alcohol (290·0 g; 5 mol) and sodium acetate (41·0 g; 0·5 mol). After heating for 60 min, the mixture was cooled and washed with ice-cold water. The upper layer was separated, neutralized with a solution of sodium carbonate, dried over magnesium sulfate and filtered. Fractionation afforded 321·7 g (64·3%) of allyl acetate, b.p. 102–103°C.

4-Oxopentyl Formate (*III*) and 7-Formyloxy-4-formyloxymethyl-2-heptanone (*V*)

A solution of allyl formate (*I*) (38·8 g; 0·45 mol) in acetaldehyde (399·5 g; 9·07 mol) was irradiated at 15–20°C with UV light for 7·5 h under simultaneous introduction of nitrogen. After distillation of excess acetaldehyde and the formed paraldehyde, the mixture was fractionated to give 34·1 g (59%) of the formate *III*, b.p. 89–90°C/1·7 kPa (reported[20] 95–97°C/2·5 kPa). ^1H NMR: 1·95 m, 2 H ($CH_2CH_2CH_2$); 2·2 s, 3 H (CH_3CO); 2·58 t, 2 H (CH_2CO, J = 7·1); 4·2 t, 2 H (CH_2O, J = 6·4); 8·1 s, 1 H (HC=O). ^{13}C NMR: 22·68 t ($CH_2CH_2CH_2$); 29·92 q (CH_3); 39·61 t (CH_2CO); 63·08 t (CH_2O); 161·26 d (HC=O); 207·64 s (C=O). Mass spectrum: m/z (relative intensity, %): 131 (M + 1, 5); 130 (1), 115 (0·2), 101 (0·6), 87 (12), 85 (90), 84 (34), 71 (5), 69 (9), 59 (7), 58 (98), 57 (7), 43 (100), 42 (32), 31 (43), 29 (23).

Fractionation of the distillation residue afforded 8·7 g (17·8%) of the heptanone *V*, b.p. 130–131°C/53 Pa. For $C_{10}H_{16}O_5$ (216·3) calculated: 55·55% C, 7·41% H; found: 55·78% C, 7·44% H. ^1H NMR: 1·4 m, 2 H ($CHCH_2CH_2$); 1·7 m, 2 H ($CH_2CH_2CH_2$); 2·16 s (CH_3); 2·33 m, 1 H (CH_2CHCH_2); 2·52 m, 2 H (CH_2CO, ^2J = 17·5, ^3J = 6·9 and 6·1); 4·12 m, 2 H (OCH_2CH, ^2J = 11·2, ^3J = 5·7 and 5·8); 4·16 t, 2 H (CH_2CH_2O, J = 6·1); 8·1 s, 2 H (HC=O). ^{13}C NMR: 25·92 t ($CH_2CH_2CH_2$); 27·61 t ($CHCH_2CH_2$); 30·38 q (CH_3); 32·86 d (CH); 45·19 t (CH_2CO);

63·49 t (CH_2—CH_2O); 65·61 t ($CHCH_2O$); 160·93 d (HC=O); 161·03 d (HC=O); 206·99 s (CH_3C=O). Mass spectrum *m/z* (relative intensity, %): 217 (M + 1, 1), 171 (38), 143 (4), 124 (6), 113 (12), 95 (6), 85 (18), 67 (32), 58 (26), 43 (100).

4-Oxopentyl Acetate (*IV*) and 7-Acetoxy-4-acetoxymethyl-2-heptanone (*VI*)

A solution of allyl acetate (*II*; 25·8 g; 0·26 mol) in acetaldehyde (340·8 g; 7·74 mol) was irradiated with UV light at 15—20°C for 7 h under constant introduction of nitrogen. The acetaldehyde and paraldehyde were distilled off and the residue was fractionated to give: *1*) 21·3 g of fraction b.p. 37—51°C/1·6 kPa; *2*) 8·6 g of fraction b.p. 74—77°C/1·4 kPa; *3*) 48 g of fraction b.p. 76 to 85°C/1·3 kPa; *4*) 29·7 g (80%) of fraction b.p. 100—101°C/1·7 kPa (ref.[20]) which was identified as the acetate *IV*. For $C_7H_{12}O_3$ (144·2) calculated: 58·32% C, 8·39% H; found: 57·89% C, 8·51% H. ^{1}H NMR: 1·90 m, 2 H ($CH_2CH_2CH_2$); 2·03 s, 3 H (CH_3COO); 2·16 s, 3 H (CH_3CO); 2·53 t, 2 H (CH_2CO, J = 7·2); 4·06 t, 2 H (CH_2O, J = 6·4). ^{13}C NMR: 20·85 q (CH_3COO); 20·85 t ($CH_2CH_2CH_2$); 29·88 q (CH_3CO) ;39·86 t (CH_2CO); 63·6 t (CH_2O); 170·91 s (COO); 207·51 s (C=O). Mass spectrum *m/z* (relative intensity, %) 144 (M^+, 0·4), 101 (14), 87 (15), 84 (15), 71 (35), 61 (19), 58 (22), 43 (100).

Further distillation of the residue gave 3·45 g (11%) of material b.p. 126—127°C/40 Pa, shown to be the diacetate *VI*. For $C_{12}H_{20}O_5$ (244·3) calculated: 59·00% C, 8·25% H, found: 59·08% C, 8·02% H. ^{1}H NMR: 1·39 m, 2 H ($CHCH_2CH_2$); 1·66 m, 2 H ($CH_2CH_2CH_2$); 2·04 s, 6 H (CH_3COO); 2·16 s, 3 H (CH_3CO); 2·30 m, 1 H (CH); 2·48 m, 2 H (CH_2CO, ^2J = 17·3, ^3J = 7); 4·0 m, 2 H ($CHCH_2O$, ^2J = 11·1, ^3J = 6·1); 4·05 t, 2 H (CH_2CH_2O, J = 6·5). ^{13}C NMR: 20·77 q and 20·87 q (CH_3COO); 26·01 t ($CH_2CH_2CH_2$); 27·83 t ($CHCH_2CH_2$); 30·36 q (CH_3CO); 33·13 d (CH); 45·57 t (CH_2C=O); 64·25 t (CH_2CH_2O); 66·42 t ($CHCH_2O$); 170·82 s and 170·93 s (COO); 207·15 s (C=O). Mass spectrum *m/z* (relative intensity, %): 245 (M + 1, 3·5), 185 (53·5), 143 (1·3), 127 (15), 111 (5·3), 95 (4·3), 85 (21), 67 (21), 54 (5·3), 43 (100).

Fraction 1 on standing deposited crystals of m.p. 114—116°C, identified as 2,5-dihydroxy-2,3,5,6-tetramethyl-1,4-dioxane (*VII*). For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·40% C, 9·17% H. ^{1}H NMR ($C_5{}^2H_5N$): 1·41 d, 6 H (CH_3CH, J = 6·5); 1·52 s, 6 H (CH_3C); 4·52 q, 2 H (CH); 7·5 bs, 2 H (OH). ^{13}C NMR ($C_5{}^2H_5N$): 16·54 q (CH_3CH); 25·63 q (CH_3C); 70·17 d (CH); 95·49 s (OCO). On standing at room temperature, the crystals turned into a mixture of solid and liquid phase. The liquid portion was identified as 2-hydroxy-3-butanone (*VIII*). ^{1}H NMR: 1·38 d, 3 H (CH_3CH, J = 7·1); 2·21 s, 3 H (CH_3CO); 3·7 bs, 1 H (OH); 4·26 q, 1 H (CHO, J = 7·1). ^{13}C NMR: 19·55 q (CH_3CH); 24·95 q (CH_3CO); 73·17 d (CH—O); 211·03 s (C=O).

Fraction 2 was a mixture of two compounds (GLC on 15% Reoplex). The minor component (20 rel. %) of shorter elution time was shown to be dioxane *VII* by comparison with a standard, the principal constituent (80 rel. %) was identified by ^{1}H NMR as 3-hydroxy-3-methyl-2,4-pentanedione (*IX*). ^{1}H NMR: 1·58 s, 3 H (CH_3C); 2·38 s, 6 H (CH_3CO); 4·9 s, 1 H (OH).

Fraction 3 was a mixture of several compounds which was analyzed by the GC–MS technique (*m/z*, (relative intensity, %)): 2,3-*butanedione* (*X*): 86 (M^+, 13), 60 (47), 45 (45), 43 (100), 42 (7); 3-*hydroxy*-2-*butanone* (*VIII*): 88 (M^+, 10), 75 (28), 57 (90), 47 (68), 46 (35), 43 (57), 29 (5); 2,3-*butanediol* (*XI*): 90 (M^+, 2), 57 (8), 47 (7), 45 (100), 43 (12); 3-*acetoxy*-2-*butanone* (*XII*): 130 (M^+, 0·5), 88 (84), 73 (7), 59 (5), 55 (30), 45 (15), 43 (100); 3-*hydroxy*-3-*methyl*-2,4-*pentanedione* (*IX*): 130 (M^+, 4), 87 (18), 43 (100); 3,4-*dihydroxy*-3,4-*dimethyl*-2,5-*hexanedione* (*XIII*), *meso*- and *dl*-form: 174 (M^+, 0·1), 131 (12), 89 (10), 88 (12), 45 (7), 43 (100).

Radiation-Initiated Addition

The additions were performed in 1 000 ml and 6 000 ml glass bottles or flasks, or in 300 ml

sealed glass ampoules. The mixtures of acetaldehyde and the ester *I* or *II* were irradiated in an irradiation facility Perun (Škoda, Plzeň, Czechoslovakia) or Gammacell 220 (AECL), the dose rate being $\dot{D} = 1{\cdot}0-1{\cdot}6$ kGy h^{-1}. Prior to the irradiation, nitrogen was bubbled through the reaction mixtures.

After irradiation, the mixture was filtered to remove metaldehyde (if formed), and acetaldehyde together with paraldehyde were distilled off. Fractionation of the residue afforded the 1 : 1 adducts *III* and *IV* and the 1 : 2 telomers *V* and *VI*. The reaction conditions and yields of the products *III*—*VI* are given in Table I (preparative reactions), Table II (studies of radiation dose effect) and Table III (experiments studying the dependence on the molar ratio of the reactants). The yield of products *III*—*VI* are calculated from the weights of the pure product fractions and from percentage of the products in the intermediate fractions.

5-Hydroxy-2-pentanone (*XIV*) and 2-Methyl-2-(4-oxopentyloxy)tetrahydrofuran (*XV*)

A) Oxopentyl acetate *IV* (21·6 g; 0·15 mol) was added to a solution of sodium methoxide in methanol, prepared from sodium (0·1 g) and methanol (150 ml), and the mixture was set aside at room temperature. The conversion was monitored by thin-layer chromatography on silica gel G in chloroform containing 5% methanol. After 4·5 h, the mixture was neutralized with gaseous carbon dioxide and methanol was evaporated on a rotatory evaporator. The residue was extracted with ether (4×) and the solvent was evaporated to give 14·7 g (96%) of chromatographically pure hydroxypentanone *XIV*. ^{1}H NMR: 1·8 m, 2 H ($CH_2CH_2CH_2$); 2·18 s, 3 H (CH_3CO); 2·58 t, 2 H (CH_2CO; $J = 6{\cdot}3$); 3·6 t, 2 H (CH_2OH, $J = 7{\cdot}2$).

Distillation of the obtained hydroxypentanone *XIV* yielded a fraction of b.p. 105—111°C/ /3·3 kPa (12·91 g) consisting (TLC) of *XIV* and another compound. Therefore, a part (5·0 g) of this fraction was extracted three times with pentane. After removal of the pentane in vacuo the obtained residue (2·46 g) was shown to be the tetrahydrofuran *XV* (ref.[20]). ^{1}H NMR: 1·42 s, 3 H (CH_3—C); 1·8 m, 2 H ($CH_2CH_2CH_2CO$); and 1·6—2·1 m, 4 H ($CH_2CH_2CCH_3$); 2·15 s, 3 H (CH_3CO); 2·52 t, 2 H (CH_2CO, $J = 7{\cdot}1$); 3·43 m, 2 H (OCH_2, $^2J = 9{\cdot}2$, $J = 6{\cdot}2$); 3·88 m, 2 H (ring CH_2—O). The pentane-insoluble portion (2·3 g) was a mixture of pentanone *XIV* (72 rel. %) and tetrahydrofuran *XV* (28 rel. %) as determined by ^{1}H NMR spectroscopy.

B) A solution of oxopentyl formate *III* (13·0 g; 0·1 mol) was treated with methanolic sodium methoxide as described in the Experiment *A*). A complete conversion was achieved after 1·5 h. Yield 9·7 g (95%) of hydroxypentanone *XIV*, identical (TLC and ^{1}H NMR) with the compound prepared according to procedure *A*).

7-Hydroxy-4-hydroxymethyl-2-heptanone (*XVI*)

A) Diacetate *VI* (9·2 g; 0·038 mol) was dissolved in a solution of sodium methoxide (prepared from 0·1 g of sodium and 100 ml of methanol). After standing at room temperature for 1·5 h the reaction mixture was neutralized by introduction of carbon dioxide. Methanol was evaporated and the residue was extracted four times with ether. Removal of the solvent in vacuo afforded 6·03 g (99%) of chromatographically pure heptanone *XVI*. For $C_8H_{16}O_3$ (160·2) calculated: 59·97% C, 10·07% H; found: 60·04% C, 9·96% H. ^{1}H NMR: 1·5 m, 4 H (CH—$CH_2CH_2CH_2$); 2·18 s, 3 H (CH_3CO); 2·3 m, 1 H (CH); 2·52 m, 2 H ($COCH_2$, $^2J = 17{\cdot}2$, $^3J = 6{\cdot}9$); 3·62 m, 2 H ($CHCH_2OH$, $^2J = 11{\cdot}3$, $^3J = 6{\cdot}0$); 3·64 t, 2 H (CH_2—CH_2O, $J = 6{\cdot}2$). Mass spectrum *m/z* (relative intensity, %): 161 ($M^+ + 1$, 0·4), 143 (40), 127 (6), 112 (4), 97 (6), 83 (24), 67 (20), 55 (22), 43 (100).

B) Diformate *V* (17·1 g; 0·08 mol) was treated with methanolic sodium methoxide as described in the procedure *A*), affording 12·7 g (99%) of heptanone *XVI*, identical (TLC and ^{1}H NMR spectra) with the compound prepared according to *A*).

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