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# LOW MOLECULAR WEIGHT PRODUCTS FROM THE AQUEOUS ALKALINE DEGRADATION OF CELLULOSE

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# LOW MOLECULAR WEIGHT PRODUCTS FROM THE AQUEOUS ALKALINE DEGRADATION OF CELLULOSE

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## ABSTRACT

Low molecular weight products from the degradation of pure cellulose in 0.6-1.3N alkali at 300°C have been identified by gas chromatography/mass spectrometry (GC/MS). Both the aqueous residual phase and the floating oil product phase were examined, and found to contain essentially the same compounds. Derivatization by trifluoroacetic anhydride was used as an ancillary method to aid identification of these compounds, which consisted primarily of unsaturated aliphatic and alicyclic hydrocarbons, aldehydes, ketones, alcohols, and furans. Many isomers were present. Specific compounds identified with a high level of confidence were cyclopentanone, cyclohexanone, phenol, cresols, 2-ethylcyclopentanone, 2- or 3-methylcyclopentanone, 2,5-dimethyl-2-cylopentenone, acrolein, 2,5-dimethyl-2,4-hexadiene, and octene. Compounds identified with a lower level of confidence include 2,4-dimethylfuran, 2,5-diethylfuran, ethylmethylfuran, 4-octyne, and decyne. The formation of these compounds from cellulose under alkaline conditions demonstrates not only the degradation of cellulose, but the resynthesis of

molecules with carbon chain lengths greater than 6 atoms (the chain length of glucose). Such resynthesis must occur to a great extent in the formation of insoluble high molecular weight oils from cellulose by heating in aqueous alkali.

## INTRODUCTION

The production of fuel and chemicals from carbonaceous materials other than coal and oil ('biomass') has been a subject of serious study for well over a century. Pyrolytic oils were obtained by Hoppe-Seyler in 1871 (1), and by numerous other authors since then (2). It was quickly determined that pyrolysis of carbonaceous material yields an oil, but in addition it yields a large amount of residual charcoal. In fact, originally it was the charcoal which was the major product and the oil which was considered as a less valuable by-product.

A modification of the pyrolysis process involved the addition of water and/or alkali to biomass. On heating under pressure, the biomass was converted to oil, gas, charcoal, and water-soluble organic compounds. The classical work on these process variations was performed in 1926-1932 (3-6). Again, there have been many reports of the production of various materials including oil from biomass, using the aqueous alkaline or 'thermochemical' route (7).

Further variations in which hydrogen and/or carbon monoxide are used as reducing gases for biomass and coal conversion into oil have been studied, beginning in 1921 - 1924 (8,9) and with a resurgence of interest within the last 20 years (10-12).

The fundamental chemistry of these processes is still very poorly understood. The mechanism of the pyrolysis process has received most attention, and some of the initial steps in the conversion of cellulose into its pyrolysis products have been elucidated, notably by Shafizadeh (13-15), Broido (16,17), and others. The thermochemical digestion process has been but little studied, and the mechanism of conversion of simple products derived from cellulose into higher molecular weight oils has been virtually ignored. There is also no data on the conversion of other biomass components such as lignin and hemi-cellulose in any of these processes.

The purpose of the present paper is to report initial results of an on-going study into the fundamental chemical mechanisms involved in the conversion of pure cellulose into an oil through thermochemical digestion in aqueous sodium carbonate or bicarbonate at temperatures in excess of 300°C.

## EXPERIMENTAL

Generation of oil and aqueous phase samples - The experiments reported here were performed with an oil sample and aqueous sample derived from 2 of a series of 130 autoclave experiments. The samples were prepared as follows: A free-floating oil product was obtained from experiment #104, in which pure cellulose (Solkafloc, Brown Co., Berlin, NH, 5.7 Kg) was mixed with distilled water (17.7 ℓ) and anhydrous sodium carbonate (0.56 Kg) in a 10 gallon autoclave, which was then sealed and brought up to 304°C over a period of 3.5 hr. The autoclave was maintained at this temperature for 1 hr and cooled to room temperature over a period of 2.5 hr. The free-floating oil product was separated from the aqueous phase and acetone-extracted in a Soxhlet apparatus until no more colored material was extracted (3 days). The acetone was then removed under reduced pressure and the product oil was air-dried at 20°C for one day before being used for GC/MS analysis.

An aqueous phase was obtained from experiment #103, in which cellulose (1.7 Kg) distilled water (5.45 ℓ), and anhydrous sodium carbonate (0.342 Kg) were heated in a 2-gallon autoclave to 307°C in 2.5 hr, maintained at this temperature for 20 min, and then cooled to room temperature over 2.5 hr. The aqueous phase was separated from any oil and then extracted directly with diethyl ether. After removal of the ether, the product was analyzed directly by GC and GC/MS. This aqueous product at no time came into contact with acetone.

All further references to 'oil' and 'aqueous extract' refer to the materials obtained as described above.

Sample analysis - Gas chromatography/mass spectrometry (GC/MS) was the principal analytical tool used for identification of components of the samples. Attempts to obtain good separation of components by direct GC of the underivatized oil were unsuccessful, although direct GC of the ether extract of the aqueous phase did give good separation. In consequence, various ways of derivatizing the oil were examined. Of the 3 approaches tried ($BF_3$/methanol methylation, silylation, trifluoroacetylation), trifluoroacetylation with trifluoroacetic anhydride gave the cleanest derivative with the best separation of components. However, the trifluoroacetate derivative (TFA-derivative) was somewhat labile in that keeping at 20°C for periods of over a week led to rearrangement of peaks in the chromatogram. Consequently, a freshly-made derivative was used (1), and compared with a derivative which had been kept for a week at 20°C (2), and with the underivatized ether extract (A) (Fig. 1). All GC work was performed on a Perkin-Elmer model 900 chromatograph, operated with a 50 ft x 0.02 in. stainless steel column. Detailed operating conditions are described in the Results section. Combined GC/MS was performed with a Perkin-Elmer mass spectrometer using the same column and conditions as for the analytical GC runs.

## RESULTS

The total ion monitor (TIM) traces for the GC/MS runs on samples A,1,2 are shown in Fig. 1, together with probable identities of some of the components. The use of 3 separate samples of similar composition allowed us to obtain up to 3 mass spectra for some of the compounds, increasing the reliability of the structural assignments. In Table 1 we show the assignments obtained by interpretation of the mass spectra. There are 3 levels assigned to the probability of a correct assignment for any compound - highly probable (H) with excellent agreement of an experimental mass spectrum with published data; probable (P), where good agreement was obtained, but there is also a chance that the compound assigned may in fact be an isomer; and tentative (T), where in most cases a good literature mass spectrum does not exist and an assignment was made on the basis of the breakdown pattern observed in the experimental mass spectrum. Published spectra were compared with observed spectra, using the 8-peak Index of Mass Spectra (18). It should be pointed out here that even the best publication available (18) frequently contains multiple reported spectra for a single compound, with considerable differences between these spectra. This makes identification difficult in cases where synthesis of a pure standard compound would be tedious - unfortunately including many of the degradation products of cellulose. However, we have assigned structures to some 23 of the major components in the volatile fraction of the cellulose thermochemical degradation products obtained in our autoclave experiments.

## DISCUSSION

The thermochemical liquefaction of pure cellulose as described in this report is part of a larger program to assess the potential of biomass as a source of chemical feedstocks and fuel oil. Little work has been done previously on pure cellulose, most of the previous work being performed on substrates such as sugar cane (19), peat, (20), sewage sludge (21), and similar ill-defined substrates. By use of a pure, well-defined substrate for our experiments we hope to be able to determine a degradation mechanism for cellulose, and to understand how degradation products are re-synthesized into the product oils and water-soluble organic materials.

To date, the most comprehensive work relevant to the mechanism of cellulose degradation in aqueous alkali was reported in a series of articles by Machell, Richards, et. al. (22-25), wherein it was found that cellulose and related carbohydrates were converted through a series of saccharinic acid derivatives to glycolic and dihydroxybutyric acids. Beyond this stage no further work has been done, either on the further degradation or the resynthesis of these compounds into higher molecular weight products.

The pyrolytic reaction with cellulose involves a dry, perhaps acid-catalyzed degradation leading to the formation of levoglucosan (_β_-D-glucopyranose-1,6-anhydride), and subsequently to levoglucosenone (1,6-anhydro-3,4-dideoxy-$\Delta^3$-_β_-D-pyranosen-2-one), 1,6-anydro-_β_-D-glucofuranose, 3-deoxy-D-erythro-hexoseulose, and other products (15). The mechanism of cellulose pyrolysis is either of the acid-catalyzed (carbonium ion) or free radical variety (26). In sharp contrast, the most active ion in thermochemical alkaline digestion is the hydroxyl ion, which tends to favor carbanion reactions rather than carbonium ion or free radical reactions. In other words, the thermochemical alkaline digestion reaction mechanism would be expected to involve reactions such as the Aldol, Claisen, and Dieckmann condensations.

The products identified by GC/MS and reported here support this conclusion, since they are capable of being formed during carbanion reactions more readily than from carbonium ion or free radical reactions.

For convenience, although the compounds identified are listed in Table 1, together with the mass spectral evidence supporting their identification, Table 2 gives a list of these same compounds but arranged in chemical class. It can be seen that the primary groups of compounds found are furans, ketones, alcohols, phenols, alkenes and alkynes. Cyclic compounds figure prominently. It is also apparent (Fig. 2) that there is much structural similarity and even homology between different products, suggesting a consistency of mechanism in their formation. The isomerism between many of the products (Fig. 3) also suggests formation of different isomers through a common intermediate. As examples, the structural similarity between the observed products cyclohexanone and phenol, the isomerism between cyclohexanone and 2-methylcyclopentanone, and the homology between phenol and the cresols may be cited. Any attempt to link these products through a reaction mechanism for their formation must therefore provide for multiple reaction products by different ways of carrying out the same reaction between the same molecules. As an example of such a reaction we cite the Aldol condensation between acetaldehyde (ethanal) and propanal, where carbanions may be generated at the $\underline{\alpha}$-carbon atoms of either aldehyde, which may then condense with another molecule of either aldehyde, giving rise to 4 products.

Thus,

$$^{-}CH_2\text{-}CH{=}0 + CH_3\text{-}CH{=}0 \xrightarrow{OH^-} CH_3\text{-}CH(OH)CH_2\text{-}CH{=}0 \text{ (Aldol)}$$

$$^{-}CH_2\text{-}CH{=}0 + CH_3\text{-}CH_2\text{-}CH{=}0 \xrightarrow{OH^-} CH_3\text{-}CH_2\text{-}CH(OH)CH_2\text{-}CH{=}0$$

$$^{-}CH(CH_3)CH{=}0 + CH_3\text{-}CH_2\text{-}CH{=}0 \xrightarrow{OH^-} CH_3\text{-}CH_2\text{-}CH(OH)CH(CH_3)CH{=}0$$

$$^{-}CH(CH_3)CH{=}0 + CH_3\text{-}CH{=}0 \xrightarrow{OH^-} CH_3\text{-}CH(OH)CH(CH_3)\text{-}CH{=}0$$

This and related types of carbanion condensation reaction can readily explain the formation of several products from a smaller number of intermediates, moreover generating the observed types of products (alcohols, aldehydes, ketones, furans, etc.). Further reactions involving reduction and elimination of water, hydroxyl-ion catalyzed rearrangements, and others, can also be invoked to explain a multiplicity of related products.

To further rationalize the observed spectrum of products from cellulose thermochemical liquefaction, it is necessary to take a step-by-step approach, working backwards from observed products to hypothetical intermediates, and from these back to compounds which might reasonably be expected to form during the degradation of cellulose. The cycle is closed when a known product can be formed from previously identified cellulose degradation products such as glycolic acid or dihydroxybutyric acid. However, the proposed mechanisms may only be confirmed when the hypothetical intermediates are isolated and identified directly in the oil products.

Formation of cyclopentane and cyclohexane derivatives - The occurrence of these compounds together in the cellulose digestion products leads intuitively to the conclusion that they were formed from similar intermediates, since they are structurally related. Also all but one of these compounds have been identified with high probability and so are a good starting point from which to attempt to deduce the mechanism of cellulose conversion to oils from simple degradation products.

The carbanion intermediate is probably a poor assumption to make for formation of these particular compounds, as such an intermediate would have to cyclize by nucleophilic substitution with loss of a leaving group such as hydroxyl, aldehyde, alkoxide, and so on, all of which are very poor leaving groups in alkaline conditions. Also, it is difficult to see how multiple products could be formed in such a direct reaction (Fig. 4a). The leaving group 'X' could not be substituted for with a double bond - this could explain the formation of multiple products, but attack of a carbanion on an electron-dense double bond is extremely rare. However, if the attacking group were a double bond, and the aldehyde group were the electron acceptor, there is a possible mechanism for formation of all of the observed cyclopentanone and cyclohexanone products, through a 6-membered ring intermediate ring-closure reaction, followed by a dehydrogenation. For instance, cyclohexanol and 2-methylcyclopentanol could be formed by internal cyclization of 5-hexenal and 4-hexenal, respectively (Fig. 4b). Both 5- and 4-hexenal could be derived by dehydration of 5-hydroxyhexanal, but no other isomer. Hence, as a first step we postulate the formation of 5-hydroxyhexanal as an intermediate in formation of cyclohexanone and 2-methylcyclopentanal and 4-hydroxypentanal as an intermediate in the formation of cyclopentanone.

In the case of cyclopentanone formation the intermediate alkenals formed by loss of water from the hydroxyl group would have been 3- and 4-pentenals; 4-pentenal could cyclize to cyclopentanone, an observed product. However, 3-pentenal would not cyclize to cyclobutanone due to steric stress effects in the resulting 4-membered ring, and would thus be expected as another product. Isolation and identification of 3-pentenal from the reaction products of cellulose conversion would be good evidence in favor of this mechanism.

2-Ethylcyclopentanone could similarly have been formed from a 2-ethyl-4-pentenal intermediate, perhaps itself derived from 4- or 5-hydroxyheptanal. If from the 4-hydroxyheptanal, we would also expect to find some of the other unsaturated dehydration product, 3-heptenal, which again for steric reasons would not be expected to cyclize to a 4-membered ring ketone.

Similar reactions could have led to the formation of the remaining cyclopentanone and cyclopentane derivatives (Fig. 4b). In the case of 2,5-dimethyl-2-cyclopentenol, dehydration of intermediate 2-methyl-5-hydroxy-2-hexenal is necessary to form an intermediate which then cyclizes by the mechanism outlined above. Rearrangement to the corresponding ketone would complete the sequence (Fig. 4c).

Formation of phenol (also identified in cellulose reaction products) from cyclohexanol is a possibility, but is unlikely in a reducing atmosphere which would strongly favor the reverse reaction - formation of cyclohexanol from phenol. Cyclohexanol may be dehydrogenated to cyclohexanone (the observed product) in a reducing atmosphere at high temperature, but this is not as unlikely as phenol formation since it involves loss of only 2 hydrogen atoms rather than 8.

<u>Furans, 4-methylpent-3-en-2-one, and 4-hydroxy-4-methyl-2-pentanone</u> - Of the products identified from cellulose conversion in alkali, furans and tetrahydrofurans figure prominently. One conventional method for furan synthesis in the laboratory involves the dehydration of a diketone, which may be crudely represented as shown in Fig. 5a. In actuality, the mechanism is rather more complicated than this would indicate, and involves formation of an ene-diol tautomer, the enolate ion form of which performs a nucleophilic attack on the adjacent carbonyl carbon atom, closing the ring (Fig. 6). Proton rearrangement of this and elimination of a molecule of water completes the change to a furan.

As an example of the conversion envisaged, we take the example of 2,4-dimethylfuran. The intermediate dicarbonyl compound required for the cyclization is 4-keto-2-methylpentanal, which cyclizes in the manner shown in Fig. 6. (R=H; R'=R"=$CH_3$). An indication that this mechanism may in fact take place is given by the observation of closely related compounds in the cellulose decomposition products, namely 4-methyl-3-pent-en-2-one and 4-hydroxy-4-methyl-2-pentanone. This relationship is brought out more clearly by formulas than by chemical names, and so the formulas are shown in Fig. 5b. A facile dehydration of 4-hydroxy-4-methyl-2-pentanone would yield the second observed product, 4-methyl-3-penten-2-one. The hypothetical intermediate in 2,4-dimethyldimethylfuran formation, 4-keto-2-methylpentanal, cannot be formed easily from either of these intermediates in any direct reaction. However, addition of water across a double bond in another intermediate, 4-methyl-4-penten-2-one (isomesityl oxide) followed by dehydrogenation, would lead to both the observed 4-hydroxy-4-methyl-2-pentanone (major product), together with a small amount of the primary alcohol 5-hydroxy-4-methyl-2-pentanone. Oxidation or dehydrogenation of the latter compound could yield the 4-keto-2-methylpentanal as a product. (Fig. 5c). An alternative sequence of reactions which could lead to the formation of 4-keto-2-methylpentanal involves the condensation between one molecule of acetone and one molecule of pyruvaldehyde, another likely (but as yet unidentified) intermediate in this class of reactions. The carbanion derived from acetone by the action of base would attack the keto carbonyl of pyruvaldehyde in a nucleophilic reaction, leading eventually to 2-hydroxy-4-keto-2-methylpentanal; dehydration and hydrogenation of the resulting double bond would yield the required 4-keto-2-methylpentanal (Fig. 5d).

It is worth noting at this point that these mechanisms represent possible, and in some cases probable ways for formation of observed products from cellulose aqueous alkaline digestion at high temperature and pressure; they are in no sense intended to be definitive, and in fact in each case will require extensive further experimentation before they may be regarded as proven. They are a guide from which a pattern for directing further experimentation may be derived.

For the moment, it will suffice that all of the observed furan and tetrahydrofuran products observed can be made from a series of chemically similar dicarbonyl compounds. 2,5-Dimethyltetrahydrofuran may be made by condensation of 2,5-hexadione and addition of hydrogen across the double bond of the resulting furan (Fig. 6a). 2-Hydroxy-2-methyl-tetrahydrofuran may be formed through condensation of 2-ketopentanal, addition of hydrogen taking place to the resulting dihydrofuran alcohol without loss of water (which would lead to another hypothetical product, 2-methylfuran. (Fig. 6, R=R"=H; R'=$CH_3$).

Using the same reaction sequence, other observed products may be formed. Thus, 5-ethyl-2-methylfuran could be formed from 2,5-heptadione, and 2,5-diethylfuran from 3,6-octadione (the alternative identification for this latter compound is 2,5-dimethyl-3-ethylfuran, which could be formed by the same route from 3-ethyl-2,5-hexadione). It is of interest to note that 3-octadienone has been tentatively identified in the cellulose conversion products, a compound structurally very similar to one of the intermediates postulated above (3,6-octadione).

Unsaturated hydrocarbons - A number of aliphatic unsaturated hydrocarbons have been tentatively identified in cellulose thermochemical conversion products. The identities of these are tentative because of the great numbers of possible isomers with closely similar mass spectra. These unsaturated compounds could conceivably have been formed by dehydration of intermediate alcohols, perhaps formed from ketones by reduction; alternatively, the unsaturated compounds could be precursors of alcohols through a hydration step, and of ketones through an oxidation of the alcohols. Work is in progress to attempt to resolve this sequence in the correct direction.

Despite the difficulty inherent in deciding whether the unsaturated hydrocarbons were the precursors of the alcohols and ketones observed, or *vice versa*, it is worthwhile for the present to assume that the unsaturated compounds were formed by elimination of water from intermediate compounds formed by reactions of simple aldehydes and ketones. As an example, we take the condensation of two molecules of acetone. Under alkaline conditions, condensation takes place with the formation of 4-hydroxy-4-methyl-2-pentanone (commonly called diacetone alcohol). This latter compound has been identified in this work as a product of cellulose conversion.

The mechanism for the reaction is shown in Fig. 7a. Apart from explaining the formation of 4-hydroxy-4-methyl-2-pentanone, this mechanism may be extended by dehydration and reduction of the above intermediate, yielding 2-methylpentadiene. Although this compound was not observed, a related compound (2,5-dimethylhexa-2,4-diene) *was* observed. This could have been formed through the identical mechanism from condensation of acetone with methyl isopropyl ketone (3-methyl-2-butanone) to form 5-hydroxy-2,5-dimethyl-3-hexanone. Reduction of this and elimination of two molecules of water would yield the observed 2,5-dimethylhexa-2,4-diene, as shown in Fig. 7b.

Alternative products of this condensation, not yet identified, are 2,3-dimethyl-2,4-pentadiene and 2,3,3-trimethyl-4-penten-2-ol, obtained by formation of intermediate carbanions at the two other available *α*-carbon atoms.

The remaining 3 unsaturated straight-chain hydrocarbons tentatively identified as 3-heptene, 3-decyne, and octyne, could not be formed by Aldol or similar condensations involving a carbanion at the *α*-carbon atom of an aldehyde or ketone, as this would result in branching in the hydrocarbon eventually formed. It is of course possible that the compounds tentatively identified as straight-chain unsaturated hydrocarbons could in fact be branched-chain isomers, but there is no evidence for this at present. One way out of this impasse is to suppose that two molecules of the same or different aldehydes condenses to form a long-chain aldehydic alcohol which then by some mechanism loses the active group responsible for the condensation. This is made clearer by giving an example, where, for instance, pentandial reacts with propanal. (Fig. 8). The intermediate branched hydroxydial could then undergo an internal Cannizzaro reaction, for which it is well set up to form a 6-membered transition state. Decarboxylation of the resulting $\underline{\alpha}$-hydroxycarboxylic acid followed by further dehydrations to an unsaturated hydrocarbon would finally yield 1,3,5-heptatriene.

Although the Canizzaro reaction is well-known, and is a type of reaction requently observed in cellulose reactions, where one group is oxidized at the same time as another is reduced, there is an alternative reaction which is possible, in this case, involving an intermediate 4-membered transition state. This is unstable and difficult to form, but results in a direct loss of a molecule of formic acid from the intermediate branched hydroxydial, with a total number of reaction steps less than that required by the Cannizzaro reaction, where the carboxylic acid must first be formed and then decarboxylated separately. This hypothetical sequence is shown in Fig. 9, and leads to 1,4-hept<u>adi</u>ene as a final product.

Thus, there are possible routes to unsaturated straight-chain hydrocarbons <u>via</u> cellulose decomposition products, notably aldehydes and ketones. However, further speculation on the formation route of these compounds is premature, since their exact structures have yet to be established.

Phenol and Cresols - The formation of aromatic structures from the decomposition of pure cellulose is not unexpected, since similar compounds have been identified in the pyrolytic tars from paper (27). Normally, they are assumed to come entirely from the lignin component of biomass, an assumption which may now be considered disproven. The exact route for aromatic phenol and cresol formation from cellulose is rather a problem, since although they could be derived from cyclohexanone and methylcyclohexanones by loss of hydrogen, the dehydrogenation reaction would have to occur in a reducing atmosphere which would favor the reverse reaction. This point will not be cleared up until radioactive tracer experiments with pure cyclohexanone and methylcyclohexanones can be carried out, and a search for radioactive tracer in the phenolic products performed.

An alternative route for phenol and cresol formation would be *via* dehydration of a polyol intermediate derived from glucose, coupled with cyclization to form a six-membered ring. Again, the exact route for this is not known.

Acrolein - Acrolein (propenal) has been identified previously in cellulose pyrolysates (28), and it is not at all unlikely as a product of aqueous degradation of cellulose also. However, acrolein was tentatively identified in the current work as the monotrifluoroacetate ester of its hydrate. This identification requires some further explanation. A GC peak at 9.9 min in the oil which had been reacted with trifluoroacetic anhydride was shown to have a mass spectrum with molecular ion at 170, and with characteristic ions due to fluoroacetate at m/e 69 and 97 ($CF_3^+$ and $CF_3CO^+$, respectively). The residual mass due to the alcohol fragment was therefore m/e 170-97, or 73.

Part of this was the alcoholic oxygen atom, mass 16, leaving a residue of 57. The only rationl way of assigning this fragment a structure was to assign it as $CH_2{=}CH\overset{+}{-}OH$ (m/e = 57), since the alternative (butanal) would have had a much lower retention time on the GC. The assignment as acrolein hydrate trifluoroacetate is made more reasonable by noting the electron-withdrawing effect of the $CF_3$-COO group in stablizing the hydrate.

Formation of aldehyde and ketone intermediates - The preceding discussion provided a structure for correlating the various compounds which have been identified by GC/MS of the cellulose alkaline digestion products, by generating a series of hypothetical intermediates using well-known mechanisms. With the exception of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone), none of these products has been identified. However, identification of diacetone alcohol in the observed products is good evidence that the postulated mechanisms are reasonable.

The hypothetical intermediates consist of 12 aldehydes and ketones, which can be used to derive all of the observed products by simple reactions such as dehydrogenation, hydrogenation, dehydration, etc., with the exception of the unsaturated hydrocarbons, phenol, and cresols. For reasons already explained, these products require the operation of different mechanisms than required for formation of aldehydes and ketones, furans, cycloalkanones, and alcohols. Also, the identifications of the unsaturated hydrocarbons are not sufficiently definite to permit much speculation on their mode of formation.

The twelve compounds postulated as intermediates are listed in Table 3, together with their structures. Without exception, they may be considered as having been derived from simple aldehydes and ketones by one of 3 different condensation routes, all well-known reactions. These reaction routes are illustrated for representative examples in Fig. 10.

The primary compounds required to condense to form all of the complex ketones and aldehydes postulated as intermediates of the observed products are all simple aldehydes and ketones, which have in most cases already been observed as products of cellulose pyrolysis or thermochemical digestion. They include acetone, acetaldehyde, propionaldehyde, acrolein, ethyl methyl ketone, propyl methyl ketones, formaldehyde, and methylpropenal. That all of the observed major products of cellulose conversion may be traced back to such simple and already observed intermediates is good circumstantial evidence for the correctness of the reaction sequences outlined.

None of this discussion is intended to replace experimental data, but merely to serve as a structure on which further experiments can be based, to confirm or deny the predictions made. The overall general sequence of reactions from cellulose through simple carbonyl intermediates through to the identified products is illustrated in Fig. 11. Further work will extend this sequence in the direction of identification of some of the higher molecular weight components of the oils derived by thermochemical alkaline digestion of cellulose, and attempt to confirm some of the tentative identification already made.

## CONCLUSIONS

The overall mechanism of cellulose conversion in hot aqueous alkali appears to be one of degradation through glucose to low molecular weight saccharinic acids, dihydroxybutyric acid, glycolic acid, and carbonyl products such as acetone, acetaldehyde, formaldehyde, and similar compounds. Although the products identified in the present report were fairly complex furans, carbocyclic ketones, unsaturated hydrocarbons, and aromatic compounds, nevertheless in most cases they could have been formed from simple carbonyl compounds through a series of condensations involving carbanion intermediates.

It is conceivable that residual alkali in the oil during acetone extraction could have given rise to diacetone alcohol as an artifact. This is refuted by examination of an aqueous residue which was extracted with diethyl ether and which was never exposed to any acetone: Compounds derived from diacetone alcohol (such as mesityl oxide or 4-methyl-3-penten-2-one) were also identified in the diethyl ether extract of the aqueous phase. Furthermore, other compounds were identified in the oil acetone extract which could not have been derived from acetone or diacetone alcohol, but which could have been formed from other carbonyl compounds by the same mechanism. Hence, diacetone alcohol is a genuine product of cellulose conversion although apparently not an intermediate in further synthesis of other products.

The further reaction of the postulated cyclic intermediates, and the route to formation of unsaturated hydrocarbons of high molecular weight is intended to be the next subject of investigation in the current work.

The fundamental difference in the mechanism of cellulose conversion to oil by pyrolysis and by aqueous alkaline digestion predicted by theory is therefore confirmed. Pyrolysis products may be explained generally by carbonium ion and free radical reactions (in fact, cellulose decomposition is acid-catalyzed), while in aqueous alkali, nucleophilic carbanion reactions are favored.

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## REFERENCES

1 F. Hoppe-Seyler, Berichte, 4 (1871) 15-16.

2 P.M. Molton, T.F. Demmitt, "Reaction Mechanisms in Cellulose Pyrolysis: A Literature Review," BNWL-2297, ERDA Contract #EY-76-C-06-1830.

3 E. Berl and A. Schmidt, Annalen, 461 (1928) 192-220.

4 E. Berl, A. Schmidt, and H. Koch, Z. Angew. Chem., 43 (1930) 1018-1019.

5 E. Berl and A. Schmidt, Annalen, 493 (1932) 97-123.

6 E. Berl and A. Schmidt, Annalen, 496 (1932) 283-303.

7 P.M. Molton and T.F. Demmitt, J. Macromol. Sci., Rev. Macromol. Chem., submitted (1977).

8 F. Fischer and H. Schrader, Brennstoff.-Chem., 2 (1921) 161-173.

9 H.I. Waterman and F. Kortlandt, Rec. Trav. Chim., 43 (1924) 691-701.

10 S. Friedman, H.H. Ginsberg, I. Wender, and P. Yavorsky, 3rd. Mineral Waste Utilization Symp., IIT Res. Inst., Chicago, IL, Mar 14-16, (1972).

11 I. Wender, F.W. Steffgen, and P.M. Yavorsky, Ann Arbor Sci., "Recycling and Disposal of Solid Wastes", ed. T.F. Yen, 1974, Ann Arbor Sci., Mich., 43-99.

12 Y.C. Fu, E.G. Illig, and S.J. Metlin, Environmental Sci. Tech., 8 (1974) 737-740.

13 F. Shafizadeh, Adv. Carbohydrate Chem., 23 (1968) 419-474.

14 F. Shafizadeh and Y.L. Fu, Carbohydrate Res., 29 (1973) 113-122.

15 F. Shafizadeh, in "Wood Chemicals - A Future Challenge", Proc. 8th. Cellulose Conf., Syracuse, N.Y., May 19-23, 1975, ed. T.E. Timell; John Wiley and Sons, N.Y., (1975) 153-174.

16 A. Broido, A.C. Javier-Son, A.C. Quano, and E.M. Barrall, J. Appl. Polymer Sci. 17 (1973) 3627-3635.

17 A. Broido, "Thermogravimetric and Differential Thermal Analysis of Potassium Bicarbonate-Contaminated Cellulose", Western States Sect., Combust. Inst., Paper Wss-Ci, 66-20 (1965), 10.

18 Mass Spectrometry Data Centre, "Eight Peak Index of Mass Spectra", Pendragon House, Inc., Palo Alto, CA, 2nd Edn. 1 (1974).

19 H. Heinemann, Petroleum Refiner, 33 (1954) 135-137.

20 G. Keppeler and E. Edler, Brennstoff-Chem., 21 (1940) 123-127.

21 H.R. Appell and J.S. Tosh, U.S. Pat. 3,733,255, (1973).

22 G. Machell and G.N. Richards, J. Chem. Soc., (1960) 1924-1931.

23 G. Machell and G.N. Richards, J. Chem. Soc., (1960) 1932-1938.

24 G. Machell and G.N. Richards, J. Chem. Soc., (1960) 1938-1944.

25 D. O'Meara and G.N. Richards, J. Chem. Soc., (1960) 1944-1945.

26 G. MacKay and M. David, U.S. Dept. Forestry, Rept. ODC 813.4 (1967) 1-23.

27 J.A.S. Gilbert and A.J. Lindsey, Brit. J. Cancer, 11 (1957) 398-402.

28 R.F. Schwenker, Jr., and L.R. Beck, Jr., J. Polymer Sci., 2C (1963) 331-340.

TABLE I

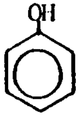
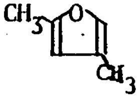
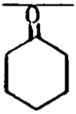
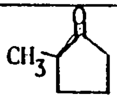
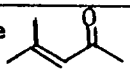
GC/MS IDENTIFICATION OF COMPOUNDS PRESENT IN CELLULOSE THERMOCHEMICAL REACTION PRODUCTS

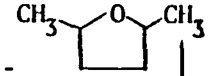
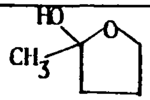
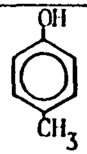
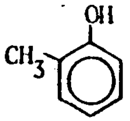
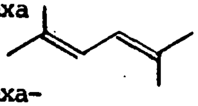
TABLE II

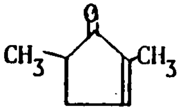
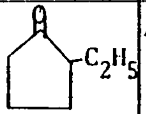
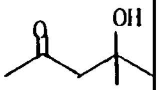
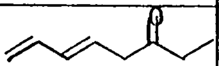
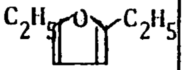
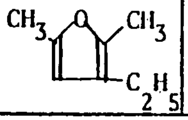
COMPOUNDS IDENTIFIED IN CELLULOSE DECOMPOSITION PRODUCTS IN ALKALI

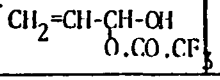
TABLE III

FORMATION MECHANISMS FOR HYPOTHETICAL DIFUNCTIONAL INTERMEDIATES

| Compound Identified[*] | Formula | Sample[†] | $R_f$(min) | M. Wt. | Major MS peaks[++] |
|---|---|---|---|---|---|
| Cyclopentanone (sample)(H)[§] |  | A,1,2 | 2.0 | 84 | 55(100),84(41),56(30),41(26),42(15), |
| " (Std.) | | - | - | 84 | 55(100),84(38),56(28),41(32),42(14), |
| Phenol (H) |  | A,1(F) | 17.5<br>2.9F | 94<br>190F | 94(100),66(27),65(25),55(11),<br>190(100),65(73),69(70),44(62),76(40),83(30),88(28),39(24) |
| Phenol (std.) | | - | - | 94 | 94(100),66(19),65(17),55(6),39(13),40(8),95(7),47(5) |
| 2,4-Dimethylfuran (P) |  | A,2 | 4.9 | 96 | 67(100),96(84),53(38),68(16),39(15),41(15),95(10),65(8) |
| 2,4-Dimethylfuran (std.) | | - | - | 96 | 67(65),96(100),53(32),68(11),39(38),81(19),95(43),65(13) |
| Cyclohexanone (H) |  | A | 3.9 | 98 | 55(100),42(60),98(37),69(33),41(29),70(26),81(24),39(18) |
| Cyclohexanone (std.) | | - | - | 98 | 55(100),42(54),98(44),69(31),41(36),70(23), - ,39(21) |
| 3-Heptene<br>Heptene isomer (T) |  | A<br>1 | 2.7<br>3.4 | 98<br>98 | 43(100),69(80),41(64),55(59),57(58),83(58),46(21),81(21) |
| Heptene (std.) | | - | - | 98 | 56(66), 69(56),41(100),55(48),39(32),98(28), |
| 2-Methylcyclopentanone (H) |  | A,1,2 | 2.5 | 98 | 42(100),55(76),98(58),69(53),41(40),70(32),56(28),83(19) |
| 2-Methylcyclopentanone (Std.) | | - | - | 98 | 42(100),55(38),98(54),69(30),41(43),70(20), - , - |
| 4-Methyl-3-penten-2-one (H) |  | 2 | 1.8 | 98 | 83(100),55(72),98(53),43(35),39(19),53(17),84(16),56(12) |
| 4-Methyl-3-penten-2-one (Std.) | | - | - | 98 | 83(100),55(87),98(59),43(51),39(23),53(13), - , - |

| Compound Identified | Formula | Sample | $R_f$(min) | M. Wt. | Major MS Peaks |
|---|---|---|---|---|---|
| 2,5-Dimethyltetrahydrofuran (H) |  | A | 8.3 | 100 | 56(100),85(65),41(37),43(32),57(20),100(11),39(7) |
| 2,5-Dimethyltetrahydrofuran (Std.) | | - | - | 100 | 56(100),85(86),41(74),43(54),57(14),100( 8),39(10) |
| 2-Hydroxy-2-methyltetrahydrofuran (T) |  | 1F<br>2F | 4.4F<br>4.4F | 102<br>102 | 71(100),43(43),69(42)[§],44(35),41(26),40(17),42(15)<br>71(100),43(36),69(31), 44(12),41(21),40(5) ,42(12) |
| 2-Hydroxy-2-methyltetrahydrofuran (Std.) | | - | - | 102 | 71(100),43(51), - , 44(8), 41(25), - ,42(11) |
| p-Cresol (H) |  | 1F | 4.2F | 108<br>(204F) | 107(100),204(64),90(40),91(37),77(37),69(31)[§],41(20) |
| p-Cresol (Std.) | | - | - | 108 | 108(100),107(99),79(23),51(22),77(28),39(18),53(17) |
| m- and/or p-Cresol (H) | | A | 20.3 | 108 | 108(100),107(89),79(37),44(24),77(28),39(22),41(17) |
| o-Cresol (H) |  | A | 18.5 | 108 | 108(100),107(88),79(39),90(27),77(29),51(18),89(18) |
| o-Cresol (Std.) | | - | - | 108 | 108(100),107(75),79(32),90(23),77(32),51(26),39(26) |
| 4-Octyne (T) |  | 2 | 7.5 | 110 | 67(100),110(70),95(28),109(19),81(18),68(18),41(17) |
| 4-Octyne (Std.) | | - | - | 110 | 67(100),110(97),95(34),52(33), 81(87),68(53),41(40) |
| Octene + Octyne (T) | | A | 5.5 | 110<br>112 | 83(100),55(80),67(63),56(59),41(50),112(35),95(32), |
| Oct-1-ene (Std.) | | - | - | 112 | 43(100),55(83),42(63),56(64),41(78),70(52),69(30) |
| 2,5-Dimethyl-2,4-hexadiene (P) |  | A<br>2 | 9.3<br>8.0 | 110<br>110 | 95(100),67(74),110(71),41(36),39(36),66(20),42(19)<br>95(100),67(59),110(83),41(33),39(26),99(26),42(26) |
| 2,5-Dimethyl-2,4-hexadiene (Std.) | | - | - | 110 | 95(100),67(51),110(56),41(44),39(40),55(35),53(22) |

| Compound Identified | Formula | Sample | $R_f$(min) | M.Wt. | Major MS Peaks |
|---|---|---|---|---|---|
| 2,5-Dimethyl-2-cyclo-pentenone (H) |  | A | 5.1 | 110 | 67(100),95(71),110(57),41(29),39(25),53(22),82(20) |
| 2,5-Dimethyl-2-cyclo-pentenone (Std.) | | - | - | 110 | 67(100),95(55),110(40),41(35),39(40),53(19),82(27) |
| Ethylmethylfuran (T) |  | A | 7.8 | 110 | 96(100),67(76),53(48),81(43),95(44),39(23),40(20) |
| 5-Ethyl-2-methylfuran (Std.) | | - | - | 110 | 95(100),67(11),53( 8),110(39),43(34),39(10),51(8) |
| 2-Ethylcyclopentanone (H) |  | A,1,2 | 4.7 | 112 | 84(100),56(65),55(61),41(49),83(40),68(35),112(30) |
| 2-Ethylcyclopentanone (Std.) | | - | - | 112 | 84(100),56(75),55(63),41(60),83(37),68(37),112(28) |
| 4-Hydroxy-4-methyl-2-pentanone (T) |  | 2F | 5.5F | 116 (212F) | 43(100),69(22)§,58(19),55(8),99(7),95(6),85(5),83(5) |
| 4-Hydroxy-4-methyl-2-pentanone (Std.) | | - | - | 116 | 43(100), - , 58(31),42(7),39(5),38(2), - ,83(1) |
| 3-Octadienone (T) |  | 2 | 10.6 | 124 | 124(100),96(96),67(84),91(69),41(63),79(59),95(53)<br>(No standard reported) |
| 2,5-Diethylfuran (T) |  | 2 | 11.8 | 124 | 109(100),124(73),95(66),67(46),123(45),81(30),39(26) |
| 2,5-Diethylfuran (Std.)<br>OR | | - | - | 124 | 109(100),124(30),95( 7),67( 7),43(23),53( 6), 39(13) |
| 2,5-Dimethyl-3-ethyl-furan (alternative) |  | - | - | 124 | 109(100),124(58),95( 8),43( 8),123(14),81( 6),39( 7) |

| Compound Identified | Formula | Sample | $R_f$(min) | M.Wt. | Major MS Peaks |
|---|---|---|---|---|---|
| Methyl-n-Propylcyclo-pentene (T) |  | A | 9.5 | 124 | 67(100),110(69),95(22),109(17),54(19),41(18),43(14)<br>(No standard reported) |
| Decyne (T) |  | 2 | 14.9 | 138 | 95(100),110(67),96(61),67(34),138(32),53(32),82(31) |
| 3-Decyne (Std.) | | - | - | 138 | 95(37), 109(67),41(57),67(100),68(40),39(34),55(30) |
| Acrolein hydrate mono-trifluoroacetate (T) |  $CH_2{=}CH\text{-}\underset{O.CO.CF_3}{CH}\text{-}OH$ | 1F | 9.9F | 170 | 141(100),69(79)§,44(32),40(24),47(21),43(16),97(12)§<br>(No standard reported) |

* Name of compound, followed by standard, where available.

† Sample 'A' - Underivatized diethyl ether extract of aqueous phase from cellulose reaction in aqueous alkali; sample '1' - derivatized oil; sample '2' - derivatized oil; derivatization with trifluoroacetic anhydride. 'F' suffix indicates that the compound was run as its trifluoroacetate ester derivative.

†† Major mass spectrum peaks, m/e(% of base peak).

§ H - Identification highly probable based on excellent agreement with literature spectrum.
P - Identification probable based on good agreement with literature spectrum, or close correlation between sample trifluoroacetate ester with underivatized (literature) compound spectrum.
T - Identification tentative based on poor agreement with reported spectra, or lack of a reported standard. However, the sample compound is highly likely to be an isomer or close structural relative to the tentatively identified compound.

§ Mass spectrum peak due to trifluoroacetate fragments $CF_3^{+}$ or $CF_3\text{-}CO^{+}$. A '-' indicates peak absent.

Aliphatic homocyclics

Cyclopentanone (H)
Cyclohexanone (H)
2-Methylcyclopentanone (H)
2,5-Dimethyl-2-cyclopentenone (H)
2-Ethylcyclopentanone (H)
Methyl-n-propylcyclopentene (T)

Aromatic homocyclics

Phenol (H)
p-Cresol (H)
o-Cresol (H)

Heterocyclics

2,4-Dimethylfuran (P)
2,5-Dimethyltetrahydrofuran (H)
2-Hydroxy-2-methyltetrahydrofuran (T)
Ethylmethylfuran (T)
2,5-Diethylfuran (T)
(or 2,5-Dimethyl-3-ethylfuran)

Aliphatic carbonyl compounds

4-Methylpent-3-en-2-one (Mesityl oxide) (H)
4-Hydroxy-4-methyl-2-pentanone
(Diacetone alcohol) (T)
3-Octadienone (T)
Acrolein (as hydrate monotrifluoroacetate)(T)

Aliphatic hydrocarbons

3-Heptene (T)
4-Octyne (T)
Octene + octyne (T)
2,5-Dimethyl-2,4-hexadiene (P)
Decyne (T)

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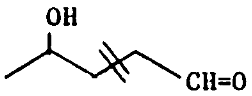
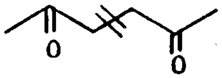
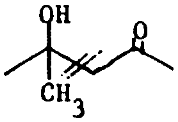
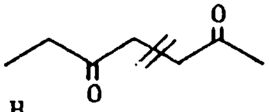
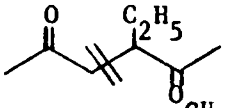
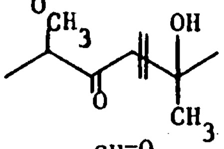
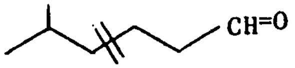
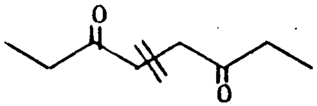
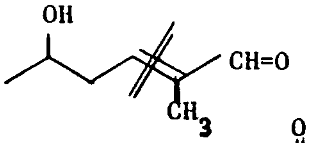
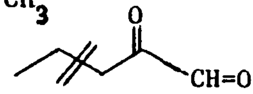
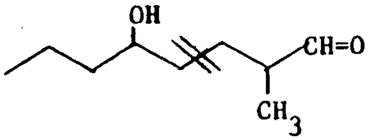
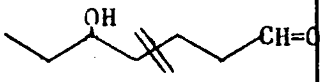
* H = Highly probable identification; P = probable; T = tentative.

| Name of Intermediate | Structure of Intermediate † | Functional Group Relation | Formed From:<br>1 + 2 | Reaction mode* |
|---|---|---|---|---|
| 4-Hydroxypentanal |  | 1,4 | Acetaldehyde + acetone | a |
| 2,5-Hexadione |  | 1,4 | Acetone + acetone | a |
| 4-Hydroxy-4-methyl-2-pentanone (Diacetone alcohol) |  | 1,3 | Acetone + acetone | c |
| 2,5-Heptadione |  | 1,4 | Ethyl methyl ketone + acetone | a |
| 3-Ethyl-2,5-hexadione |  | 1,4 | Methyl n-propyl ketone + acetone | a |
| 5-Hydroxy-2,5-dimethyl-3-hexanone |  | 1,3 | Methyl iso-propyl ketone + acetone | c |
| 5-Hydroxyhexanal |  | 1,5 | Acrolein + acetone | b |
| 3,6-Octadione |  | 1,4 | Ethyl methyl ketone + ethyl methyl ketone | a |
| 2-Methyl-5-hydroxy-2-hexenal |  | 1,5 | Pyruvaldehyde + methyl vinyl ketone | b |
| 2-Ketopentanal |  | 1,2 | Acetaldehyde + pyruvaldehyde | c |

| Name of Intermediate | Structure of Intermediate † | Functional Group Relation | Formed from: 1 + 2 | Reaction mode* |
|---|---|---|---|---|
| 5-Hydroxy-2-methyl-octanal |  | 1,5 | Methyl n-propyl ketone + methacraldehyde‡ | b |
| 5-Hydroxyheptanal |  | 1,5 | Ethyl methyl ketone + acrolein‡ | b |

* Corresponds to mechanisms outlined for simple intermediates in Figure 10.

† Linkage points between the two carbonyl compounds are indicated by a //

‡ Acrolein = acraldehyde = propenal; methacraldehyde = methylpropenal

Fig. 1. Gas chromatography was performed using a Perkin-Elmer Series 900 gas chromatograph with helium carrier gas at a column gas flow rate of 4 ml/min, through a 50 ft x 0.02 in stainless steel support-coated open tubular column with LB 550X stationary phase. Operating conditions were, initial temp. 70°C, programmed at 4°C/min to 130°C, held at 130°C for 30 min. Attenuation used was x20 for a 0.5 μℓ injection, split 99:1, chart speed was 0.5 in/min. (Attenuation was x80 for the diethyl ether extract of product aqueous phase.)

Fig. 2. Structural similarity and homology in cellulose thermochemical reaction products.

Fig. 3. Isomerism in cellulose thermochemical reaction products.

Fig. 4. Hypothetical carbonyl intermediates in the formation of observed cyclopentanones and cyclohexanone.

Fig. 5. Formation of intermediate dicarbonyl compounds required for cyclization to furans.

Fig. 6. Formation of observed furan derivatives from dicarbonyl compounds.

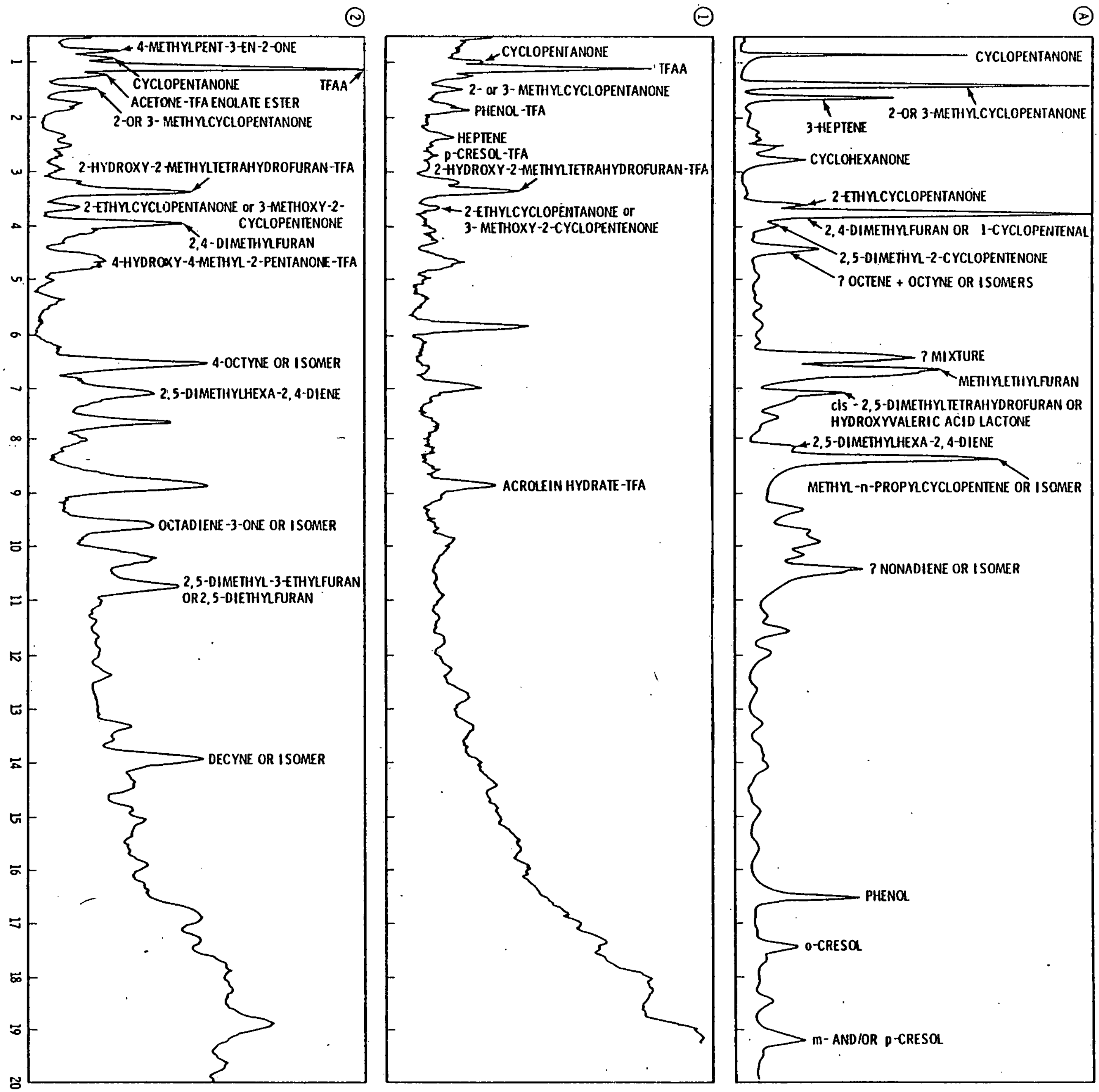
Fig. 7. Possible route to alkadienes from carbonyl intermediates.

Fig. 8. Possible formation route for unsaturated hydrocarbons via the Aldol and Cannizzaro reactions.

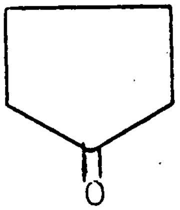
Fig. 9. Alternative route for unsaturated hydrocarbon formation by direct elimination of formic acid.

Fig. 10. Formation mechanisms for hypothetical difunctional intermediates.

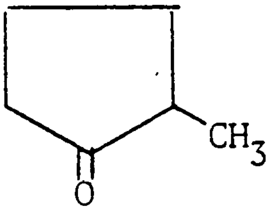
Fig. 11. Summary of intermediate product classes in the formation of oils and tars from cellulose.



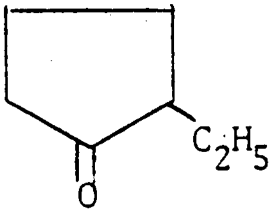
②
4-METHYLPENT-3-EN-2-ONE
CYCLOPENTANONE
TFAA
ACETONE-TFA ENOLATE ESTER
2-OR 3- METHYLCYCLOPENTANONE
2-HYDROXY-2-METHYLTETRAHYDROFURAN-TFA
2-ETHYLCYCLOPENTANONE or 3-METHOXY-2-CYCLOPENTENONE
2,4-DIMETHYLFURAN
4-HYDROXY-4-METHYL-2-PENTANONE-TFA
4-OCTYNE OR ISOMER
2,5-DIMETHYLHEXA-2,4-DIENE
OCTADIENE-3-ONE OR ISOMER
2,5-DIMETHYL-3-ETHYLFURAN OR 2,5-DIETHYLFURAN
DECYNE OR ISOMER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
①
CYCLOPENTANONE
TFAA
2- or 3- METHYLCYCLOPENTANONE
PHENOL-TFA
HEPTENE
p-CRESOL-TFA
2-HYDROXY-2-METHYLTETRAHYDROFURAN-TFA
2-ETHYLCYCLOPENTANONE or 3- METHOXY-2-CYCLOPENTENONE
ACROLEIN HYDRATE-TFA
Ⓐ
CYCLOPENTANONE
2-OR 3-METHYLCYCLOPENTANONE
3-HEPTENE
CYCLOHEXANONE
2-ETHYLCYCLOPENTANONE
2,4-DIMETHYLFURAN OR 1-CYCLOPENTENAL
2,5-DIMETHYL-2-CYCLOPENTENONE
? OCTENE + OCTYNE OR ISOMERS
? MIXTURE
METHYLETHYLFURAN
cis - 2,5-DIMETHYLTETRAHYDROFURAN OR HYDROXYVALERIC ACID LACTONE
2,5-DIMETHYLHEXA-2,4-DIENE
METHYL-n-PROPYLCYCLOPENTENE OR ISOMER
? NONADIENE OR ISOMER
PHENOL
o-CRESOL
m- AND/OR p-CRESOL



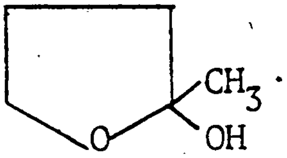
Cyclopentanone



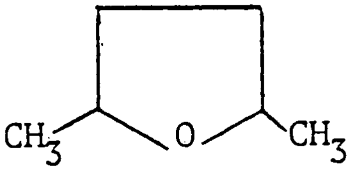
2-Methylcyclopentanone



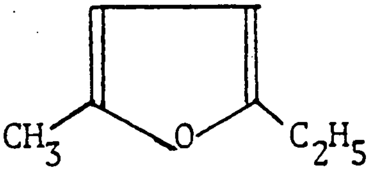
2-Ethylcyclopentanone



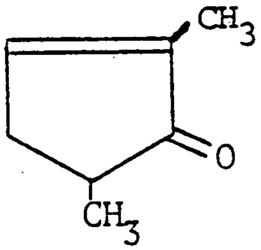
2-Hydroxy-2-methyl -tetrahydrofuran



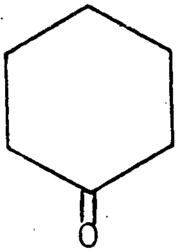
2,5-Dimethyltetrahydrofuran



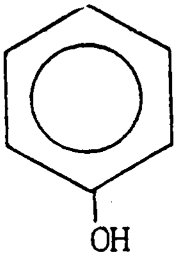
Ethylmethylfuran



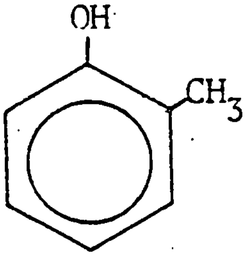
2,5-Dimethyl-2-cyclopentenone



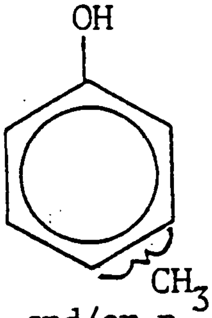
Cyclohexanone



Phenol

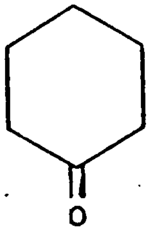


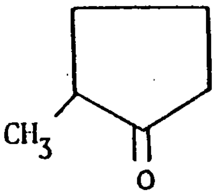
o-Cresol

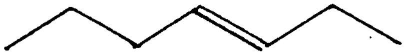


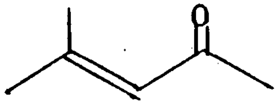
m- and/or p- Cresol

**M.Wt. 98**

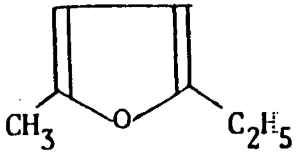

Cyclohexanone
(3.9)*

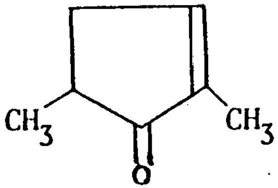

2-Methylcyclopentanone
(2.5)

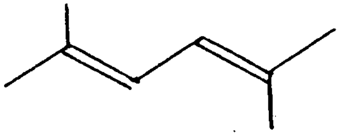

Heptene isomer
(2.7,3.4)

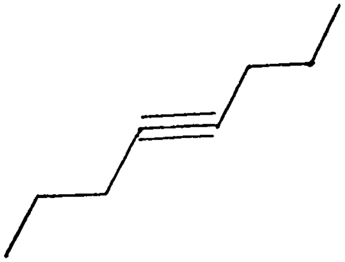

4-Methyl-3-penten-2-one
(1.8)

**M.Wt. 110**


5-Ethyl-2-methyl-furan
(7.8)

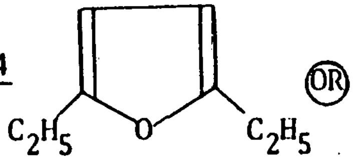

2,5-Dimethyl-2-cyclopentenone
(5.1)


2,5-Dimethyl-2,4-hexadiene
(8.0,9.3)


Octyne isomer

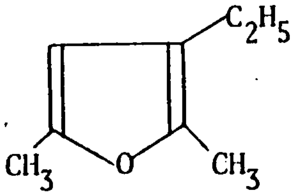
(7.5)

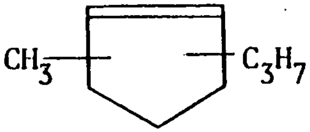
**M.Wt. 124**

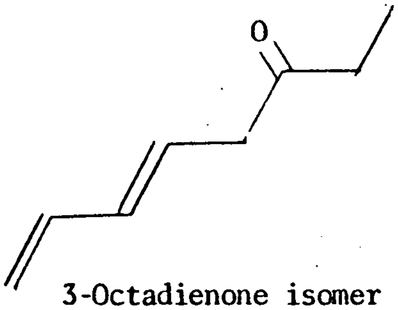

2,5-Diethylfuran

(11.8)

OR


2,5-Dimethyl-3-ethyl-furan
(-)

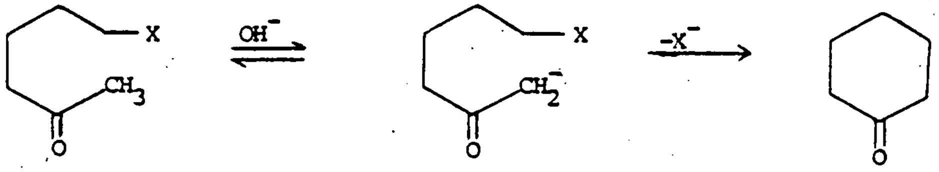

Methyl-n-propyl-cyclopentene isomer
(9.5)


3-Octadienone isomer

(10.6)

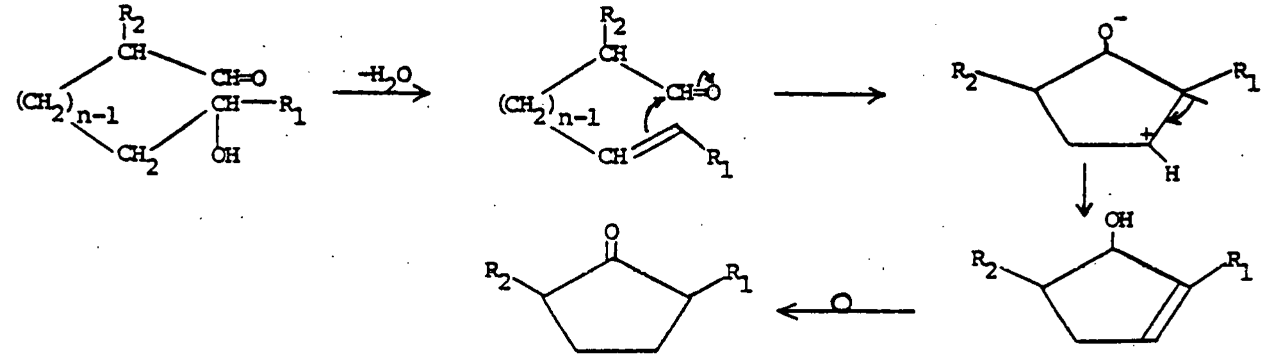
* $R_f$ values (min).

(a)



($X^- = HO^-$, $C_2H_5O^-$, etc.)

(b)



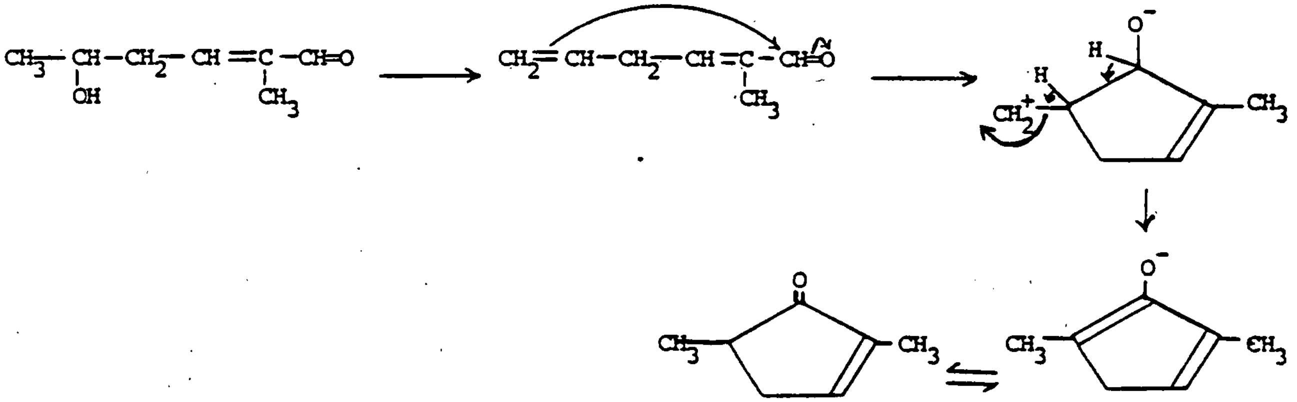
**KEY:**

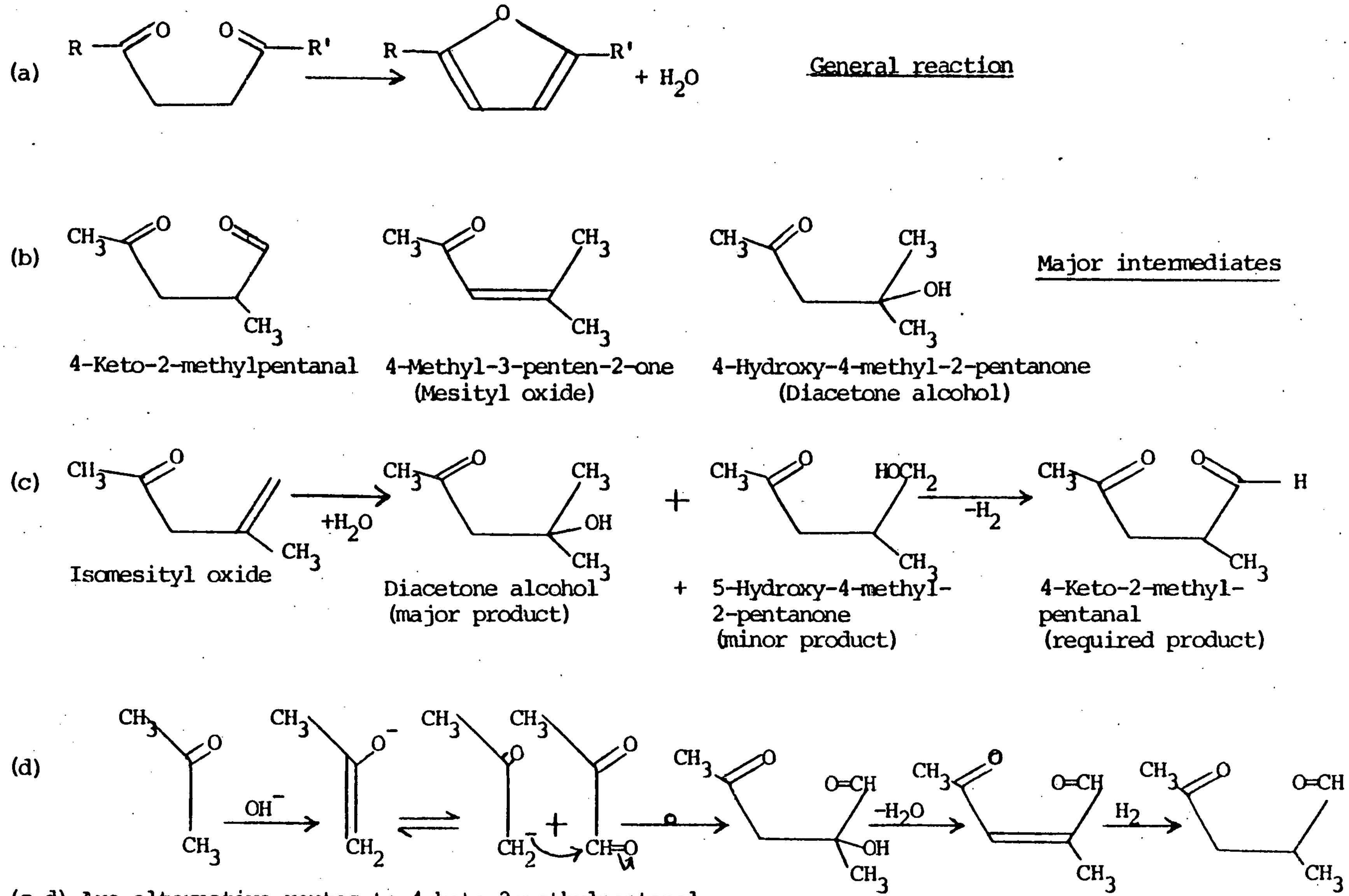
| $R_1$ | $R_2$ | n | Starting material | Intermediate Product | Final Product |
|---|---|---|---|---|---|
| $CH_3$ | H | 1 | 4-Hydroxypentanal | 4-Pentenal* | Cyclopentanone |
| $CH_3$ | H | 2 | 5-Hydroxyhexanal | 5-Hexenal* | Cyclohexanone |
| $CH_3$ | H | 2 | 5-Hydroxyhexanal | 4-Hexenal | 2-Methylcyclopentanone |
| $C_2H_5$ | H | 2 | 5-Hydroxyheptanal | 4-Heptenal | 2-Ethylcyclopentanone |
| $C_3H_7$ | $CH_3$ | 2 | 5-Hydroxy-2-methyloctanal | 2-Methyl-4-octenal | 2-Methyl-5-propylcyclopentene† |

* Double bond formed to $R_1$ carbon.

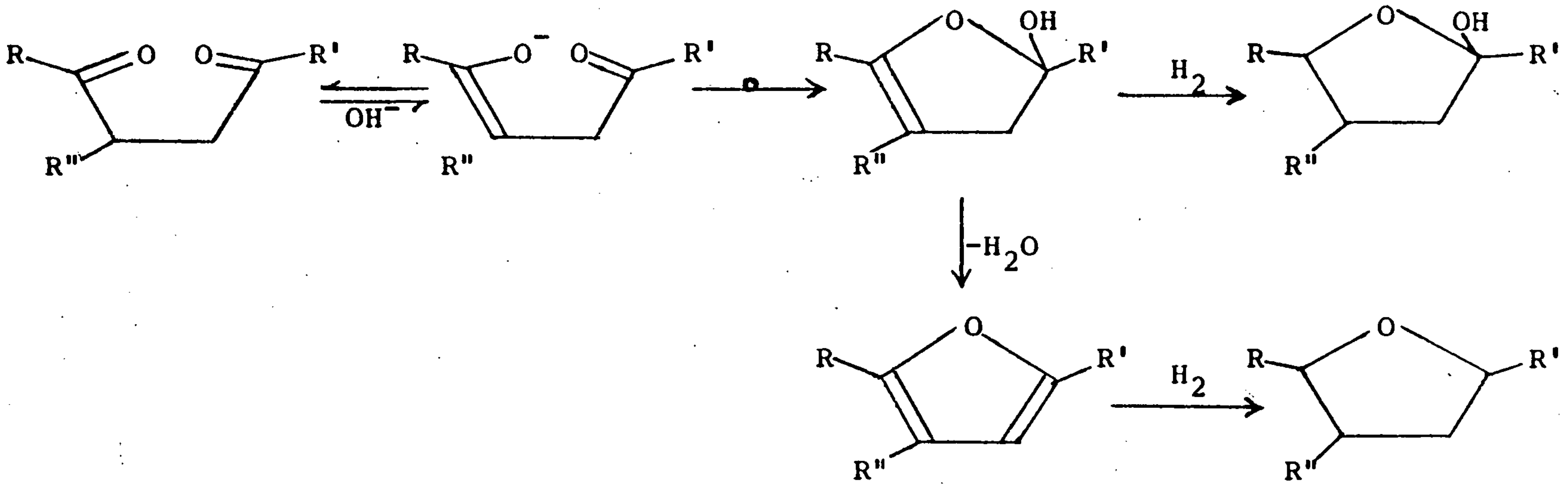
† Elimination of water and addition of hydrogen instead of rearrangement of the intermediate cyclohexenol.

(c)



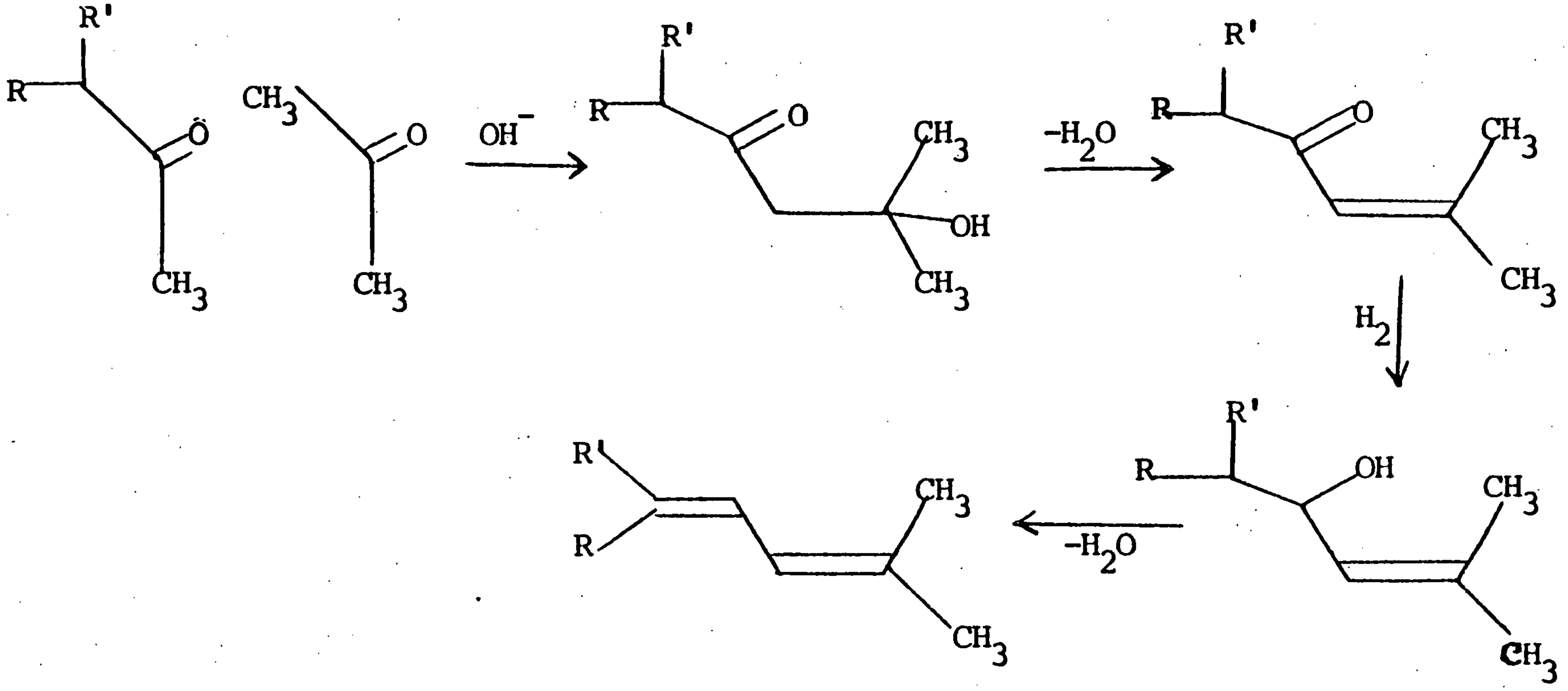


(c,d) Are alternative routes to 4-keto-2-methylpentanal.

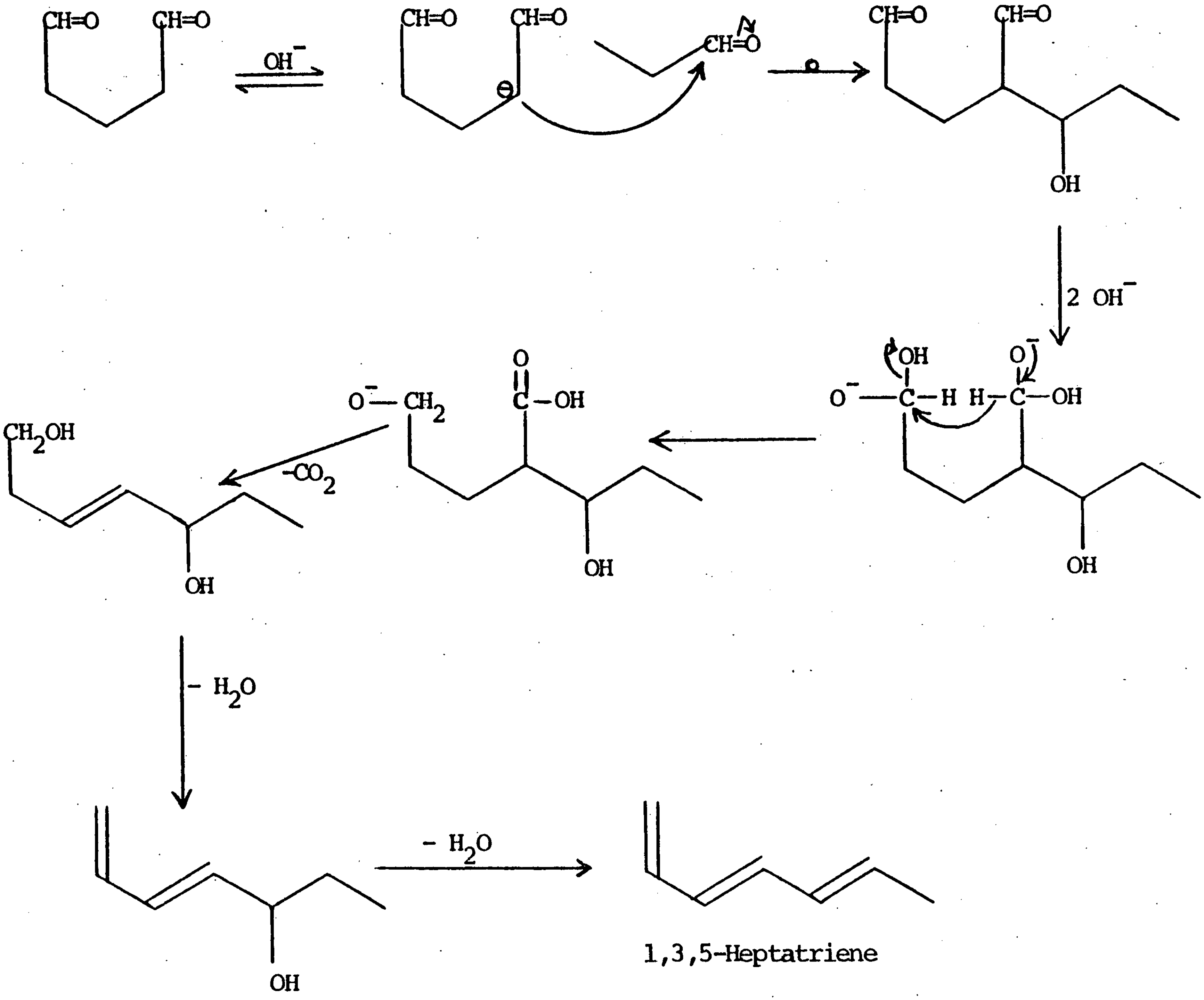


KEY:

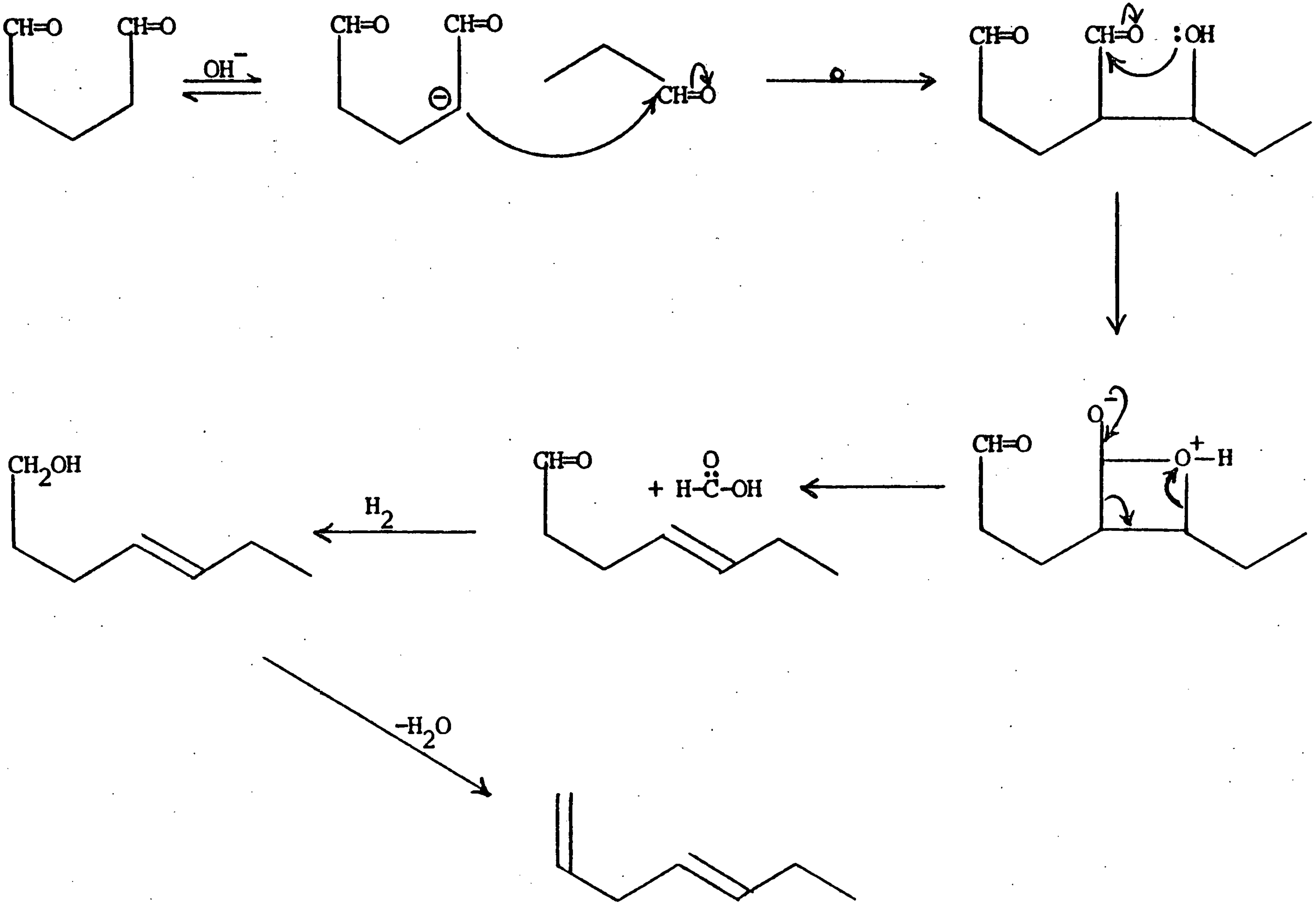
| R | R' | R" | Starting Material | Final Product |
|---|---|---|---|---|
| H | $CH_3$ | H | 2-Ketopentanal | 2-Methylfuran; 2-Hydroxy-2-methyltetrahydrofuran |
| $CH_3$ | $CH_3$ | H | 2,5-Hexadione | 2,5-Dimethylfuran; 2,5-Dimethyltetrahydrofuran |
| H | $CH_3$ | $CH_3$ | 2-Methyl-4-ketopentanal | 2,4-Dimethylfuran |
| $C_2H_5$ | $CH_3$ | H | 2,5-Heptadione | 5-Ethyl-2-methylfuran |
| $C_2H_5$ | $C_2H_5$ | H | 3,6-Octadione | 2,5-Diethylfuran |
| $CH_3$ | $CH_3$ | $C_2H_5$ | 3-Ethyl-2,5-hexadione | 3-Ethyl-2,5-dimethylfuran |



R = R' = H, product is 2-methyl-2,4-pentadiene;
R = R' = $CH_3$, product is 2,5-dimethyl-2,4-hexadiene.

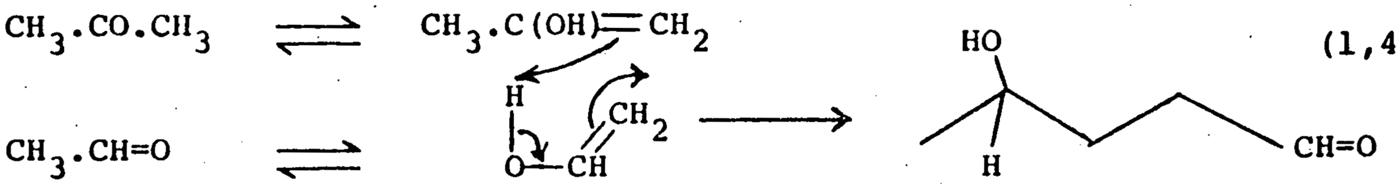


1,3,5-Heptatriene



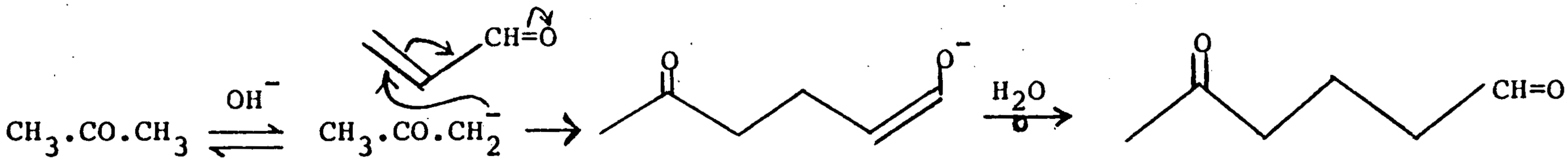
1,4-Heptadiene

(a) Addition between the enol forms of two carbonyl compounds:



(1,4-product)

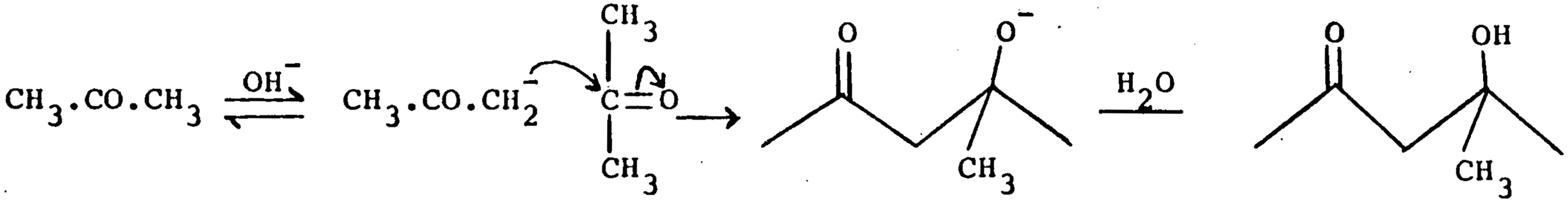
(b) Nucleophilic attack of carbonyl compound α-carbanion on the β-position of an α,β-unsaturated carbonyl compound:

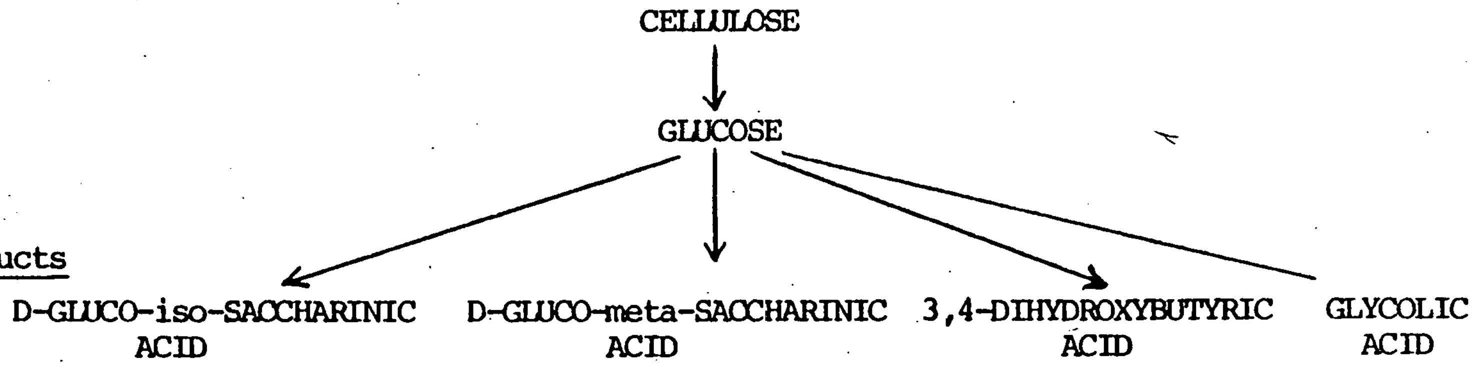


(1,5-product)

(c) Nucleophilic attack of carbonyl compound α-carbanion on the carbonyl function of a second carbonyl compound:

(1,3-product)





**Primary Products**

D-GLUCO-iso-SACCHARINIC ACID; D-GLUCO-meta-SACCHARINIC ACID; 3,4-DIHYDROXYBUTYRIC ACID; GLYCOLIC ACID

**Secondary Products**

FORMALDEHYDE; ACETALDEHYDE; PROPIONALDEHYDE; ACROLEIN; ACETONE; ETHYL METHYL KETONE

METHYL PROPYL KETONE; METHYL iso-PROPYL KETONE; METHYL VINYL KETONE; PYRUVALDEHYDE;

METHACRALDEHYDE

**Tertiary Products**

| | DIKETONES | HYDROXYALDEHYDES | ALKYLHYDROXYKETONES |
|---|---|---|---|
| (e.g.) | 3,6-Octadione | 5-Hydroxyheptanal | 4-Hydroxy-4-methyl-2-pentanone<br>(Diacetone alcohol) |

**Quaternary Products**

AROMATICS FURANS TETRAHYDROFURANS CYCLOALKANONES HYDROCARBONS

↓

**Final Products**

**OIL + TAR**