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Methods of synthesis of acrolein and its α-substituted derivatives

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Abstract. The methods of synthesis of acrolein and its α-alkyl-substituted derivatives are examined: (a) catalytic oxidation of propene, isobutene, propane, isobutane, propyl and *tert*-butyl alcohols, *tert*-butyl alkanoates, propionaldehyde isobutyraldehyde, and allyl alcohol and its ethers and esters; (b) condensation of formaldehyde with aliphatic aldehydes by the Mannich reactions and also in the vapour phase over heterogeneous catalysts. Both general methods (the Mannich reaction, *ipso*-substitution of a α-halogen in the acrylic system, and interaction of 1-bromo–2-ethoxycyclopropyllithium with electrophiles) and various special methods are used in the synthesis of α,β-unsaturated aldehydes with functional-group-substitutents. The bibliography includes 323 references.

I. Introduction

Acrolein and methoacrolein and industrial products produced on a large scale. The world production of the former compounds runs into hundreds of thousands of tonnes annually. The acrylic and methacrylic acids obtained from acrolein and methacrolein, as well as their esters have found extensive applications as monomers in the manufacture of various polymeric materials, synthetic fibres, emulsions, adhesives, etc. Industrial methods of synthesis of acrylonitrile, methionine, glycerol, allyl alcohol, glutaraldehyde, β-picoline, pheromones, pesticides, perfumes, and medicinal drugs from acrolein have been developed. The high reactivity of acrolein and its substituted derivatives has created extensive possibilities for its use in fine organic synthesis. During the last decade up to 300 articles and patents devoted to the methods of synthesis of acrolein and its derivatives and their involvement in various syntheses have been published annually. Acrolein itself is used as a herbicide and algicide and prevents the growth of biomass on technical water supply systems, as a slimicide which destroys slime in the manufacture of paper, as a binder in solutions for building purposes, as a component for the purification of waste water containing hydrogen sulfide and cyanide ions, as an ingredient in compositions for the protection of wood against water, as a stabiliser used in the finishing of textile materials, etc. It has been shown recently that latex microbeads based on polyacrolein can be used in immunoanalysis. All the expanding applications of acrolein and its derivatives have made it necessary to improve the known methods and to seek new ones for their synthesis using cheaper and more readily available raw materials.

The principal industrial method for the synthesis of acrolein and methacrolein available at present involves the incomplete selective vapour-phase oxidation of propene and isobutene respectively on heterogeneous catalysts. The last systematic review devoted to the oxidation of propene to acrolein covers the literature published up to 1981.[1] Review articles on other methods of synthesis of acrolein and its derivatives were published even earlier.[2–6] We therefore had to deal in the present review with studies published mainly during the last 15–20 years. In addition α,β-unsaturated aldehydes α-substituted by functional groups, the chemical reactions of which are extremely varied and frequently unexpected, have been scarcely represented in the review literature (with the exception of one publication by the authors of the present review[7]). As far as possible, they will be considered exhaustively in the text below.

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II. Methods of synthesis of acrolein and α-alkylacroleins

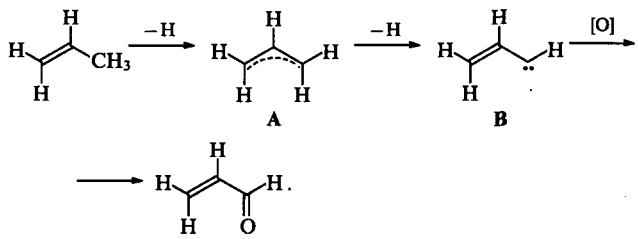
1. Oxidation of propene and isobutene

The partial vapour-phase oxidation of propene and isobutene on heterogeneous catalysts is at present the main industrial method of synthesis of acrolein and methacrolein respectively:

$$CH_2=CR-CH_3 + O_2 \longrightarrow CH_2=CR-CHO + H_2O;$$
$$R = H, Me.$$

This reaction constitutes the first stage of the large scale industrial production of acrylic and methacrylic acids from which acrylates and polyacrylates are obtained in their turn. Data on the improved methods of the oxidation of propene and isobutene available up to 1981 are surveyed in the existing reviews.[1,4–6,8–14]

The catalytic oxidation of propene is one of the most important allylic oxidation reactions.[12] In allylic oxidation, the alkene, for example propene, is activated as a result of the elimination of a hydrogen atom from the methyl group with formation of the allyl intermediate A. This stage determines the rate of the entire process.[12,15–18]



The intermediate **B** formed subsequently interacts with the oxygen of the catalyst lattice and is converted into acrolein. All the known selective oxidation catalysts have oxidation-reduction properties. They must be capable of not only being reduced during the formation of acrolein but also of being reoxidised with incorporation of oxygen from the gas phase into the catalyst lattice in the form of the O^{2-} ions, which results in the refilling of the free vacancies. A procedure in which the properties of various polyvalent oxides are combined has become one of the fruitful methods for the selection of catalysts of the process under consideration.[12] The participation of oxygen from the crystal lattice of bismuth molybdate or the three-component bismuth–vanadium–molybdenum oxide catalyst in the oxidation of propene has been confirmed experimentally using $^{18}O_2$ as the oxidant.[19,20]

Among the complex oxide catalysts for the selective oxidation of propene, molybdenum-containing catalysts have come to be most widely used during the last 20 years.[21–26] However, molybdenum catalysts are frequently used only for research purposes, for example, in the study of the dependence of the activity on the surface structure[27] or for the determination of the orientation of MoO_3 in the catalyst layers, which influences the selectivity of the reaction.[28,29] Bimetallic catalysts, which contain, apart from molybdenum oxide, also bismuth,[30] cobalt,[31] or vanadium[32] oxide, are much more active. The incorporation of bismuth in an amount of even several tenths per cent increases the conversion of butene and the reaction selectivity with respect to methacrolein by tens per cent.[33] The addition of bismuth increases the effectiveness of the oxidation of propene on $PbMoO_4$[34] or on the multicomponent molybdenum catalysts $Mo_{12}Bi_xFe_yTl_z$ and $Mo_{12}Bi_xFe_yTl_zNi_6Zn_3$.[35]

Systematic studies have been made on the oxidation of isobutene on Fe–Mo–Te and Fe–Mo–Sb oxide catalysts,[36–39] as well as on Co–Mo–Bi–Fe oxides.[40] On one of the specimens of the Fe–Mo–Te catalysts, it has been possible to attain the virtually complete conversion of the olefin in the oxidation of an isobutene–air mixture containing 1.8 vol.% of isobutene at 370 °C. The selectivity with respect to methacrolein was then 77% and the yield of the latter relative to the isobutene passed through the system was 75%–80%.

However, the multicomponent oxide catalysts containing added Co, Ni, Fe, K,[21] Ni, Co, Fe, K, P, Si,[41] and certain other elements,[42–43] apart from molybdenum and bismuth, are the most effective and selective. With the aid of such catalysts, it has been possible to achieve 93%–98% conversion of propene and a 79%–88% yield of acrolein.[41,44] Equally high parameters were obtained in the oxidation of butene, but the catalysts employed had a more complex composition:

$$Mo–Co–Fe–Bi–Tl–X–Y–Z–O,$$

where X = V and/or NB, Y = La and/or Ce, and Z = Cs and/or Te;[45]

$$Mo–Co–Fe–Ni–Pb–X–SmO,$$

where X represents two elements from the Rb, Cs, Tl triad:[46]

$$Mo–Bi–M^1–M^2–M^3–M^4–M^5–ZnO,$$

where M^1 = In, La, Ga or Al; M^2 = Fe or Fe and Cu; M^3 = Ni and/or Co; M^4 represents several elements from the P, W, Cr triad (usually W + P or W + Cr) and sometimes B, As, or V, and M^5 is one or several of the elements from the set Cd, Ta, Sm, Nb, Ag, Pb, Mn, Re, Sn, Ge, Mg, Ca, or Ba.[47] Each of the eight or nine elements is a necessary component for the attainment of a high productivity. For example, the last of the catalysts enumerated, with added zinc, is distinguished by an increase in selectivity and a higher stability.[47]

Since the catalysts are multicomponent systems, the choice of the composition ensuring the attainment of the optimum activity and selectivity is a task of enormous difficulty.

The stability and activity of the catalyst play an important role in the industrial manufacture of acrolein. For example, at the start of the catalyst bed, where the temperature has increased owing to the evolution of the heat of the reaction with the water present in the reacting gas, molybdic acid is formed and vaporises.[48] The vaporised molybdenum condenses in the colder part of the reactor. As a result of this, the yield of methacrolein is low at the beginning of the bed.

Apart from molybdates, metal anitmonates[49] and tellurates as well as multicomponent systems based on them[50,51] and phosphates of the type $2Bi_2O–P_2O_5$ [17] are active catalysts. The introduction of 0.2%–0.8% of Na_2O into the last catalyst increases the amount of basic surface centres and leads to the conversion of propene not into acrolein but into hexa-1,5-diene and benzene.[52]

Vanadium and titanium–vanadium oxide catalysts exhibit an increased selectivity, which depends on the presence of nonstoichiometric V–Na compounds.[53,54]

Iron–tin[16] and tin–antimony[27,55–58] catalysts constitute a separate group of effective catalysts of the oxidation of propene. The latter exhibit an especially high activity in the oxidation of isobutene to methacrolein.[59–64] Depending on the composition, the optimum temperature at which the highest activity of the catalyst is attained is in the range from 430 to 675 °C.[59] The activity and selectivity of the tin–antimony catalysts depend greatly on the method of their preparation. The dissolution of the metal in boiling nitric acid,[64] the coprecipitation of the corresponding Sn and Sb salts followed by heat treatment of the deposits,[49] the deposition of Sb oxides onto the SnO_2 matrix, mixing of SnO_2 and Sb_2O_4 or Sb_6O_3,[27] and spray drying of an aqueous suspension of the initial oxides with subsequent heat treatment at 800 °C [65] are most often used. The Sb–Sn oxide catalyst obtained in the last case exhibits a high mechanical strength and ensures a high yield of methacrolein (up to 85% relative to the initial isobutene). Highly active and selective tin–antimony catalysts of the gas-phase oxidation of isobutene to methacrolein (yield up to 72%) are obtained from a moist paste of tin(II) and antimony (preferentially Sb_2O_5) oxides by drying it and subsequent heat treatment.[61] The conditions in the preparation of the tin–antimony catalysts influence their structure and properties so significantly that the method of preparation of the catalyst is frequently more important than its chemical composition.[66]

It has been suggested that catalysts be compared in terms of their maximum selectivity attained for a specified conversion of isobutene and yield of methacrolein.[62] According to this criterion, the catalysts investigated can be arranged in the following series:

$$Sn–Sb > Bi–Mo–V–O > Bi–Mo–W–O.$$

The Sn–Sb–O mixed oxide catalyst is 1.5–2 times less active at 425 °C than the analogous Mo–Bi–O catalyst for the same initial selectivity with respect to methacrolein (80%).[67]

A series of the catalysts of the oxidation of propene to acrolein described in the literature have been compared using the thermal desorption method: $Co_6Mo_{12}Bi_{0.5}Fe_{0.75}O_x$, Bi_2MoO_6, 5 at.% Sb in SnO_2, USb_3O_3, $BiFeMoO_x$, $Bi_3FeMo_2O_x$, Cu_2O, $CoMoO_4$.[68]

It was established that the active intermediates arising from propene can be converted into acrolein via two pathways: they interact either with the oxygen of the catalyst lattice or with the adsorbed oxygen. The rate of the selective oxidation of propene on modified cobalt molybdate is determined by the acrolein desorption stage.

Overall, the idea that it is mainly the oxygen ions of the crystal lattice which participate in the selective oxidation of alkenes over the $MoO_3-Bi_2O_3$ or $Bi_{1-x/3}V_{1-x}Mo_xO_4$ catalysts while gaseous oxygen reoxidises the catalyst became firmly established towards the beginning of the 1990s.[19,20,34] The use of oxides with a scheelite structure of the type $Pb_{1-3x}Bi_{2x}\Phi_xMoO_4$ (Φ = cationic vacancy, x = 0 and 0.04) as the catalysts in the electrochemical oxidation of the alkenes made it possible to determine the mobility of the lattice oxygen ions, which is satisfactorily correlated with the catalytic activity.[20,34] The electrolyser cell incorporating the yttrium oxide-stabilised zirconium oxide (Y–s–Zr) as the solid electrolyte, namely $P(O_2)$, M/Y–s–Zr/M′, $P(O_2)'$, where M and M′ are electrodes, can perform the function of an oxygen pump, in which the oxygen stream passing through the electrolyte is regulated by the electric potential applied to the electrodes.[34,69] Under the conditions of the partial oxidation of alkenes in this system at 450–475 °C, the gaseous oxygen chemisorbed on the catalyst surface dissociates into ions, which diffuse into the bulk phase and are then incorporated in the allyl intermediate, forming oxidised compounds. On the other hand, the chemisorbed oxygen remaining on the surface accelerates only the more extensive oxidation of the alkenes to CO and CO_2. The ideas concerning the mechanisms of the oxidation of propene to acrolein current up to 1976 have been examined in detail in a monograph[13] (pp 81–102 and 120–132).

The copper catalyst for the oxidation of propene to acrolein, which was most effective in the 1940s, is little used. Nevertheless, the influence of reoxidation and of water vapour on the ion-exchange process catalysed by copper(II)-containing zeolites was studied recently.[70]

Apart from the composition of the catalysts and the method of mixing the components,[39,71] the valence state of the elements and hence the activity of the catalyst are influenced decisively by the heat treatment temperature,[33,50] the size and geometrical shape of the particles employed, and also their specific surface.[13,33,72]

The oxidation of olefins is usually carried out at 250–450 °C at a pressure close to atmospheric. A stationary catalyst bed is most often employed, but sometimes a fluidised bed is also used.[16,57] The effectiveness of reactants of different types in the oxidation process can be estimated by mathematical modelling methods.[60]

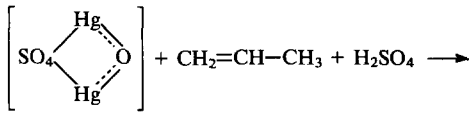
In order to make industrial processes more economical, it is essential to achieve in the latter a high conversion of the olefin and a greater selectivity with respect to the aldehyde in order to eliminate the cost of the recirculation of the unreacted initial alkene. An excess of oxygen 2–20 times greater than the concentration of the alkene is used for this purpose.[16,39,45,46,73] In order to prevent the overheating of the catalyst and to reduce the formation of the extensive oxidation product, the reacting gases are diluted with 10%–40% of water vapour,[23,24,36–39,45,46,74,75] nitrogen,[32,47,76] helium or argon,[46] or inert hydrocarbons — for example, but-1-ene.[73]

An increase in the conversion and selectivity during the oxidation of olefins to unsaturated aldehydes on a catalyst of the type $Mo_{12}BiCo_3NiFeK_{0.1}O_x$ is attained by introducing an inert material into the catalyst (up to 75% by volume). This promotes a more uniform distribution of the heat of reaction throughout the catalyst bed and the attainment of the optimum rate of the process.[74] The inert carriers employed are porcelain, quartz,[3,39,77] α-Al_2O_3,[37] SiO_2,[46,78] and 'inert' glass particles.[79] The Fe–Sb–O catalyst was diluted with silica gel containing 30% of SiO_2 (the SiO_2 content in the heat-treated catalyst was 2, 10, or 25 mass%).[16]

Acetone and acetaldehyde[53] and acetic and acrylic or methacrylic acids are encountered in small amounts, in addition to CO and CO_2,[46] among the side products of the oxidation of lower alkenes to acrolein and methacrolein respectively.[36,37,39,46,47] The side reactions involving the extensive oxidation of the initial alkenes and the unsaturated aldehydes formed can be suppressed by introducing promoting agents, for example thallium,[33,80] or by reducing the contact time.[39] The crystal structure,[27–30] phase composition,[75,81–83] and a number of other physicochemical properties of the catalysts of the vapour phase oxidation of lower alkenes[16,84,85] were investigated by IR, Raman,[51,86] UV, visible[87] and Mössbauer spectroscopy, electron microscopy,[88] and also X-ray diffraction.[61,88] The study of the kinetics of this process showed that the rate of formation of acrolein on a multicomponent molybdenum catalyst at 320 °C is independent of the partial oxygen and water vapour pressures, increasing with increase in the propene pressure.[89] The reaction involving the oxidation of propene to acrolein on a bismuth–molybdenum oxide catalyst with added Ni, Co, Fe, K, and P in the temperature range 300–390 °C is autocatalytic. Water vapour promotes the formation of acids as side products, but suppresses the extensive oxidation reactions of acrolein and acrylic acid.[64] Optimisation of the catalytic composition containing Mo, Co, Fe, Bi, and K oxides by Fabian's statistical method made it possible to attain the maximum selectivity with respect to acrolein.[90] The π-complexes of the allyl anion with transition metals have been investigated *ab initio* by the molecular orbital method.[91]

Technological schemes for the partial oxidation of propene on a multicomponent oxide catalyst have been developed with the aid of the mathematical modelling method.[21,60,89,90,92]

An effective laboratory liquid-phase method for the oxidation of propene to acrolein (in 85% yield) in an acid aqueous solution of mercury salts (preferentially the sulfate and perchlorate)[93] can be described schematically as follows:



$$\longrightarrow CH_2{=}CH{-}CHO + 2Hg_2SO_4 + 2HgSO_4 + 2H_2O.$$

An electrochemical process involving the allylic oxidation of propene to acrolein and acrylic acid has been patented.[94] When a palladium anode and 25% phosphoric acid as the electrolyte were used in this process, a high selectivity with respect to acrolein could not be attained.[95]

Acrolein and methacrolein are also formed in the oxidation of butadiene to isopropene by molecular oxygen in the presence of a rhodium catalyst (80 °C, 50 atm). However, the yield of the unsaturated aldehyde is only ~1%, so that this reaction is of no practical interest.[96]

2. Oxidation of propane and isobutane

Attempts were made in the 1980s to select a catalyst for the direct oxidation of propane by oxygen to the corresponding unsaturated aldehydes and acids.[97–99] The highest conversion (20%–30%) for a selectivity with respect to C_3 oxidation products of 13%–40% was attained on mixed oxide catalysts containing boron and phosphorus or molybdenum and tellurium at 500–550 °C. The selectivity with respect to acrolein of silver-doped bismuth vanadomolybdate exceeded 60%, but the conversion of propane was only 13%.[100]

Isobutane is oxidised by atmospheric oxygen to methacrolein at 250–450 °C over a reduced catalyst prepared from heteropolyacids, for example $H_3PMo_{12}O_{40} \cdot 30H_2O$.[101] The conversion of the alkane is 7%–8%, under these conditions, while the selectivity with respect to methacrolein and methacrylic acids is 12% and 48% respectively. Unsaturated aldehydes may be synthesised from the corresponding alkanes more conveniently in two stages without the isolation of intermediates.[102] The first stage involves the dehydrogenation of the mixture of alkanes (propane, isobutane, etc.) at 650 °C (approximately 45% conversion), while the second involves the oxidation of the products in another reactor at 340 °C (82% conversion).

3. Oxidation of propanol and *tert*-butyl alcohol

The vapour-phase oxidation of propanol by atmospheric oxygen to acrolein has been achieved using a two-bed catalyst.[103] Dehydration and oxidation occurred in the first and second catalyst beds respectively. BPO_4 coprecipitated with SiO_2 and Al_2O_3 and also WO_3 and Al_2O_3 were used as the dehydration catalyst. The second bed contained either the Fe–Co–Bi–P–Mo–K, Fe–Co–W–Bi–Mo–Mg, and Sb–U mixed oxides or a mixture of bismuth molybdate and phosphoromolybdate. The mixture of propanol and oxygen supplied to the reactor was diluted with an inert gas (N_2, He, CO_2) or water vapour and the process was carried out at 350–500 °C and pressures in the range 0.5–10 atm.

tert-Butyl alcohol is a side product of the processing of the butane–butene fraction and in many other industrial processes. A highly efficient process involving the direct oxidation of the alcohol to methacrolein without the preliminary dehydration to isobutene has been proposed for its utilisation.[104] The yield of methacrolein on the Fe–Te–Mo (1 : 0.85 : 1) oxide catalyst[36] is more than 80%. The reaction is carried out at 400–420 °C, a space velocity of 0.1–0.15 s^{-1}, and an alcohol concentration in the initial reaction mixture of 4–5 vol.%. The synthesis of methacrolein by the partial oxidation of *tert*-butyl alcohol is similar to the oxidation of isobutene examined above.[22,25,26,45,46,105,106] Both processes are carried out on the same incomplete oxidation catalyst. Comparison of the dependence of the selectivities of the processes (with respect to methacrolein and CO and CO_2) on the degree of conversion of the initial isobutene or *tert*-butyl alcohol showed that the oxidation reaction proceeds by a consecutive-parallel mechanism. *tert*-Butyl alcohol is initially dehydrated to isobutene, which is converted into methacrolein and extensive oxidation products.[105–107] The selectivity with respect to methacrolein in the oxidation of *tert*-butyl alcohol on the Co–Mo–Bi–Fe–Sb–K–O catalyst is somewhat higher than in the oxidation of isobutene.[105] As in the oxidation of isobutene, the initial mixture of the alcohol and oxygen is diluted with water vapour and nitrogen.[25,26,105,108–110] A yield of methacrolein of 80%–90% for a virtually complete conversion of *tert*-butyl alcohol can be achieved on modern multicomponent oxide catalysts based on Mo–Co–Bi.[45,46] The use of complex catalytic compositions of the type $Sm_aFe_bBi_cX_dNi_eZ_fQ_gMo_{12}O_h$, where X = K, Rb, Cs, or Tl, Z = B, Co, Si, Au, Ag, Cd, Hg, V, Ti, Zr, Nb, Ta, Cr, W, U, Tc, Re, Be, Mg, Ca, Sr, or Ba and Q = Gd, Sc, Tb, Ho, Hf, Lu, or Dy, and a selection of catalyst carriers (SiO_2, SiC_2, Al_2O_3) and partial pressures of $(CH_3)_3COH$, O_2, N_2 and H_2O make it possible to raise the conversion of the alcohol to 92% for a selectivity of 90%.[111] According to patent data, the modified Mo–Fe–Co catalyst to which other elements have been added exhibits a high resistance to compression and wear, has a high catalyst activity, and is long lived.[112] Silicon dioxide is the commonest carrier for multicomponent catalysts of the processes described[22,108,113] but granulated activated charcoal can be used instead.[114]

In contrast to the one-reactor method described, it has been suggested that, in order to obtain methacrolein from *tert*-butyl alcohol, the latter should be dehydrated to isobutene over the γ-Al_2O_3 (90%)–SiO_2 (10%) catalyst at 80 °C. The isobutene obtained in this way is oxidised further to methacrolein. This greatly increases the lifetime of the second catalyst bed prepared from the Mo–Bi–Fe–Co–Cs oxide composition.[115]

A method of synthesis of methacrolein involving the oxidation of *tert*-butyl alcohol and/or its isobutyl ether as well as isobutene by oxygen-containing gases at 100–300 °C with the Hg, Ba, Cr, Mo, V, Mn oxides and halides as catalysts has been described.[114]

Highly effective catalysts of the oxidation of methyl and butyl ethers of *tert*-butyl alcohol, having the composition $Mo_aW_bBi_cFe_dX_eY_fZ_gQ_hO_x$ (X = Ni and/or Co; Y is an alkali or alkaline earth metal and/or Tl; Z = P, Te, Sb, Sn, Ce, Pb, Nb, Mn, Zn, Ge, Ga, La, In, Cd, V, Cr, U and/or Ag; and Q = Si, Al, Ti, or Zr) have been proposed. The conversion of the ethers is 98% and the selectivity with respect to methacrolein is 82%.[116]

Acetic and methacrylic acids, but-1-ene or but-2-ene, buta-1,3-diene, CO, CO_2, and polymers are side products of the oxidation of *tert*-butyl alcohol.[117,118]

4. Oxidation of *tert*-butyl alkanoates

A continuous method of synthesis of methacrolein by the gas-phase oxidation of *tert*-butyl alkanoates with oxygen or air over the isobutene oxidation catalyst in the presence of water vapour has been proposed.[119]

$$RCOOC(CH_3)_3 \xrightarrow{[O]} CH_2{=}C(CH_3){-}CHO.$$

The Mo–Co, Mo–Bi, Mo–Fe, Mo–P, Mo–Bi–Fe–Co oxide mixtures, preferably with added Ni, Sb, W, Te, Cs, K, Cu, or their mixtures, are used as catalysts. The reaction is carried out at 200–600 °C with the molar ratio oxygen : ester = (0.5–10) : 1. Under optimum conditions, the conversion of the ester is 61% and the selectivity with respect to methacrolein is 88%.

5. Oxidative dehydrogenation of propionaldehyde and isobutyraldhyde

The vapour phase oxidative dehydrogenation of propionaldehyde and isobutyraldehyde to acrolein and methacrolein respectively can be carried out at 280–390 °C over catalysts containing Mo, P, and O as well as Zn, Cu, or Ag on Al_2O_3 or Si–C.[120]

$$CH_3CHRCHO + 0.5O_2 \longrightarrow CH_2{=}CRCHO + H_2O;$$

R = H, Me.

It is recommended that the initial aldehyde–air mixture be diluted with water vapour or nitrogen. When the mixture of isobutyraldehyde, air, steam, and nitrogen is used in proportions of 3.4 : 18.6 : 70 : 8.0, it is possible to obtain methacrolein in 61.5% yield. The corresponding unsaturated acid is a side product. There has been no demand for isobutyraldehyde, which is a waste product in the manufacture of 2-ethyl-hexanol[121] and a side product in oxo-synthesis,[122] but there arises now the prospect of using it to obtain polyacrylates via methacrolein and methacrylic acid. The competitiveness of the oxidative dehydrogenation process depends greatly on the efficiency of the catalyst. The most effective catalytic systems for the oxidative dehydrogenation of isobutyraldehyde are presented in Table 1.

Table 1. Conditions in the oxidative dehydrogenation of isobutyraldehyde (IBA) to methacrolein.

Catalytic system	Initial reactants	T/°C	Yield (%)	Conversion (%)	Selectivity (%)	Ref.
Bi–P–Mo–O	IBA + air	320	80 [a]			123
Mo–Co–O (W or W + Te)	IBA : O_2 : H_2O : N_2 = 5 : 10 : 30 : 55		21			124
Mg–Cr–Fe–O_4	IBA : O_2 = 1 : (1.5–3)	350		68	88	125
Zn–Cr–Fe–O_4	IBA : O_2 = 1 : (1.5–3)	350		65	87	125
$H_5Mo_{10}V_2PO_{40}$	IBA : O_2 : N_2 = 4.7 : 12.7 : 82.6	288	68			126
Bi_2O_3 + Group I and II metal oxides	IBA + lattice oxygen	450	47		65.5	127
Mo–P–Zr–V–X–X′–O (X = K, Pb, Cs or Tl; X′ = Li, Na, Mg or Ca)	IBA + air + water	260	76.5	100	65.5	128
		310	17			
	IBA : air : H_2O = 4 : 40 : 56	320	18.1			129
		280	65.3	10		
$A_aFe_bP_cO_x$ (A = Cs, Tb, Mn, U, Ag, Tl)	IBA : O_2 : H_2O = 1 : 3.7 : 26	250–600	80	100		130
$H_5Mo_{10}V_2PO_{40}$	IBA + air + nitrogen	205–210	100	>90		131
$H_5Mo_{10}V_2PO_{40}$	O_2 : IBA = 1.23–1.92					122
Sb_2O_5	IBA + air	325	81.5	20		134
Fe, Te, and Mo oxides (1 : 0.85 : 1)	IBA : air = 2.5 : 97.5	285		88	42	132
Fe, Te, Mo, and Mg oxides (1 : 0.85 : 1 : 0.1)	IBA : air = 2.5 : 97.5	340		100	39	132
$Mo_3Sb_2Te_{0.1}O_x$	IBA : air = 2.5 : 97.5	310		12	67	132
		420		53	40	132
$Mo_{12}Sb_2Te_{0.2}O_x$	IBA : air = 2.5 : 97.5	385		100	41	132
$Mo_{12}SbTe_2O_x$	IBA : air = 0.5 : 10	360		>90	60	133

[a] The overall yield of methacrolein and methyl methacrylate is quoted.

The table shows that catalysts based on heteropolyacids of the type $H_{3+x}Mo_{12-x}V_xPO_{40}$ ensure the highest conversion and selectivity of the process at a comparatively low temperature. However, for technological use, they must be deposited on inert supports. The problem of the long time stability of the catalyst, associated mainly with retention of molybdenum, must then be solved.[131]

The study of the kinetics and mechanism of the oxidative dehydrogenation of isobutyraldehyde[131,135,136] on the Sb_2O_3 and MoO_3 catalysts by a pulsed method showed that the aldehyde reacts with the catalyst oxygen, forming methacrolein. The catalyst surface is then reduced. The methacrolein molecule is also adsorbed and, when oxygen is passed over the system, the latter is oxidised by gaseous oxygen to side products. The catalyst surface is reoxidised.[135]

The influence of the alternate changes in the composition of the gases entering the reactor on the selectivity of the oxidative dehydrogenation of isobutyraldehyde (IBA) over the heteropolyacid catalyst $H_5Mo_{10}V_2PO_{40}$ has been investigated. The alternation of two gas streams—IBA/N_2 and O_2/N_2 (for the reoxidation of the catalyst)—ensures the conversion of isobutyraldehyde into methacrolein with a greater selectivity than for the continuous supply of oxygen under comparable conditions.[137]

6. Synthesis of acrolein from allyl alcohol and its ethers and esters

Acrolein and methacrolein can be readily obtained by the vapour-phase oxidation of allyl alcohol, allyl acetate, and methylallyl acetate over a heterogeneous catalyst containing Pd with added Cu or Ag and Au at 150–200 °C.[138–140]

$$CH_2{=}CH{-}CH_2OH + 0.5O_2 \longrightarrow CH_2{=}CH{-}CHO + H_2O.$$

Methacrolein, suitable for oxidation to the acid without further purification, has also been obtained in a high yield by oxidising 2-methylallyl alcohol in the presence of the $A_aFe_bBi_eX_dMo_eO_f$ catalyst, where A = Co and/or Ni and X = Li, Na, K, Rb, Cs, or Tl.[141] However, this reaction, to which numerous studies have been devoted, has not found extensive application.[142]

The mechanism of the oxidation of allyl alcohol on MoO_3, $Bi_2O_3 \cdot nMoO_3$ (n = 1, 3), and multicomponent molybdenum-bismuth oxide[15] and silver[142] catalysts has been investigated. In the last case, the π-allyl intermediate, of the kind observed in the case of the oxide catalyst, is not observed, and the process should be regarded as oxidative dehydrogenation.

Much more attention has been devoted to the liquid-phase oxidation of allyl alcohol with the aid of special oxidants. Thus, by oxidising it in an aqueous acid medium by divalent silver ions at 20 °C, it is possible to obtain acrolein in 70% yield.[143] Oxidation of allyl alcohol by palladium chloride in aqueous solution at 25 °C leads to the formation of acrolein and α-hydroxyacetone in 30% and 15% yields respectively.[144] The use of deuteriated derivatives in this reaction showed that the reaction mechanism includes a stage involving the transfer of a hydride ion from the carbon atom linked to the hydroxyl.

A convenient method of synthesis of acrolein (and some of its derivatives) is based on the oxidation of allyl alcohol (and its γ-substituted derivatives) with chromic acid adsorbed on silica gel.[145]

$$RR^1C{=}CHCH_2OH \xrightarrow{H_2CrO_4/SiO_2,\ CCl_4} RR^1C{=}CHCHO; \quad (70\%-80\%)$$

R = R^1 = H; R = H, R^1 = Me; R = H, R^1 = Cl.

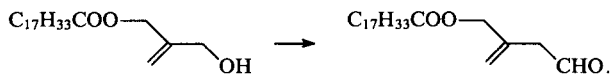
In the laboratory, acrolein can be obtained by oxidising alkyl allyl ethers with atmospheric oxygen in the presence of palladium chloride at 50–60 °C.[146] It has been demonstrated by the EPR method that an intermediate allyl radical is formed in this reaction.

$$CH_2{=}CH{-}CH_2{-}OR \xrightarrow[-RO^{\bullet}]{PdCl_2} CH_2{=}CH{-}CH_2^{\bullet} \xrightarrow{0.5\,O_2} CH_2{=}CH{-}CHO;$$

R = Me, Et, Bu^t, $C(C_2H_5)_3$.

The electrochemical oxidation of allyl alcohol to acrolein in a water–acetonitrile mixture is possible. By maintaining a potential difference of 2.3–2.6 V, it has been possible to attain a yield of acrolein of 30%.[147]

The oxidation of the α-substituted allyl alcohol **1** with manganese dioxide in hexane leads to the corresponding methacrolein **2** derivative in 60% yield.[148]



1 **2**

It has been found possible to obtain α-(4-methylcyclohexyl)acrolein in yields up to 50% by oxidising the corresponding α-substituted allyl alcohol **3** with lead tetraacetate in a non-polar solvent.[149]

$$CH_2{=}CR{-}CH_2OH \xrightarrow{80\,^{\circ}C} CH_2{=}CR{-}CHO;$$

3

R = 4-MeC_6H_{10}.

Highly effective oxidation of the allyl alcohols **4** to the corresponding aldehydes **5** has been achieved in the presence of the bis(η^5-cyclopentadienyl)zirconium(IV) complexes Cp_2ZrH and $Cp_2Zr(OPr^i)_2$ (the Oppenauer reaction).[150,151] The reaction is carried out in boiling toluene in the presence of 0.02 molar equivalent of the catalyst and an equimolar amount of benzaldehyde or benzophenone[15] as hydrogen acceptors (A). The yields of α,β-unsaturated products are 75%–95%.

$$R^1R^2C{=}CR^3CH_2OH + A \xrightarrow[\text{boiling toluene, 8 h}]{\text{Cat.}} R^1R^2C{=}CR^3CHO + AH_2$$

4 **5**

7. The aldol-crotonic condensation of formaldehyde with aliphatic aldehydes

The vapour-phase catalytic condensation of acetaldehyde with formaldehyde was the main industrial method of synthesis of acrolein in 1940–1960.[5,8]

$$H_2CO + CH_3CHO \xrightarrow{SiO_2} CH_2{=}CHCHO + H_2O.$$

In this process, formaldehyde (in the form of a 30% aqueous solution) and acetaldehyde, in proportions of 1 : 1 or 2 : 1, are passed over silica gel impregnated with NaOH,[152] Na_2SiO_3,[153] Li_2CO_3,[154] or KOH[155] at 260–320 °C. The yields of acrolein are 75%–90%.[8,156] Other catalysts have also been proposed: TiO_2,[155] Al_2O_3/SiO_2 mixtures in various proportions including catalysts impregnated with HF solution,[157,158] Ni, Mn, Fe, and V phosphates,[159] and a cation-containing diatomite.[160] CsOH proved to be the most active catalyst.[161]

Acetone, propionaldehyde, and ethyl methyl ketone are side products of the process considered.[157,162] The factorial experimental design method can be used to optimise the technological process involving the condensation of CH_2O with CH_3CHO.[163]

The study of the catalytic reactions of mixtures of formaldehyde with ethanol on metal phosphates and W, Zn, Ni, and Mg oxides deposited on silica gel at 240–320 °C[164] led to the conclusion that ethanol is dehydrogenated to acetaldehyde under these conditions.

Instead of acetaldehyde, its homologues can react with formaldehyde. This results in the formation of α-alkyl-substituted α,β-unsaturated aldehydes in 88%–94% yields.[165–167]

$$H_2CO + RCH_2CHO \xrightarrow{180-500\,^{\circ}C} CH_2{=}CRCHO + H_2O;$$

R = H, Me, Et.

The molar ratio H_2CO : RCH_2CHO ranges from 6.8 : 0.7 to 1 : 20. The catalysts may be phosphorus and vanadium pentoxides,[168] borosilicate molecular sieves on the Al_2O_3 carrier,[165] and even unmodified silica gel (its impregnation with KOH or alkali metal carbonates lowers the yield of α,β-unsaturated aldehydes).[166,169]

8. Condensation of formaldehyde with aldehydes in the presence of amines

Systematic study of the condensation of formaldehyde with aldehydes in an aqueous medium in the presence of an equimolar amount of an amine (preferably a secondary amine) salts made it possible to develop a method of synthesis of α,β-unsaturated aldehydes in nearly quantitative yields.[5] The hydrochloride of the Mannich base is an intermediate of this reaction:

$$RCH_2CHO + CH_2O + R'_2NH\cdot HCl \xrightarrow[-H_2O]{40-120\,^{\circ}C} [RCH(CHO)CH_2NR'_2\cdot HCl] \xrightarrow[90\%-99\%]{} RC(CHO){=}CH_2 + R'_2NH\cdot HCl;$$

R = Me, Et, Pr^i.

This process was developed up to the technical application stage.[170,171] Later this method was used to synthesise higher α-alkylacroleins.[172–179]

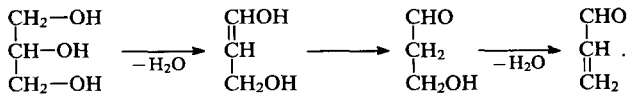
A convenient and economical version of the above procedure for the synthesis of α,β-unsaturated aldehydes involves the condensation of CH_2O with RCHO in the presence of only catalytic amounts of a secondary ammonium salt (10.3 and even 0.05 mol.%).[170,180–182]

Judging from patent data, the duration of the syntheses of α-alkylacroleins under the conditions of the Mannich reaction can be greatly reduced by carrying out the interaction between the reagents above 150 °C under pressure.[183]

9. Catalytic vapour-phase thermolysis of glycerol, 3-alkoxypropanal, and 3-acetoxypropanal

The method of synthesis of acrolein by the dehydration of glycerol, preferably in the presence of $KHSO_4$ or other acid catalysts, which was developed as early as the past century, is nowadays recognised as uneconomical. Furthermore, it proved cheaper to synthesise glycerol from acrolein.[10] However, the inevitable return to the renewable nature sources of organic raw materials in connection with the exhaustion of the resources of petroleum and gas will apparently again draw attention to the use of glycerol and then possibly also of biomass as sources of acrolein.[184,185] The replacement of $KHSO_4$ as the catalyst of the thermal dehydration of glycerol by phosphoric acid made it possible to obtain acrolein at 250 °C in 95% yield.[186]

The thermal conversion of glycerol into acrolein in 'supercritical' water, which has unusual properties, has been investigated recently.[184,185] At 360 °C under a pressure of 335 atm and in the presence of $NaHSO_4$, glycerol is converted into acrolein and acetaldehyde. The yield of acrolein reaches 70% and its formation is represented by the following scheme:



A method of synthesis of acrolein in yields up to 87% by the catalytic vapour-phase thermolysis of 3-alkoxypropanals, which are side products in the synthesis of acrylates, has been patented.[187,188] This reaction is catalysed by Al, Cu, Ca, Mn, Fe, Co, and Zn sulfates or their mixtures.

$$ROCH_2CH_2CHO \xrightarrow{250\,^\circ C} CH_2{=}CH{-}CHO + ROH.$$

Methacrolein has been obtained by the catalytic decomposition of 3-acetoxy-2-methylpropanol in the presence of tertiary amines, aluminosilicates, or zeolites.[189]

10. Thermolysis of unsaturated ethers, acetals, acylals, and other oxygen-containing compounds

The thermolysis of diallyl and allyl methylallyl ethers leads to the formation of the corresponding aldehydes together with other decomposition products.[190]

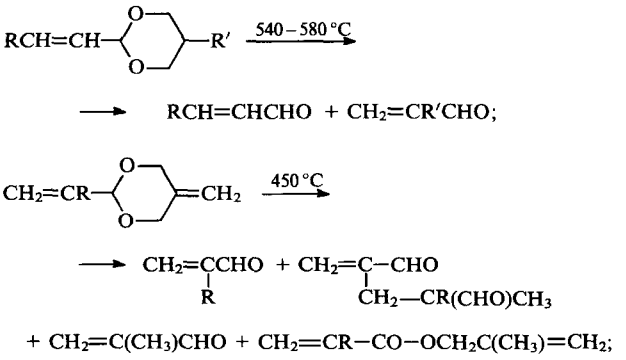
$$CH_2{=}CRCH_2OCH_2CH{=}CH_2 \xrightarrow{430-560\,^\circ C} CH_2{=}CRCHO + CH_3CH{=}CH_2.$$

When R = H, the yield is 88%, whereas for R = Me it is 28%. α,β-Unsaturated aldehydes are also obtained on thermal decomposition of diallyl acetals of alkenals.[191-193]

$$RCH{=}CR^1CH(OCH_2CR^2{=}CH_2)_2 \xrightarrow{360-420\,^\circ C} CH_2{=}CR^2CHO + RCH{=}CR^1CHO + CH_2{=}CR^2CH_2CR^1(CH_2R)CHO + RCH{=}CR^1{-}CO{-}OCH_2{-}CR^2{=}CH_2;$$

R = H, Me; R^1 = H, Me, $(CH_2)_2CN$; R^2 = H, Me.

The thermolysis of 2-(1-alkenyl)-5-alkyl-1,3-dioxanes[191] and 2-(2-alkenyl)-5-methylene-1,3-dioxanes leads to α,β-unsaturated aldehydes.[193,194]

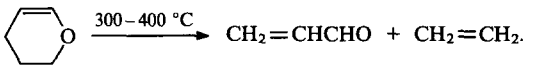


R = H, Me.

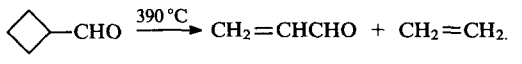
Acrolein is formed together with acetic anhydride in the catalytic thermolysis of 3,3-diacetoxypropene (and also 1,3-diacetoxypropane) in the presence of palladium or zinc halides.[195] The conversion and selectivity reach 98%.

$$CH_2{=}CHCH(OCOMe)_2 \xrightarrow{100-150\,^\circ C} CH_2{=}CHCHO + O(COMe)_2.$$

Acrolein and methacrolein can also be obtained in low yields (5%–30%) by the thermolysis of many oxygen-containing organic compounds. Thus, for example, dihydropyran decomposes preferentially to acrolein and ethylene over activated charcoal, platinised charcoal, or quartz.[196]



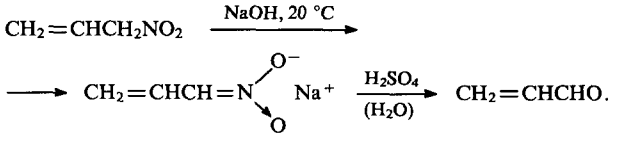
The thermal decomposition of formylcyclobutane also leads to the formation of acrolein and ethylene.[197]



Small amounts of acrolein and methacrolein (up to 10%) are produced on thermal decomposition of acrylates,[198] glucose,[199] allyl and methylallyl benzoates,[200] and diorganyl(2-propenyl)-*N*-oxides[201] and also on joint thermolysis of methanol with 1,2-dichloropropane.[202]

11. Other methods of synthesis

A novel method of synthesis of acrolein from 3-nitropropene is based on the Nef reaction.[203,204]

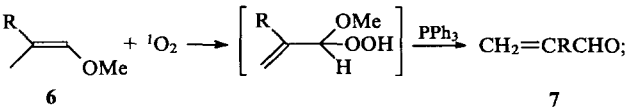


Acrolein is formed on photochemical oxidation of allyltrimethylsilane in the presence of palladium(II) salts.[205]

$$CH_2{=}CHCH_2SiMe_3 \xrightarrow{Pd^{2+},\ h\nu,\ O_2} CH_2{=}CHCHO.$$

The photochemical reaction of allene and ozone at 12 K leads to the formation of acrolein together with cyclopropane.[206]

The photochemical oxidation of the (*E*)-forms of the methyl ethers of corresponding enols **6** in the presence of triphenylphosphine made it possible to obtain α-cyclopropyl- and α-benzyl-acroleins **7** in 75%–90% yield. The addition of singlet oxygen in the (*Z*)-forms of the same ethers leads to a mixture of hydroperoxides, which are converted on treatment with PPh_3 not only into the α,β-unsaturated aldehydes mentioned above but also to their isomers cyclo-PrHC=CMeCHO and PhCH=CMeCHO.[207,208]



6 **7**

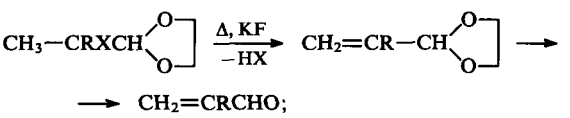
R = $(CH_2)_2CH-$, $PhCH_2-$.

The synthesis of α,β-unsaturated aldehydes by the dehydrohalogenation of the corresponding saturated aldehydes[209] was improved by using tetramethylammonium dimethyl phosphate as the hydrogen halide acceptor. The use of this reagent makes it possible to obtain methacrolein and its β-alkyl substituted derivatives.[210]

$$(CH_3)_2C(X)CHO \xrightarrow[-HX]{} CH_2=C(CH_3)CHO;$$

X = Br, Cl.

Acrolein and its α-organyl substituted derivatives can be obtained by dehalogenating 2-(1-haloorganyl)-1,3-dioxolans.[211]



$$\longrightarrow CH_2=CRCHO;$$

R = H, Me, Ph; X = Cl, Br.

Propargyl alcohol isomerises to acrolein over Mo, W, and Re oxides deposited on silica gel.[215-217] The yields of acrolein reach 70%–90%.

$$HC\equiv C-CH_2OH \xrightarrow[10-15\ mmHg]{300-400\ ^\circ C} CH_2=CHCHO.$$

The hydroformylation of acetylene catalysed by a mixture of $Co_2(CO)_8$ with polyvinylpyridine also leads to the formation of acrolein.[218]

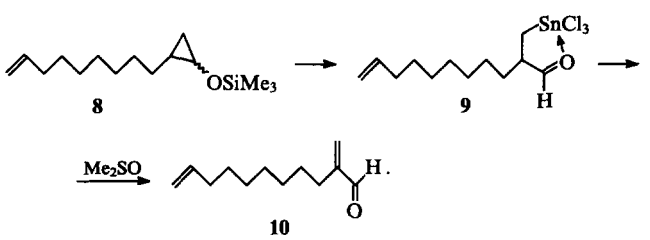
$$HC\equiv CH + CO + H_2 \longrightarrow CH_2=CHCHO.$$

Acrolein can be obtained in 81%–91% yield by the reaction of vinylacetic or crotonic anhydride with pyridine *N*-oxide.[219]

$$(H_2C=CHCH_2CO)_2O + 2C_5H_5N\rightarrow O \xrightarrow{140\ ^\circ C}$$

$$\longrightarrow CH_2=CHCHO + CH_2=CHCH_2COOH + 2C_5H_5N + CO_2.$$

The reaction of 1-(8-nonenyl)-2-(trimethylsiloxy)cyclopropane **8** with $SnCl_4$ in CH_2Cl_2 leads to 2-trichlorostannylmethylundecan-10-al **9**. Treatment with dimethyl sulfoxide in hexane converts it into α-(8-nonen-1-yl)acrolein **10**.[220]



8 **9**

10

It has been suggested that α-alkylacroleins be obtained by the reaction of substituted enamines **11** with phenylselenyl chloride and subsequent oxidative elimination of α-phenylselenoaldehyde **12** by treatment with *m*-chlorobenzoic acid or sodium periodate.[221]

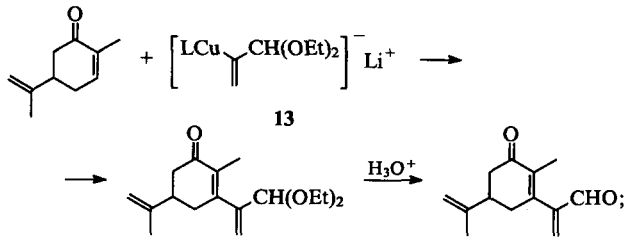
$$CH_3CR=CH-NC_5H_{10} \xrightarrow{PhSeCl} CH_3-CR(SePh)CHO \longrightarrow$$

11 **12**

$$\longrightarrow CH_2=CR-CHO;$$

R =  -Me.

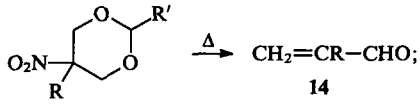
It is recommended that 3,3-diethoxyisopropenylcuprates **13**, which are carriers of the carbonyl functional group in a latent form, be used as synthons which make it possible to introduce the acrolein fragment into an organic molecule.[222,223] Their condensation with cycloalkenones and subsequent hydrolysis of the acetal formed permit the quantitative synthesis of acrolein derivatives containing a complex substituent in the α-position.



13

L = PhS–, $CH_2=\overset{|}{C}-CH(OEt)_2$.

Thermolysis[224] of 5-alkyl-5-nitro-1,3-dioxanes at 390 °C or their interaction with polyphosphoric acid at 160 °C in the presence of copper powder[225] leads to the formation of α-alkylacroleins **14.**



14

R = Me, Et; R′ = H, Pr^i.

It has been suggested that acrolein be stored and transported in the form of linear or cyclic acetals $CH_2=CHCH(OR')OR''$, where R′ and R″ are C_{1-6} alkyls or R′ + R″ are cycloalkyls $(CH_2)_{2-6}$. It can be regenerated quantitatively from these products by hydrolysis in the presence of perfluorinated ion-exchange resin.[226]

The synthesis of acrolein by the 'alcohol–aldehyde' exchange reaction catalysed by the microbial aldehyde dismutase from *Pseudomonas putida* has been described recently.[227] An equimolar mixture of allyl alcohol and isobutyraldehyde is converted into acrolein and isobutyl alcohol to the extent of 69% at 30 °C in 1 h:

$$CH_2=CHCH_2OH + Pr^iCHO \longrightarrow$$

$$\longrightarrow CH_2=CHCHO + Pr^iCH_2OH.$$

The microorganism *Coryne bacterium*, which transforms glycerol into acrolein, has been isolated from sugar cane.[228] It is suggested that the odour which sometimes appears in rum is due to the vital activity of this microorganism.

III. Methods of synthesis of α,β-unsaturated aldehydes α-substituted by functional groups

1. α-Haloacroleins

An effective method of synthesis of 2-chloropropenal is based on the dehydrochlorination of 2,3-dichloropropenal, which is obtained in its turn by chlorinating acrolein.

$$CH_2=CHCHO + Cl_2 \longrightarrow ClCH_2CHClCHO \longrightarrow$$

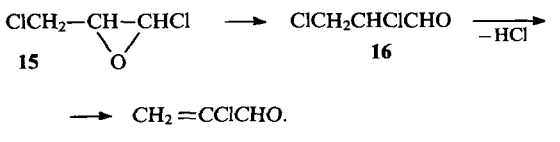
$$\longrightarrow CH_2=CClCHO.$$

Hydrogen chloride may be eliminated by a thermal method involving the passage of a mixture of acrolein vapour, chlorine, and nitrogen through a quartz tube at 75–200 °C. The maximum yield of α-chloroacrolein (91%) is obtained for the acrolein : chlorine ratio = 1 : 1.7 and for a contact time of 3 s.[229,230]

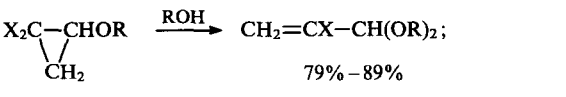
The liquid-phase dehydrochlorination of 2,3-dichloropropanal at 0–5 °C [231,232] or 20 °C [233,234] is more widely used. Diethylaniline is usually employed as the HCl acceptor. The yield of α-chloroacrolein reaches 80%.

α-Bromoacrolein is obtained by a similar procedure: by brominating acrolein and subsequent dehydrobromination of 2,3-dibromopropanal.[233,235,236] The yield of α-bromoacrolein is appreciably lower (45%–68%).

1,3-Dichloro-1,2-epoxypropane **15** is converted at 200 °C into α-chloroacrolein in 23% yield.[237] The isomerisation of 1,3-dichloro-1,2-epoxypropane to 2,3-dichloropropanal **16** and the subsequent dehydrochlorination of the latter to α-chloroacrolein in aqueous tetrahydrofuran in the presence of a phosphate buffer occur already at 37 °C.[238]

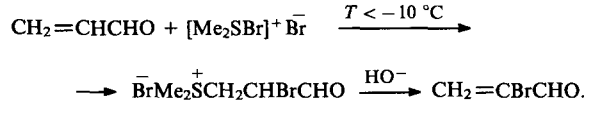


The ethanolysis of 2-alkoxy-1,1-dihalocyclopropanes in the presence of bases (K_2CO_3, NaOR) is widely used to obtain the acetals of 2-halopropenals.[239–241] The subsequent hydrolysis of the acetal makes it possible to obtain pure α-haloacrolein.[240]



X = Cl, Br, F; R = Et, Bu.

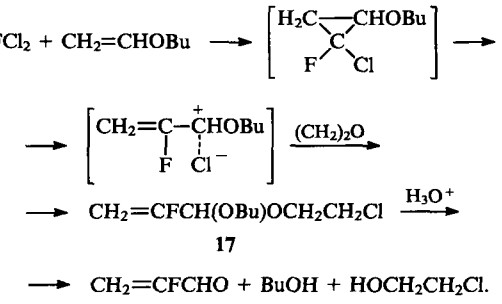
The interaction of bromodimethylsulfonium bromide with acrolein constitutes an elegant and simple method of synthesis of α-bromoacrolein in a satisfactory yield:[242]



Account must be taken of the fact that α-chloro- and α-bromo-acroleins are powerful direct-action mutagens.[243,244] The latter was identified in the organism as the metabolite of certain domestic preparations, for example the fumigant 1,2-dibromo-3-chloropropane and the fire extinguishing agent tris(2,3-dibromopropyl)phosphate.[243,245]

Traces of α-acrolein are formed on chlorination of humic acids.[246] It has been suggested that this induces a mutagenic activity in chlorinated drinking water. α-Chloroacrolein is also obtained by treating 2-chloroallyl alcohol with dehydrogenase.[247] It is also formed when the carcinogenic herbicide *S*-2,3-dichloroallyl diisopropylthiocarbamate (diallate) is treated with liver microsomal monoxygenase of *m*-chloroperbenzoic acid.[231,248,249] The photochemical decomposition of diallate also leads to α-acrolein.[250]

Like other α-haloacroleins, α-fluoroacrolein was first obtained by opening the ring in 2-alkoxy-1,1-difluorocyclopropanes.[239] A modified version of this method constitutes a continuous process proceeding in a single reactor (autoclave) and involves the formation of chlorofluorocarbene *in situ*.[251] For this purpose, a mixture of dichlorofluoromethane, butyl vinyl ether, epoxyethane, and tetraethylammonium bromide is heated at 150 °C.



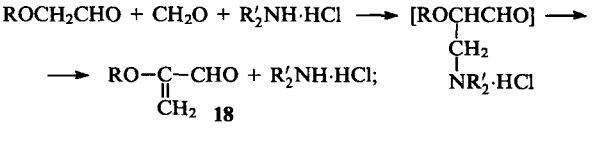
The resulting acetal **17** is hydrolysed with 5% H_2SO_4, which leads to the formation of α-fluoroacrolein (yield 41%). This lachrymatory substance polymerises rapidly during storage (in the absence of hydroquinone) and explodes during combustion when it is subjected to elemental analysis. When an attempt is made to synthesise more than one mole of α-fluoroacrolein, the pressure in the autoclave suddenly rises sharply from 20 to 300 atm, which makes this method too dangerous.[252] It has therefore been suggested that α-fluoroacrolein be synthesised in two stages using the mild phase transfer catalytic conditions.[252–255] The yield reaches 53% relative to the initial butyl vinyl ether. This method may be used on a large scale (for the synthesis of up to 200 moles of α-fluoroacrolein).

3-Alkyl-2-halo-2-alkenals can also be readily obtained by converting the corresponding enol ethers into cyclopropane derivatives under the conditions of phase transfer catalysis[256,257] or in the presence of potassium butoxide[258] with subsequent stereoselective opening of the ring in the cyclopropanes produced.

2. α-Organyloxy- and α-acetoxy-acroleins

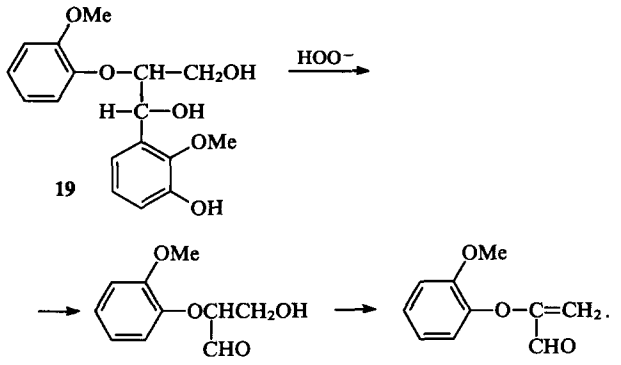
α-Alkoxy- and α-phenoxy-acroleins were first obtained by the aminomethylation of the corresponding organyloxyacetaldehydes followed by the decomposition of the hydrochloride of the Mannich base.[259–262]

Under optimum conditions (equivalent reactant proportions) at 60 °C, pH 7–7.1, 1.5–2 h), the yields of acroleins reach 66%–78%.



R = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**), Ph (**e**), 2-$MeOC_6H_4$ (**f**), $PhCH_2$ (**g**).

This convenient method of synthesis of α-alkoxy-(phenoxy)acroleins using the Mannich reaction was subsequently used frequently.[263–267] For example α-guaiacoxyacrolein was obtained by this procedure from 2-(2′-methoxyphenoxy)-acetaldehyde and formaldehyde.[267] This acrolein derivative is also an intermediate in the oxidation of guaiacylglyceryl β-guaiacyl ether **19**—the most common structural fragment of lignin—in the technical peroxide bleaching process.[267,268]



Like aryloxyacroleins, α-benzyloxyacrolein **18g** can be obtained by the aminomethylation of benzyloxyethanal.[265]

2-Phenoxybutenal is formed from the diethyl acetal of 3-ethoxy-2-phenoxybutanal as a result of acid hydrolysis accompanied by the elimination of ethanol.[269]

$$MeCH(OEt)-CH(OPh)-CH(OEt)_2 \xrightarrow{H_3O^+} MeCH=C(OPh)-CHO.$$

However this procedure is unsuitable for the synthesis of α-ethoxycrotonaldehyde apparently owing to the hydrolytic instability of this compound in an acid medium.

2-Methoxypropenal was synthesised in 69% yield by the β-elimination of methanol from 2,3-dimethoxypropanal in an alkaline medium.[270,271]

$$MeOCH_2CH(OMe)CHO \xrightarrow{25\,^\circ C,\ pH\ 12} CH_2=C(OMe)CHO + MeOH.$$

69%

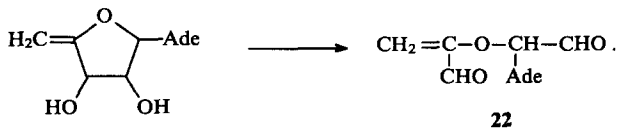
We shall now consider the kinetics and the proposed mechanism of this reaction.[272] α-Alkoxyacroleins **21** with functional group substituents are obtained from 2-alkoxy-3-vinylthiopropanols **20** by the mild Swern oxidation followed by the elimination of ethylenethiol.[273]

$$CH_2=CHSCH_2CH(OR)CH_2OH \xrightarrow[2.\ Et_3N\ (10\ equiv.)]{1.\ DMSO/ClCOCOCl/-78\,^\circ C} CH_2=C(OR)CHO$$

20 → **21**

R = $O(CH_2)_2OCH_3$, $CH=CH_2$, $\overline{CH_2OCH}$, $(CH_2)_3Br$, $(CH_2)_3N_3$.

Certain α-organyloxyacroleins containing an organic moiety with a functional group substituent play a definite role in biochemical reactions. They include the α-organyloxy-α,β-unsaturated aldehyde **22** – the first representative of the group of the so called nucleoside dialdehydes. It was obtained by the periodate oxidation of 9-(5-deoxy-*b*-D-*erythro*-pent-4-enofuranosyl)adenine.[274]

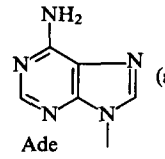
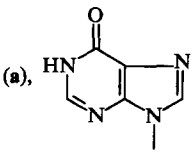


22

Purine-containing α-organyloxyacroleins **24a, b** are readily formed on heating the nucleoside dialdehydes **23a, b** to 100 °C.[275]

$$HOCH_2CH(CHO)OCHRCHO \xrightarrow[H_2O(EtOH)]{100\,^\circ C,\ 1\ h} CH_2=C(CHO)OCHRCHO;$$

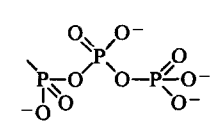
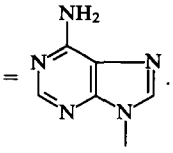
23 → **24**

R =  (a),  (b), —OMe (c).

This reaction was first observed in enzymic studies involving adenosinedeaminase. The purine ring does not play a significant role in the process described and elimination takes place readily also in the case of the aldehyde **23c**, which have been confirmed by UV spectroscopic data. The adenosine triphosphate oxidised by periodate (*o*-ATP) at 20 °C and pH 7 slowly gives rise to the adenosine-containing β,β-dihydroxyethoxyacrolein **25** as a result of the β-elimination of the triphosphate group.[276]

$$ROCH_2CH(CHO)OCH(CHO)-Ade \xrightarrow{Na_2B_2O_7} CH_2=C(CHO)O-CH(Ade)-CH(OH)_2;$$

ortho-ATP → **25**

R = , Ade = .

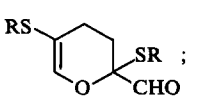
α-Acetoxyacrolein has been synthesised by acetylating the diethyl acetal of acetoxymercuriomethylglyoxal.[277] The reaction is accompanied by the formation of a number of side products, the principal of which is the hemiacylal of acetoxymethylglyoxal.

$$AcOHgCH_2COCH(OEt)_2 + CH_3COCl \longrightarrow [CH_2=C(OAc)CH(OEt)_2] \xrightarrow{Ac_2O} CH_2=C(OAc)CHO.$$

3. α-Organylthio- and α-organylseleno-acroleins

The attempts to obtain α-organylthioacroleins by the Mannich reaction (by analogy with α-alkoxyacroleins) led to the isolation of their cyclic dimers — 2,5-dialkylthio-2-formyl-2,3-dihydro-4*H*-pyrans (yield 31% – 61%).[278–280]

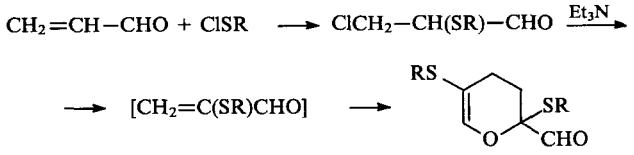
$$RSCH_2CHO + CH_2O + R^1_2NH\cdot HCl \longrightarrow RSCH(CHO)CH_2NR^1_2\cdot HCl \longrightarrow [CH_2=C(SR)CHO] \longrightarrow$$



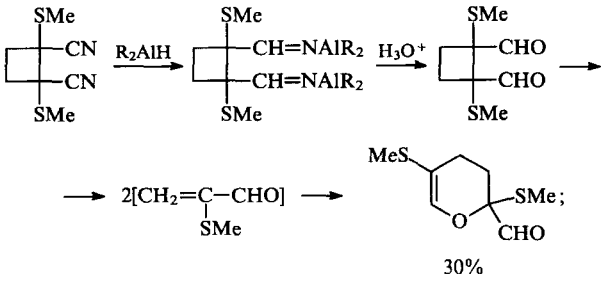
R = Me, Et, Pr, Bu, Bu^i, Pe^t, C_6H_{13}; R^1 = Et, Me.

The study of this process by the ^1H NMR method at 6 – 10 °C made it possible to observe the intermediate formation of the monomeric α-alkylthioacrolein.[281]

The extreme instability of α-alkylthioacroleins has been confirmed when an attempt was made to obtain them by the reaction of alkanesulfenyl chlorides with acrolein.[282] The labile alkylthiochloropropanals formed afford only the dimers of α-alkylthioacroleins in approximately 50% yield on dehydrochlorination with triethylamine at −15 °C.

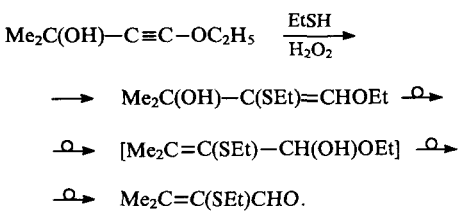


A cyclic dimer of α-methylthioacrolein has been obtained from 1,2-bis(methylthio)-1,2-dicyanocyclobutane.[283]

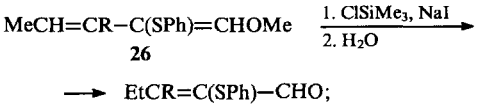


R = Bu^i.

In contrast to α-alkylthioacroleins, their β-alkyl derivatives exist in a monomeric form. Thus α-ethylthio-β,β-dimethylacrolein has been obtained from ethoxyethynyldimethylcarbinol by carrying out consecutive reactions involving thiylation, rearrangement, and elimination of the alcohol in accordance with the following scheme:[284]

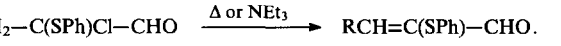


The specially synthesised dienes **26** have been used to synthesise β-alkyl-α-phenylthioacroleins.[285]

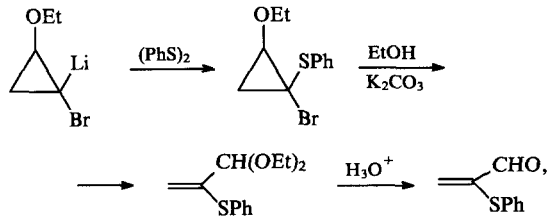


R = H, Me.

The synthesis of 2-phenylthio-2-alkenals in 65% yield by the dehydrochlorination of α-chloro-α-phenylthioaldehydes has also been described.[286]

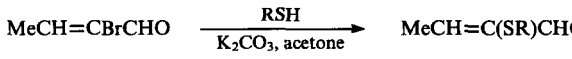


The possibility of obtaining α-phenylthioacrolein by treating 1-bromo-2-ethoxycyclopropyllithium with diphenyl disulfide with subsequent transformation of the reaction product via the scheme



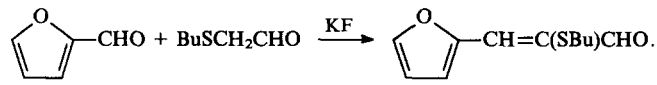
which is universal for the synthesis of 2-substituted alkenals, has been reported.[240]

The *ipso*-substitution of the halogen in vinyl halides activated by a geminal aldehyde group can also be used to synthesise β-alkyl-α-organylthioacroleins.[287,288]

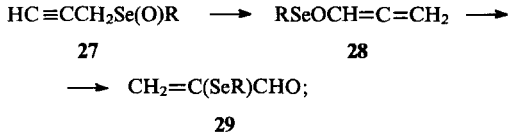


R = Bu, Ph.

The use of the aldol-crotonic condensation of butylthioacetaldehyde with furfural in the presence of KF with added tetraethoxysilane made it possible to obtain 2-butylthio-3-(2′-furyl)propenal in 60% yield.[289]

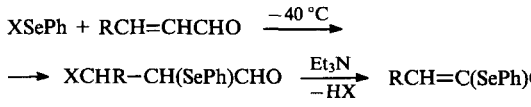


The formation of the α-phenylselenoacrolein **29a**, which is unstable at room temperature, was observed for the first time on isomerisation of phenylpropargyl selenoxide **27a** in methylene chloride at −31 °C.[290-292]



R = Ph (**a**), *m*-$F_3CC_6H_4$ (**b**), *o*-$O_2NC_6H_4$ (**c**).

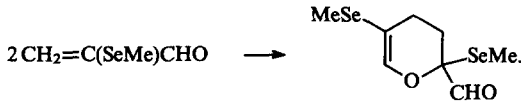
The trifluoromethyl analogue **27b** rearranges 1.6 times faster than the selenoxide **27a**. In both cases, the intermediate reaction product was not detected. The existence of the intermediate **28c** with the allenol structure, formed on isomerisation of 2-nitrophenylpropargyl selenoxide **27c**, has been demonstrated by ^{1}H NMR and IR spectroscopy and mass spectrometry. The allene **28c** was identified at −45 °C. Above −10 °C, it rearranges to the aldehyde **29c**.



R = H (**a**), Me (**b**); X = Br, Cl.

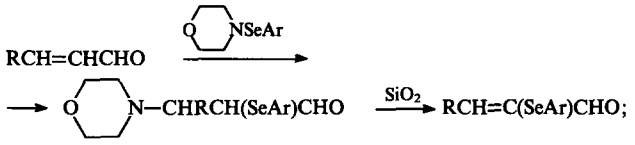
Later α-phenylselenoalkenals were obtained in 68% yield by the haloselenation of the corresponding unsaturated aldehydes and subsequent elimination of hydrogen halides with triethylamine.[293,294]

In contrast to the unstable phenylselenoacrolein **29a**, its homologue **29b** can be vacuum-distilled. In order to obtain α-methylselenoacrolein in accordance with a scheme similar to that presented above, the dehydrohalogenation stage was carried out at −40 °C, but the expected aldehyde cyclodimerised fully and very rapidly (in 20 min at 20 °C). It was characterised only by the NMR method.[294,295]



$$2\,CH_2{=}C(SeMe)CHO \longrightarrow$$

N-Arylselenomorpholines are effective α-selenating agents for α,β-unsaturated aldehydes.[296,297]



$$RCH{=}CHCHO \xrightarrow{\text{NSeAr}} \longrightarrow N{-}CHRCH(SeAr)CHO \xrightarrow{SiO_2} RCH{=}C(SeAr)CHO;$$

R = H, Me, Pr, MeCH = CH, Ph;
Ar = Ph, 4-ClC_6H_4.

A single-stage method of synthesis of α-arylseleno-α,β-unsaturated aldehydes is based on the electrochemical oxidation of 3-hydroxyalkynes in the presence of diaryl diselenides.[298,299]

$$RCHOH{-}C{\equiv}CH \xrightarrow[(ArSe)_2]{-2e} RCH{=}C(SeAr)CHO;$$

74%–87%

R = Me, Et, Pe, Ph.

4. α-Dialkylaminoacroleins and their homologues

β-Alkyl-α-piperidinoacroleins were first synthesised by treating β-dialkylamino-α-piperidinoacroleins with Grignard reagents.[300]

$$C_5H_{10}NCH{=}C(NC_5H_{10})CHO \xrightarrow[2.\ NH_4Cl/\,aq]{1.\ RMgX} \longrightarrow RCH{=}C(NC_5H_{10})CHO;$$

R = Me, Et, Pr, Bu.

Although the yields of the final products are fairly high (60%–80%), the initial diaminoacroleins can be obtained in only 10%–30% yield by formylating the corresponding diaminoethylenes.

Subsequently the reaction involving the *ipso*-substitution of the halogen atom in 2-halo-2-alkenals was used to synthesise 2-dialkylamino-2-alkenals.[301–304] The interaction takes place even at room temperature and the substitution products **30** are formed as a mixture of (*E*)- and (*Z*)-isomers.

$$RR^1C{=}CX{-}CHO + HNR_2^2 \longrightarrow RR^1C{=}C(NR_2^2)CHO;$$

30

R = Me; R^1 = H, Me; X = Hal;

NR_2^2 = , , NEt_2, $N(Bu^n)_2$.

5. Organosilicon derivatives of acrolein

α-Trialkylsilylacroleins (in a mixture with the β-isomers) are formed when the product of the hydrosilylation of propargyl alcohol or its trimethylsilyl ether by trialkylsilanes is oxidised by chromium trioxide.[305,306]

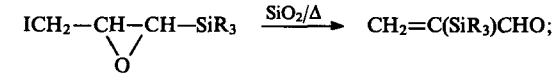
$$HC{\equiv}CCH_2OR + HSiR^1R_2^2 \longrightarrow CH_2{=}C(SiR^1R_2^2)CH_2OR \xrightarrow[H_2SO_4]{CrO_3} \longrightarrow CH_2{=}C(SiR^1R_2^2)CHO;$$

R = H, $SiMe_3$; R^1, R^2 = Me, Et.

A mixture of α- and β-triethylsilylacroleins is also formed on hydrosilylation of propynal,[307] the yields of the α- and β-adducts being 28% and 26% respectively.

$$HSiEt_3 + HC{\equiv}C{-}CHO \xrightarrow{H_2PtCl_6} CH_2{=}C(SiEt_3)CHO.$$

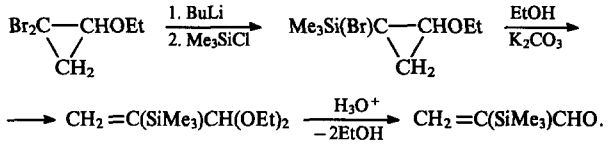
α-Triisopropylsilylacrolein is formed in a low yield from 2-iodomethyl-3-triisopropylsilyloxiran together with 3-iodo-2-triisopropylsilylpropanal.[308]



$$ICH_2{-}CH(O){-}CH{-}SiR_3 \xrightarrow{SiO_2/\Delta} CH_2{=}C(SiR_3)CHO;$$

R = Pr^i.

α-Trimethylsilylacrolein has been synthesised in 80% yield from 1,1-dibromo-2-ethoxycyclopropane in accordance with the following scheme: [240,309]



$$Br_2C(CH_2){-}CHOEt \xrightarrow[2.\ Me_3SiCl]{1.\ BuLi} Me_3Si(Br)C(CH_2){-}CHOEt \xrightarrow[K_2CO_3]{EtOH} \longrightarrow CH_2{=}C(SiMe_3)CH(OEt)_2 \xrightarrow[-2EtOH]{H_3O^+} CH_2{=}C(SiMe_3)CHO.$$

The most convenient method of synthesis of α-trimethylsilylacrolein is based on the reaction of 2-bromo-3,3-diethoxypropene **31** with butyllithium and subsequent interaction with chlorotrimethylsilane.[310] The removal of the acetal protecting group in an acid aqueous acetone solution leads to the formation of α-trimethylsilylacrolein from the initial acetal **31** in 73% yield.

$$CH_2{=}CBrCH(OEt)_2 \xrightarrow[2.\ ClSiMe_3]{1.\ BuLi} CH_2{=}C(SiMe_3)CH(OEt)_2 \longrightarrow$$

31

$$\longrightarrow CH_2{=}C(SiMe_3)CHO.$$

α-Trimethylsilylmethacrolein has been obtained by oxidising α-trimethylsilyl methylallyl alcohol with oxalyl chloride in dimethyl sulfoxide (DMSO) [311] (cf. also Trost and Grese [312]).

$$CH_2{=}C(CH_2SiMe_3)CH_2OH \longrightarrow CH_2{=}C(CH_2SiMe_3)CHO.$$

2-Dimethylphenylsilylmethylpropen-2-al has been synthesised in a yield up to 94% by the reaction of diorganylpropargylamines with a twofold excess of dimethylphenylsilane and carbon monoxide in the presence of ruthenium carbonyl.[313]

$$HC{\equiv}C{-}CH_2NR_2 + 2\,Me_2PhSiH + CO \xrightarrow{Ru_4(CO)_{12}} \longrightarrow CH_2{=}C(CH_2SiMe_2Ph)CHO;$$

R = Me, CH_2Ph.

α-(*tert*-Butyldimethylsiloxymethyl)acrolein **32** has been synthesised from acrolein, the latter part of the synthesis being[314]

$$CH_2{=}CBrCH(OEt)_2 \xrightarrow[2.\ H_2CO]{1.\ BuLi} CH_2{=}C(CH_2OH)CH(OEt)_2 \longrightarrow$$

72%

$$\xrightarrow[2.\ (COOH)_2]{1.\ ClSiMe_2(Bu^i)} CH_2{=}C(CH_2OSiMe_2)CHO.$$

Bu^i

32 (87%)

The reaction of methylglyoxal with chlorotrimethylsilane in the presence of triethylamine leads to α-trimethylsiloxyacrolein.[315]

$$CH_3COCHO + Me_3SiCl \xrightarrow[-HCl]{Et_3N} CH_2{=}C(OSiMe_3)CHO.$$

6. Dialkylphosphonoacroleins

α-Dialkylphosphonoacroleins **36** have been synthesised by hydrolysing a mixture of the corresponding organophosphorus derivatives **33**–**35**, obtained in their turn by phosphorylating alkyl allyl ether with phosphorus pentachloride.[316] The unstable individual α-phosphorylated acroleins **36** were not isolated and were identified as products of the diene synthesis **37**.

$$(RO)_2P(O)C(=CHOR)CH_2OR + (RO)_2P(O)CH(CH_2OR)CH(OR)_2$$

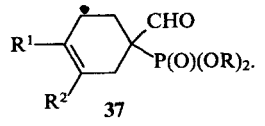
33 **34**

$$+ (RO)_2P(O)C(=CH_2)CH(OR)_2 \xrightarrow{H_3O^+}$$

35

$$\longrightarrow [(RO)_2P(O)C(=CH_2)CHO] \xrightarrow{CH_2=CR^1-CR^2=CH_2}$$

36

$$\longrightarrow$$ 

37

7. Oxygen and sulfur derivatives of α-alkylacroleins

Hydrolysis of the diethyl acetal of 3-hydroxy-2-hydroxymethylpropanal leads to the formation of the free aldehyde **38**, which is readily hydrated in the presence of bases to α-hydroxymethylacrolein **39**.[317]

$$(HOCH_2)_2CHCH(OEt)_2 \xrightarrow[-2\,EtOH]{H_3O^+} (HOCH_2)_2CHCHO \longrightarrow$$

38

$$\longrightarrow CH_2{=}C(CH_2OH)CHO.$$

39

An elegant method of synthesis of α-hydroxyalkylacroleins **42** is based on the condensation of the organolithium derivative of the diethylacetal of α-bromoacrolein **40** with various aldehydes at a low temperature. The subsequent cautious removal of the acetal protecting group in the acetals **41** leads to the formation of α-hydroxyalkylacroleins in 95% yield.[318]

$$CH_2{=}CLiCH(OEt)_2 + RCHO \longrightarrow$$

40

$$\longrightarrow CH_2{=}C[CH(R)OH]CH(OEt)_2 \xrightarrow[H_2O]{H_2SO_4} CH_2{=}C[CH(R)OH]CHO;$$

41 **42**

R = Me, Et, Pe, Ph.

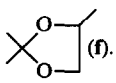
The single-stage alkylcarbonylation of 3,3-diethoxy-2-lithiopropene **40** with dimethylformamide or the dimethylamides of other carboxylic acids makes it possible to obtain α-diethoxymethylacrolein **43a** or the diethyl acetals of α-alkylcarbonylacroleins in 20%–70% yields.[319]

$$CH_2{=}CLiCH(OEt)_2 + RCONMe_2 \longrightarrow$$

40

$$\longrightarrow CH_2{=}C(COR){-}CH(OEt)_2;$$

43

R = H (**a**), Me (**b**), Bu^i (**c**), Pe (**d**), Ph (**e**),  (**f**).

Unfortunately the hydrolysis of the latter to the corresponding acroleins has not been achieved.

The reaction of 1-bromo-2-ethoxycyclopropyllithium **44** (the synthetic equivalent of 2-lithiopropenal) with heptanol leads to the intermediate **45**, the interaction of which with alcohol on heating in the presence of K_2CO_3 makes it possible to obtain the diethyl acetal of α-(1-hydroxy)heptylacrolein **46**. Hydrolysis of the latter leads to the corresponding aldehyde **47** (yield 77%).[240,309]

$$Li(Br)C{-}CHOEt + C_6H_{13}CH_2OH \longrightarrow X(Br)C{-}CHOEt \longrightarrow$$

44 **45**

$$\xrightarrow[K_2CO_3]{EtOH} CH_2{=}CX{-}CH(OEt)_2 \longrightarrow CH_2{=}C(X)CHO;$$

46 **47**

X = $-CH(OH)C_6H_{13}$.

The aldehyde **49** was synthesised by acetylating the acetal **46** with subsequent hydrolysis of the resulting acetal **48**.

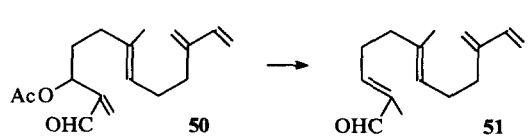
$$\mathbf{46} \xrightarrow[-AcOH]{Ac_2O} CH_2{=}C[CH(OAc)C_6H_{13}]CH(OEt)_2 \xrightarrow{H_3O^+}$$

48

$$\longrightarrow CH_2{=}C[CH(OAc)C_6H_{13}]CHO.$$

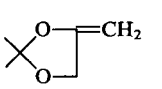
49

The method developed for the synthesis of α-substituted acroleins has been used to synthesise β-sinensal **51**, which determines the taste and smell of the oil of Chinese oranges.[309] The initial triene aldehyde **50** was obtained in the same way as the aldehyde **49**, from 4-methyl-8-methylenedecene-4,9-dienal:



50 **51**

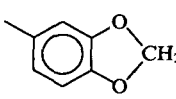
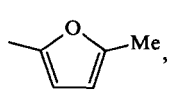
Various α-hydroxyalkylacroleins **54** can be synthesised in 65%–77% yield by adding to aldehydes a nucleophile such as allenoxylithium **53** (equivalent of 2-lithiopropenal), obtained from 2,2-dimethyl-4-methylene-1,3-dioxolan **52**.[320]

 $\xrightarrow{Bu^tLi,\ -78\,^\circ C}$ $CH_2{=}C{=}CHOLi$ $\xrightarrow{RCHO}$

52 **53**

$$\longrightarrow CH_2{=}C(CHO)CH(OH)R;$$

54

R = C_6H_{13}, Ph, , ,

$-CHMeOCH_2OMe$.

The reaction of α-(methoxymetoxyethyl)acrylonitrile with diiso-propylaluminium hydride in toluene leads to the formation of the corresponding α-substituted acrolein in 73% yield.[321]

$$CH_2{=}CR{-}CN \xrightarrow{HAlR^1_2} CH_2{=}CR{-}CH{=}NAlR^1_2 \xrightarrow{5\%\ H_2SO_4} CH_2{=}CR{-}CHO;$$

R = $CH_2CH_2OCH_2OCH_3$; R^1 = Pr^i.

α-Carboxyacrolein has been obtained from the diethyl acetal of α-bromoacrolein by successive treatment with butyllithium, carbon dioxide, and water.[322]

$$CH_2{=}CBrCH(OEt)_2 \xrightarrow{BuLi} CH_2{=}CLiCH(OEt)_2 \xrightarrow[2.\ H_2O]{1.\ CO_2} CH_2{=}C(COOH)CHO.$$

The β-alkylthioacetals **55** are converted into the enals **56** on treatment with formalin and dimethylamine hydrochloride.[179, 323]

$$RSCH_2CH(OEt)_2 + CH_2O \xrightarrow[-H_2O]{Me_2NH\cdot HCl} CH_2{=}C(CH_2SR)CHO;$$

55 **56**

R = Et, Ph.

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