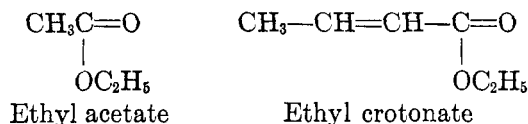# THE PRINCIPLE OF VINYLOGY

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It has long been recognized that, in a molecule containing a system of conjugated double linkages, the influence of a functional group may sometimes be propagated along the chain and make itself apparent at a remote point in the molecule. For example, the methyl group in ethyl crotonate behaves in some respects as it does when it is attached directly to the ester group as in ethyl acetate.

$$CH_3C{=}O \qquad\qquad CH_3{-}CH{=}CH{-}C{=}O$$
$$\mid \qquad\qquad\qquad\qquad\qquad \mid$$
$$OC_2H_5 \qquad\qquad\qquad\qquad OC_2H_5$$

Ethyl acetate Ethyl crotonate

Similarly, the methyl group in *p*-nitrotoluene resembles that in *o*-nitrotoluene, and both of these groups resemble the methyl group in nitromethane, which is attached directly to the nitro group. It is as though the influence of the nitro group were felt even when the methyl group is located in a distant part of the molecule.

Another characteristic property of conjugated systems is that in addition reactions the extremities of the system may be involved even though they be widely separated. The 1,4-addition of certain reagents to α, β-unsaturated ketones and esters is an example. In these cases, carbon atom 4 may be said to usurp the function of carbon atom 2:

$$\overset{4}{R}{-}\overset{3}{CH}{=}\overset{2}{CH}{-}\overset{1}{C}{=}O$$
$$\mid$$
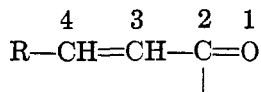
Phenomena of the foregoing general types have been effectively correlated by many authors, notably Angeli (2, 3), Lapworth (50), Koenigs (44), Thiele (70), and Claisen (17), who have dealt with the problem primarily on an empirical basis. Others, especially in recent years, have, by reference to theoretical considerations, succeeded in greatly clarifying the problems involved.[1]

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[1] See, for example, Robinson: J. Soc. Dyers Colourists *Jubilee Journal*, 65 (1934).

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Examples of such effects have increased rapidly in variety as well as in number, and it seemed worth while to attempt to formulate an expression which would make the significance of this wealth of material more readily apparent. The present review is presented as a contribution to this problem. An empirical principle has been worked out which is designed to embrace a wide variety of phenomena and which, at the same time, can be stated in relatively simple terms.

If E_1 and E_2 be made to represent non-metallic elements, the generalization takes the following form: *When, in a compound of the type* A—E_1=E_2 *or* A—E_1≡E_2, *a structural unit of the type* —(C=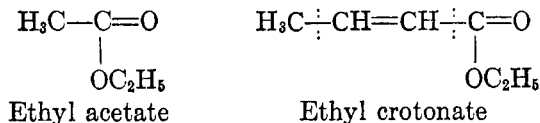C)$_n$= *is interposed between A and* E_1 *the function of* E_2 *remains qualitatively unchanged but that of* E_1 *may be usurped by the carbon atom attached to* A. The resulting compound will have the form A—(C=C)$_n$—E_1=E_2 or A—(C=C)$_n$—E_1≡E_2, and in any given series of this type the members will differ from each other by one or more vinylene residues.[2] It is proposed to term such a group of compounds a vinylogous series. The members of a vinylogous series will then be vinylogs of one another.[3]

In what follows, a number of different vinylogous series are pointed out and, in each case, illustrative reactions have been cited to show the application of the general principle under consideration. In view of the fact that each of these classes represents a broad field of study, it has not seemed desirable in any instance to attempt an exhaustive review of the literature.

ESTERS

In this series the operation of the principle of vinylogy may be illustrated by a comparison of the esters of saturated fatty acids with their vinylogs, the α, β-unsaturated esters. Ethyl acetate and ethyl crotonate may be
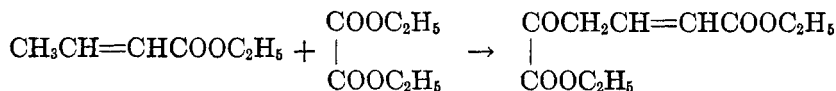
$$H_3C—C=O \qquad\qquad H_3C\!\!\mid\!\!-CH=CH-\!\!\mid\!\!C=O$$
$$\mid \qquad\qquad\qquad\qquad\qquad\qquad \mid$$
$$OC_2H_5 \qquad\qquad\qquad\qquad\qquad OC_2H_5$$

Ethyl acetate   Ethyl crotonate

used as typical examples. In each case A = CH_3 and E_1=E_2 is —C=O.
$$\mid$$
$$OC_2H_5$$

In the first n = 0; in the second n = 1. A function of the carbonyl carbon atom in ethyl acetate (acting in conjunction with the carbonyl oxygen

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[2] It is understood, of course, that the vinylene residues will be disposed in a linear arrangement.
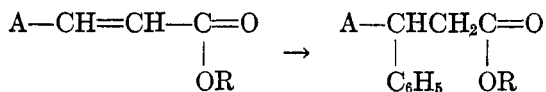
[3] The term "vinylene homologs" has been used to designate the simplest type of vinylogs, namely, those differing by —(CH=CH)$_n$—, i.e., one or more *unsubstituted* vinylene groups. See, for example, König: Ber. **55**, 3297 (1922).

atom) is to activate the hydrogen atoms of the methyl group attached to
it. In ethyl crotonate this function is usurped by the carbon attached to
the methyl group (A). Thus, ethyl crotonate condenses with ethyl oxa-
late (50) in a manner which is analogous to the behavior of ethyl acetate
under similar conditions (78):

$$CH_3CH{=}CHCOOC_2H_5 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \rightarrow \begin{array}{l} COCH_2CH{=}CHCOOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$
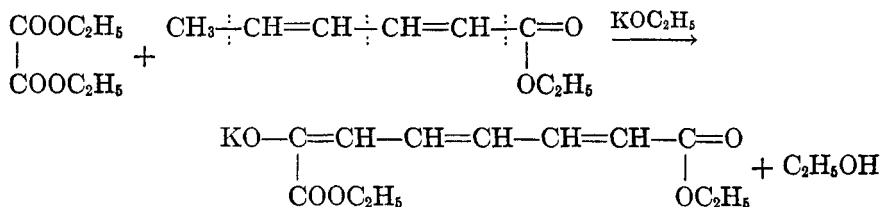
Ethyl β-ethoxycrotonate behaves similarly (81).

Again, when phenylmagnesium bromide is added to saturated esters the
phenyl group becomes attached to the carbon atom of the carbonyl group;
in α, β-unsaturated esters the phenyl group may attach itself instead to the
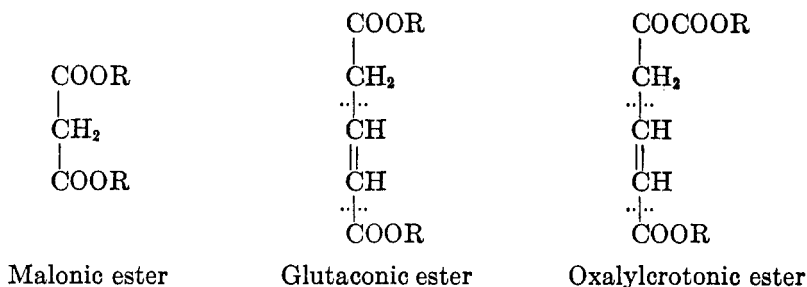carbon atom in position 4, i.e., to the carbon atom joined to A (45):

$$\begin{array}{l} A{-}CH{=}CH{-}C{=}O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OR \end{array} \rightarrow \begin{array}{l} A{-}CHCH_2C{=}O \\ \quad\;\; | \qquad\;\; | \\ \quad\;\; C_6H_5 \quad OR \end{array}$$

It has recently been shown that the next higher vinylog (n = 2), ethyl
sorbate, also has an active methyl group. Like the acetic and crotonic
esters, it condenses with ethyl oxalate (15):

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + CH_3{\div}CH{=}CH{\div}CH{=}CH{\div}C{=}O \quad \xrightarrow{KOC_2H_5} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad OC_2H_5$$

$$\begin{array}{l} KO{-}C{=}CH{-}CH{=}CH{-}CH{=}CH{-}C{=}O \\ \qquad | \qquad\qquad\qquad\qquad\qquad\qquad\;\; | \qquad + C_2H_5OH \\ \qquad COOC_2H_5 \qquad\qquad\qquad\qquad\quad OC_2H_5 \end{array}$$

Sorbic ester also undergoes 1,6-addition (25, 12). It will be seen that in
both of these types of reaction the function of the carbon atom of the car-
bonyl group has been usurped by that adjoining the group which corre-
sponds to A in the general formula.

Among esters of dibasic acids, glutaconic ester and oxalylcrotonic ester
are recognizable as vinylogs of malonic ester:

$$\begin{array}{ccc} & COOR & COCOOR \\ & | & | \\ COOR & CH_2 & CH_2 \\ | & ..|.. & ..|.. \\ CH_2 & CH & CH \\ | & || & || \\ COOR & CH & CH \\ & ..|.. & ..|.. \\ & COOR & COOR \\ \text{Malonic ester} & \text{Glutaconic ester} & \text{Oxalylcrotonic ester} \end{array}$$
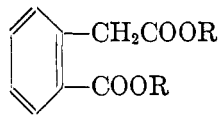
In reactions with alkylating agents (33, 11), diazo compounds (60), and other reagents the behavior of the methylene group in these esters shows a very close parallel to that of the malonic esters.

Similarly, the methylene group in the esters of homophthalic acid is known to be very much more reactive than that of the phenylacetic esters (21, 20):
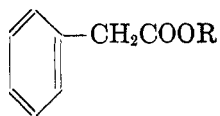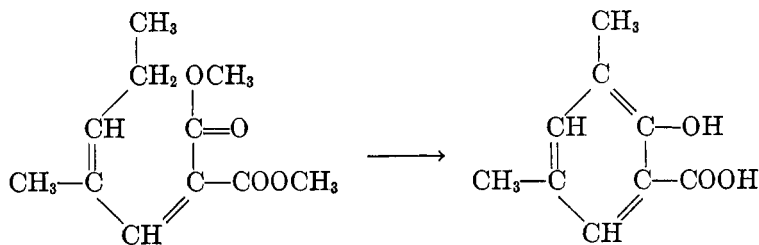

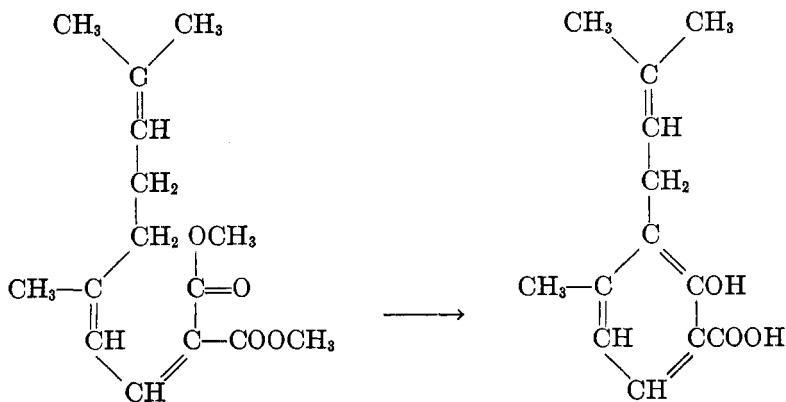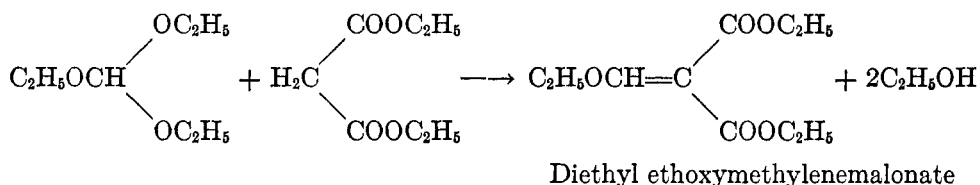Phenylacetic ester   Homophthalic ester

Meerwein's conversion of dimethyl α-methyl-β-ethylacrylidenemalonate and dimethyl citralidenemalonate into the corresponding derivatives of salicylic acid illustrates the behavior of the next higher vinylogs (55):

Dimethyl
α-methyl-β-ethylacrylidenemalonate
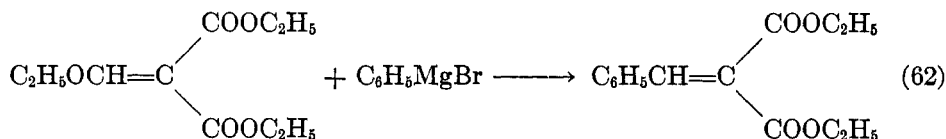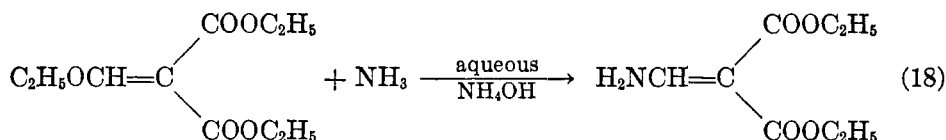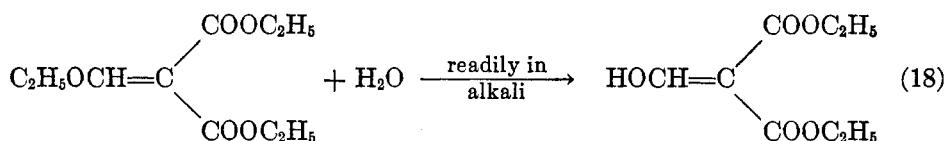

Dimethyl
citralidenemalonate

The latter case is of particular interest, inasmuch as the ester contains a methyl as well as a methylene group in position to condense with the carbomethoxyl group. It seems probable that the course of the ring-closure may depend on the configuration of the ester. Moreover, it may be that negative results in similar cases (19, 55) may be explained by assuming an unfavorable configuration.
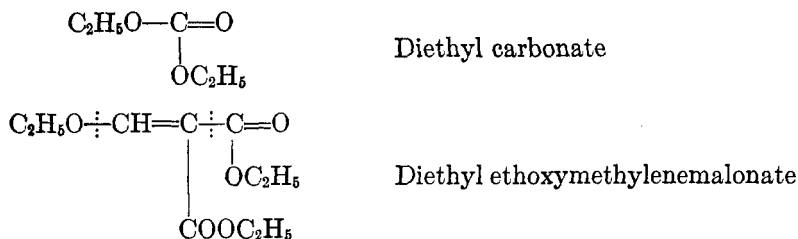
β-Alkoxyacrylic esters

The alpha-substituted β-alkoxyacrylic esters which form when ethyl acetoacetate, ethyl cyanoacetate, and similar substances are condensed with orthoformic ester behave in a manner which has long been regarded as anomalous. As an example may be cited diethyl ethoxymethylenemalonate which is formed according to the following equation:

$$C_2H_5OCH \begin{matrix} OC_2H_5 \\ \\ OC_2H_5 \end{matrix} + H_2C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} \longrightarrow C_2H_5OCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} + 2C_2H_5OH$$

Diethyl ethoxymethylenemalonate

Among the peculiar reactions of this substance are the following:

$$C_2H_5OCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} + H_2O \xrightarrow[\text{alkali}]{\text{readily in}} HOCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} \qquad (18)$$

$$C_2H_5OCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} + NH_3 \xrightarrow[\text{NH}_4\text{OH}]{\text{aqueous}} H_2NCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} \qquad (18)$$

$$C_2H_5OCH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} + C_6H_5MgBr \longrightarrow C_6H_5CH{=}C \begin{matrix} COOC_2H_5 \\ \\ COOC_2H_5 \end{matrix} \qquad (62)$$
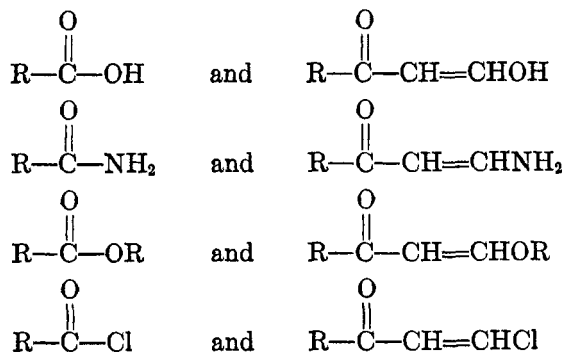
The great ease with which the ethoxyl group suffers direct replacement by the hydroxyl, amino, and phenyl groups in the above reactions ceases to appear anomalous when we reflect that we are dealing with a vinylog of diethyl carbonate:

$$C_2H_5O-C=O$$
$$\hspace{1.2cm}|$$
$$\hspace{1cm}OC_2H_5$$

Diethyl carbonate

$$C_2H_5O\dot{-}CH=C\dot{-}C=O$$
$$\hspace{2cm}|$$
$$\hspace{2cm}OC_2H_5$$
$$\hspace{0.3cm}|$$
$$\hspace{0.3cm}COOC_2H_5$$

Diethyl ethoxymethylenemalonate

This principle suggests that o- and p-alkoxybenzoic acids would undergo cleavage more readily than would the corresponding meta derivatives. The conversion of 3, 4, 5-trimethoxybenzoic acid into syringic acid (31, 32) is in accord with this point of view, for the trimethoxyl compound is vinylogous with carbonic ester only with reference to the methoxyl group in position 4:

Syringic acid
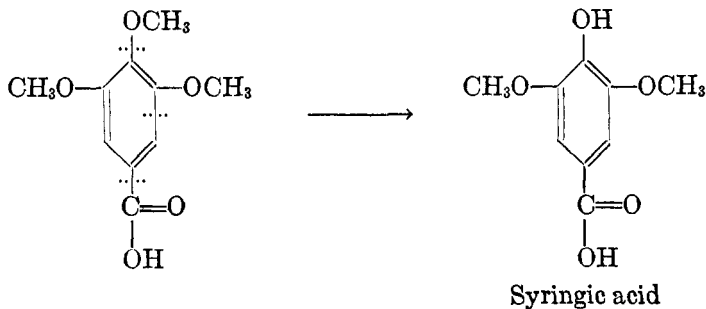
This general point of view has been elaborated by Claisen (17, 4), who pointed out certain similarities between the following pairs of structures:
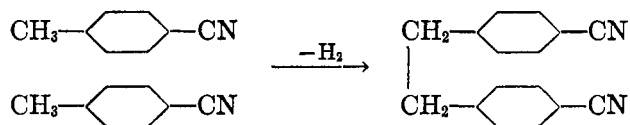
$$\underset{\text{R—C—OH}}{\overset{\displaystyle O \atop \displaystyle \|}{}} \quad \text{and} \quad \underset{\text{R—C—CH=CHOH}}{\overset{\displaystyle O \atop \displaystyle \|}{}}$$

$$\underset{\text{R—C—NH}_2}{\overset{\displaystyle O \atop \displaystyle \|}{}} \quad \text{and} \quad \underset{\text{R—C—CH=CHNH}_2}{\overset{\displaystyle O \atop \displaystyle \|}{}}$$

$$\underset{\text{R—C—OR}}{\overset{\displaystyle O \atop \displaystyle \|}{}} \quad \text{and} \quad \underset{\text{R—C—CH=CHOR}}{\overset{\displaystyle O \atop \displaystyle \|}{}}$$

$$\underset{\text{R—C—Cl}}{\overset{\displaystyle O \atop \displaystyle \|}{}} \quad \text{and} \quad \underset{\text{R—C—CH=CHCl}}{\overset{\displaystyle O \atop \displaystyle \|}{}}$$

NITRILES

Acetonitrile, crotonitrile, and sorbic nitrile form a vinylogous series in which the activity of the hydrogen atoms of the methyl group is qualitatively independent of n.
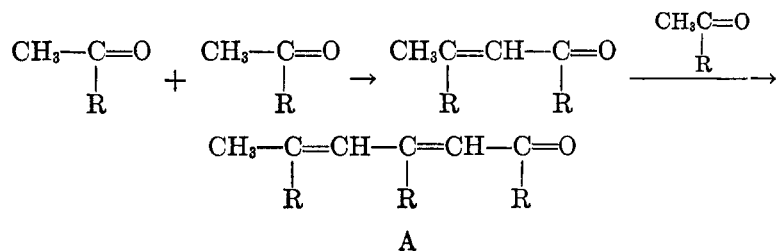
$$CH_3—CN \qquad \text{Acetonitrile (n = 0)}$$

$$CH_3\dot{-}CH{=}CH\dot{-}CN \qquad \text{Crotonitrile (n = 1)}$$

$$CH_3\dot{-}CH{=}CH\dot{-}CH{=}CH\dot{-}CN \qquad \text{Sorbic nitrile (n = 2)}$$

In this series $A = CH_3$, $E_1 = C$, and $E_2 = N$. It has long been known that acetonitrile condenses with oxalic ester in the presence of sodium ethoxide (28):

$$CH_3CN + \begin{array}{c} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \rightarrow \begin{array}{c} COCH_2CN \\ | \\ COOC_2H_5 \end{array} + C_2H_5OH$$

Borsche and Manteuffel (16) have recently shown that, by using potassium ethoxide, a similar result is obtained with crotonitrile and sorbic nitrile:

$$CH_3 - CH{=}CHCN + \begin{array}{c} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \rightarrow \begin{array}{c} KOC{=}CHCH{=}CHCN \\ | \\ COOC_2H_5 \end{array} + C_2H_5OH$$

$$CH_3{—}CH{=}CH{—}CH{=}CHCN + \begin{array}{c} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \rightarrow$$

$$\begin{array}{c} KOC{=}CH{—}CH{=}CH{—}CH{=}CHCN \\ | \\ COOC_2H_5 \end{array} + C_2H_5OH$$

The term vinylogous series has been defined in such a manner as to include many of the correlations which have been made by Angeli, whose celebrated rule (3) states that in ortho- and para-disubstituted benzene derivatives ($A{—}C_6H_4{—}B$) the substituents (A and B) react as though the benzene ring were not present (i.e., as $A{—}B$). This rule was extended to include compounds of more complex types, such as $A{—}C_6H_4{—}C_6H_4{—}B$, $A{—}C_6H_4CH{=}CHC_6H_4{—}B$ and $A{—}C_6H_4N{=}NC_6H_4{—}B$, as well as groups separated by an unsaturated chain.

In the vinylogous series under discussion would also be included o- and p-tolunitrile, but not the meta isomer.

$$\begin{array}{c} CH_3{—}C{=\!=}C{—}CN \\ \diagup \qquad \diagdown \\ CH \qquad\quad CH \\ \diagdown\!\diagdown \qquad \diagup\!\diagup \\ CH{—}CH \end{array} \qquad \text{o-Tolunitrile (n = 1)}$$

$$\begin{array}{c} CH_3 - C{=}CH{—}CH{=}C{—}CN \\ \diagdown \qquad\qquad \diagup \\ CH{=}CH \end{array} \qquad \text{p-Tolunitrile (n = 2)}$$

$$\begin{array}{c} CH_3{—}C{—}CH{=}C{—}CN \\ \| \qquad\quad | \\ CHCH{=}CH \end{array} \qquad \text{m-Tolunitrile}$$

The implication of the generalization under consideration, as well as that of Angeli, is that in the o- and p-tolunitriles the activity of the hydrogen atoms of the methyl groups will be greater than that of the corresponding atoms in toluene or in m-tolunitrile. Some evidence is at hand in support of this. Kattwinkel and Wolffenstein (41) found that when p-tolunitrile is oxidized with potassium or ammonium persulfate, 4,4'-dicyanodibenzyl results:
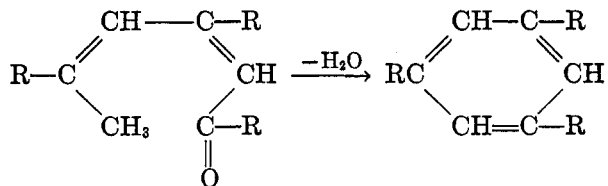
$$CH_3-\langle\ \rangle-CN \quad \xrightarrow{-H_2} \quad \begin{array}{l} CH_2-\langle\ \rangle-CN \\ | \\ CH_2-\langle\ \rangle-CN \end{array}$$

$$CH_3-\langle\ \rangle-CN$$

The meta isomer does not undergo this reaction.

KETONES

It seems probable that the formation of mesitylene and other 1,3,5-trialkyl- and triaryl-benzenes depends on the activation of a methyl group joined to a ketone group by a butadiene chain. By condensing together in a linear fashion three molecules of a methyl ketone we would get a vinylog (A) of the parent ketone:

$$\begin{array}{l} CH_3-C{=}O \\ | \\ R \end{array} + \begin{array}{l} CH_3-C{=}O \\ | \\ R \end{array} \rightarrow \begin{array}{l} CH_3C{=}CH-C{=}O \\ | \qquad\quad | \\ R \qquad\quad R \end{array} \xrightarrow[\;R\;]{CH_3C{=}O} \rightarrow$$

$$\begin{array}{l} CH_3-C{=}CH-C{=}CH-C{=}O \\ | \qquad\quad | \qquad\quad | \\ R \qquad\quad R \qquad\quad R \end{array}$$

$$A$$

The cyclization may then be formulated as an intramolecular condensation which depends on the activity of the methyl group of this vinylog:

$$R-C\begin{array}{c} CH{-\!\!\!-}C-R \\ \diagup \qquad\qquad \diagdown \\ \qquad\qquad CH \\ \diagdown \qquad\qquad \diagup \\ CH_3 \quad C-R \\ \| \\ O \end{array} \xrightarrow{-H_2O} RC\begin{array}{c} CH{-}C-R \\ \diagup \qquad\qquad \diagdown \\ \qquad\qquad CH \\ \diagdown \qquad\qquad \diagup \\ CH{=}C-R \end{array}$$

The transformation of α- and β-ionone into ionene is an example of a similar condensation. Bogert and Fourman (13) have recently shown the correctness of Barbier and Bouveault's (8) structure for ionene as opposed to the earlier structure proposed for this hydrocarbon by Tiemann and

Kruger (73, 74). The new structure permits a formulation of the condensation as that of a vinylog of acetone:
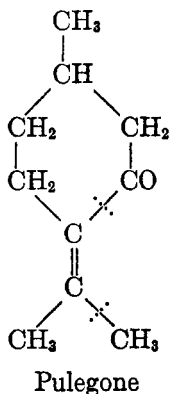
$$
\begin{array}{ccc}
\text{CH}_3 \quad \text{CH}_3 & \text{CH}_3 \quad \text{CH}_3 \\
\end{array}
$$

CH₃   CH₃
   \ /
    C   CH=CHCCH₃
   / \   ‖
 CH₂ CH   O   →
  | ‖
 CH₂   C
   \ / \
    CH   CH₃
   α-Ionone

CH₃   CH₃
   \ /
    C   CH=CH⁞C—CH₃
   / \   ‖
 CH₂   C   O   →
  | ‖
 CH₂   C
   \ / \
    CH₂   CH₃
   β-Ionone

CH₃   CH₃
   \ /
    C   CH
   / \   ‖   ‖
 CH₂   C   CH
  | ‖ |
 CH₂   C   C—CH₃
   \ / \ ‖
    CH₂   CH
   Ionene
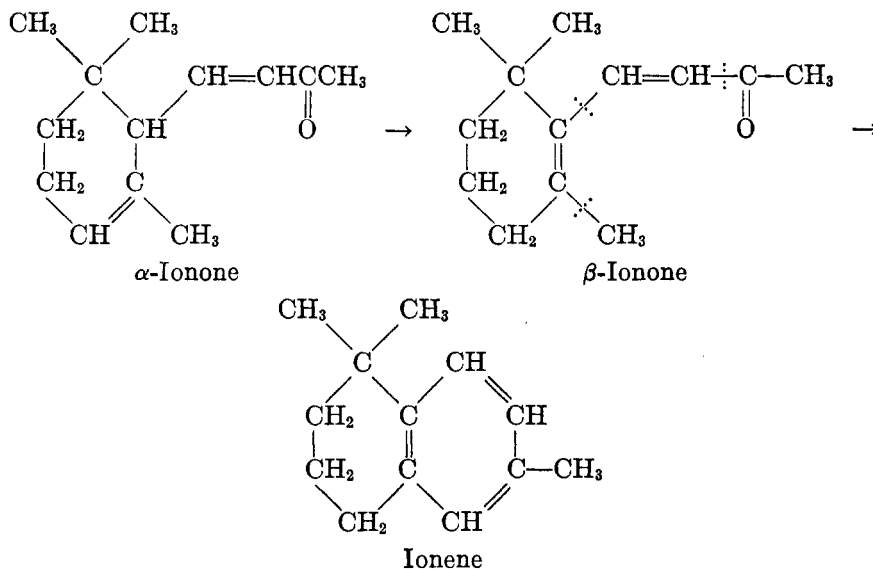
In the case of α-ionone the first step in the condensation would be the isomerization to the beta isomer.

Barbier and Bouveault's syntheses of pseudocumene and 2,4-diisopropyltoluene rest on condensations similar to that indicated for ionene (7):

        CH   CH
       ‖   ‖   ‖   ‖
CH₃—C   CH   CH₃—C   CH
    ‖   ⁞   →   ‖ |
   CH   C—CH₃   CH   C—CH₃
    \   ‖   \   ‖
     CH₂ O   C
      | |
     CH₃   CH₃
                          Pseudocumene

CH₃   CH   CH₃   CH
   \   ‖ ‖   \   / ‖
   CH—C   CH   CH—C   CH
   /   ‖   ⁞   →   /   ‖ |
CH₃   CH C—CH₃   CH₃   CH C—CH₃
       \ ‖   \ ‖
        CH₂ O   C
         | |
    CH₃—CH—CH₃   CH₃—CH—CH₃
                          2,4-Diisopropyltoluene
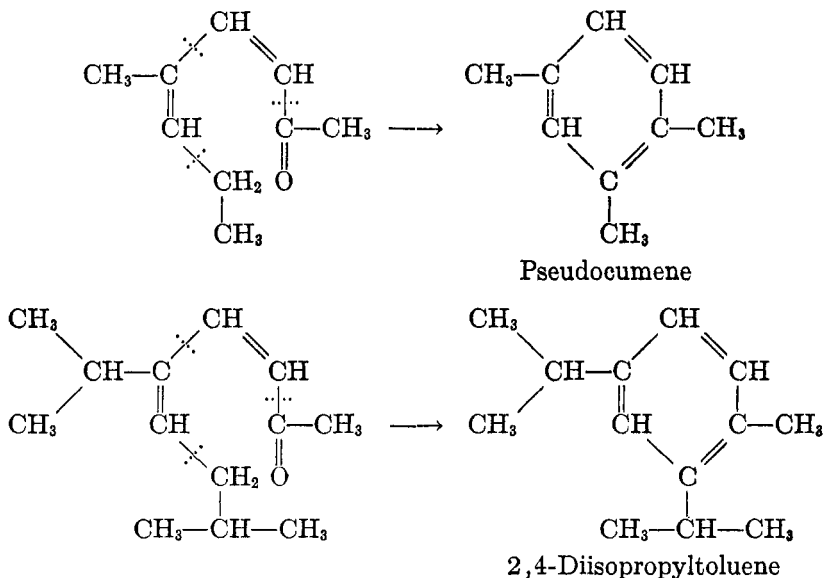
When we consider the configurational possibilities of an open chain molecule containing two ethylenic linkages, it is not surprising that ring-closures of this type frequently fail to take place. Examples are Dautwitz's failure to obtain p-xylene from acetone and tiglic aldehyde (19), and Kekulé's unsuccessful attempt to obtain benzene by cyclization of sorbaldehyde (42).

Poggi's discovery that pulegone gives the iodoform test (59) is interesting in view of the fact that this ketone is vinylogous with methyl ketones.

$$
\begin{array}{c}
CH_3 \\
| \\
CH \\
\diagup \quad \diagdown \\
CH_2 \qquad CH_2 \\
| \qquad\qquad | \\
CH_2 \qquad CO \\
\diagdown \quad \diagup \\
C \\
\| \\
C \\
\diagup \quad \diagdown \\
CH_3 \qquad CH_3
\end{array}
$$

Pulegone

It is possible that a trichloromethyl derivative is formed as an intermediate. This suggests that compounds such as trichloroethylideneacetophenone (43), which are vinylogous with trichloromethyl ketones, might undergo cleavage with alkali to give chloroform:

$$RCO\!-\!CCl_3$$

$$C_6H_5CO\dot{\div}CH\!=\!CH\dot{\div}CCl_3$$
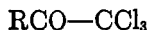
QUINONES

Methylquinones are vinylogous with methyl ketones and might, therefore, be expected to have active methyl groups:

$$
\begin{array}{c}
CH_3\dot{\div}C\!=\!\!=\!CH\dot{\div}C\!=\!O \\
| \qquad\qquad\quad | \\
CO\!-\!CH\!=\!CH
\end{array}
$$
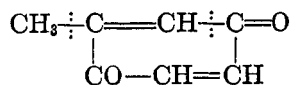
The peculiar condensation of malonic ester with duroquinone observed by Smith and Dobrovolny (69, 68) indicates that one of the methyl groups of the quinone is active. The following is a possible mechanism based

upon the assumption that the hydrogen atoms of the methyl groups are sufficiently mobile to undergo a 1,4-prototropic shift:

$$
\begin{array}{ccc}
\underset{\substack{\text{O}\\\|\\\text{C}\\ \text{CH}_3\text{C}\quad\text{CCH}_3 \\ \text{CH}_3\text{C}\quad\text{CCH}_3 \\ \text{C}\\\|\\\text{O}}}{}
&\rightarrow&
\underset{\substack{\text{O}\\\|\\\text{C}\\ \text{CH}_3\text{C}\quad\text{C}=\text{CH}_2 \\ \text{CH}_3\text{C}\quad\text{CCH}_3 \\ \text{C}\\ \text{OH}}}{}
&\rightarrow&
\underset{\substack{\text{OH}\\ \text{C}\\ \text{CH}_3\text{C}\quad\text{C}-\text{CH}_2\text{CH}\begin{smallmatrix}\text{COOC}_2\text{H}_5\\ \text{COOC}_2\text{H}_5\end{smallmatrix} \\ \text{CH}_3\text{C}\quad\text{CCH}_3 \\ \text{C}\\ \text{OH}}}{}
\end{array}
$$

<div align="center">I</div>
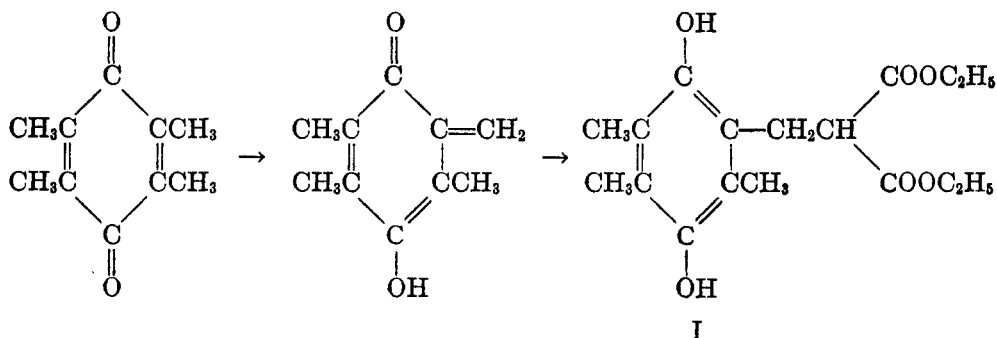
By a process involving oxidation, a succession of prototropic changes, and a ring-closure, the final product (II) may be produced from I.

$$
\begin{array}{c}
\text{H}\quad\quad\text{O}-\text{CO}\\
\text{C}\quad\quad\quad\text{CCOOC}_2\text{H}_5\\
\text{CH}_3\text{C}\quad\text{C}-\text{CH}\\
\text{CH}_3\text{C}\quad\text{C}-\text{CH}_3\\
\text{C}\\
\|\\
\text{O}
\end{array}
$$

<div align="center">II</div>
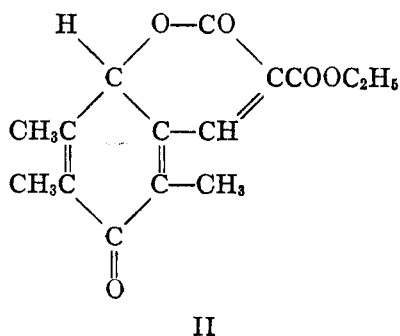
It seems likely also that a methyl group is involved in the dimerization of certain methylquinones. Thus Rügheimer and Hankel (63) write diduroquinone as follows:

$$
\begin{array}{c}
\text{O}\quad\quad\quad\text{CH}_3\ \text{CH}_3\\
\text{C}\quad\quad\quad\text{C}=\text{C}\\
\text{CH}_3\text{C}\quad\text{CCH}_2-\text{C}\quad\quad\text{C}=\text{O}\\
\text{CH}_3\text{C}\quad\text{CCH}_3\quad\text{C}=\text{C}\\
\text{C}\quad\quad\quad\text{OH}\ \text{CH}_3\ \text{CH}_3\\
\|\\
\text{O}
\end{array}
$$

<div align="center">Diduroquinone</div>

NITRO COMPOUNDS

Among nitro compounds may be cited nitromethane, *o*-nitrotoluene, and *p*-nitrotoluene (but not *m*-nitrotoluene), which form a vinylogous series in which $A = CH_3$, $E_1 = N$, and $E_2 = O$.

$$CH_3—N{=}O$$
$$O$$

Nitromethane (n = 0)

$$CH_3{\doteq}C{=}C{\doteq}N{=}O$$
$$CH \qquad CH$$
$$CH—CH$$

o-Nitrotoluene (n = 1)

$$CH_3{\doteq}C{=}CH{\doteq}CH{=}C{\doteq}N{=}O$$
$$CH{=}CH$$

p-Nitrotoluene (n = 2)

$$CH_3—C—CH{=}C—N{=}O$$
$$CH—CH{=}CH$$

m-Nitrotoluene

As is well known, the methyl group in nitromethane enters into a wide variety of reactions involving the removal of one or more of its hydrogen atoms (34, 71). As has been repeatedly pointed out by Angeli and others, the *o*- and *p*-nitrotoluenes, in contrast to the meta isomer, undergo similar reactions. With diethyl oxalate, for example, they yield keto esters (61):

$$O_2NC_6H_4CH_3 + (COOEt)_2 \rightarrow O_2NC_6H_4CH_2COCOOEt + EtOH$$

2,4-Dinitrotoluene (72), 4,6-dinitro-*m*-xylene (14), trinitrotoluene (58), and other similarly constituted compounds behave analogously when treated with benzaldehyde:

$$NO_2{-}\langle\ \rangle{-}CH_3 + C_6H_5CHO \rightarrow NO_2{-}\langle\ \rangle{-}CH{=}CHC_6H_5 + H_2O$$
$$NO_2 \qquad\qquad\qquad\qquad\qquad NO_2$$

$$O_2N\ CH_3 \qquad\qquad\qquad\qquad O_2N\ CH{=}CHC_6H_5$$
$$\langle\ \rangle \quad + 2C_6H_5CHO \rightarrow \quad \langle\ \rangle \qquad + 2H_2O$$
$$O_2N\ CH_3 \qquad\qquad\qquad\qquad O_2N\ CH{=}CHC_6H_5$$

$$NO_2 \qquad\qquad\qquad\qquad\qquad NO_2$$
$$O_2N{-}\langle\ \rangle{-}CH_3 + C_6H_5CHO \rightarrow O_2N{-}\langle\ \rangle{-}CH{=}CHC_6H_5 + H_2O$$
$$NO_2 \qquad\qquad\qquad\qquad\qquad NO_2$$

Similar results are obtained by the use of nitroso compounds in place of benzaldehyde (65).

An extremely interesting comparison of these vinylogs was made by Angeli (5), who pointed out that in each case it was possible to effect coupling by oxidation:

$$\underset{NO_2}{\overset{R}{\underset{|}{\overset{|}{CH_2}}}} + \underset{NO_2}{\overset{R}{\underset{|}{\overset{|}{CH_2}}}} \xrightarrow{\text{oxidation}} \underset{NO_2}{\overset{R}{\underset{|}{\overset{|}{CH}}}}-\underset{NO_2}{\overset{R}{\underset{|}{\overset{|}{CH}}}}$$

$$\underset{NO_2}{\overset{CH_3}{\underset{|}{\overset{|}{C_6H_4}}}} + \underset{NO_2}{\overset{CH_3}{\underset{|}{\overset{|}{C_6H_4}}}} \xrightarrow{\text{oxidation}} \underset{NO_2}{\overset{CH_2-CH_2}{\underset{|}{\overset{|}{C_6H_4 \quad C_6H_4}}}}$$

(ortho or para)
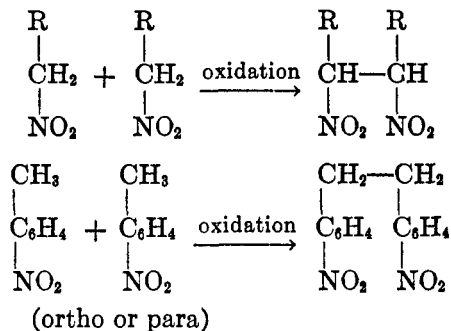
Angeli (1) showed also that p-nitrotoluene was converted by the action of nitrous acid to the oxime analogous to the nitrolic acid derived from nitromethane in the same manner:

$$\underset{NO_2}{\overset{CH_3}{\underset{|}{\overset{|}{}}}} + HONO \rightarrow \underset{NO_2}{\overset{CH=NOH}{\underset{|}{\overset{|}{}}}}$$

$$\underset{NO_2}{\overset{CH_3}{\underset{|}{\overset{|}{C_6H_4}}}} + HONO \rightarrow \underset{NO_2}{\overset{CH=NOH}{\underset{|}{\overset{|}{C_6H_4}}}}$$
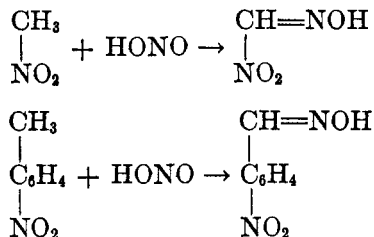
Angeli has also noted the interesting parallel between nitrogen peroxide and its vinylogs. The hydrolysis of nitrogen peroxide shows a formal similarity to that of o- and p-dinitrobenzene:

$$\underset{NO_2}{\overset{NO_2}{\underset{|}{\overset{|}{}}}} + \underset{H}{\overset{HO}{\underset{|}{\overset{|}{}}}} \rightarrow \overset{HONO_2}{\underset{HNO_2}{}}$$
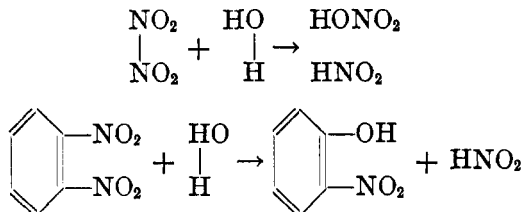
The replacement of a nitro group in o-dinitrobenzene by a hydroxyl group (51), an amino group (52), or a methoxyl group (54) takes place when the dinitro compound is treated, respectively, with aqueous alkali, ammonia, or sodium methoxide. Similar reactions take place with p-dinitrobenzene (54). m-Dinitrobenzene, on the other hand, resists the action of such

reagents; heating with solid potassium hydroxide fails to displace the nitro groups.   Wohl (82) showed that in this case the product was 2,4-dinitrophenol:

OH
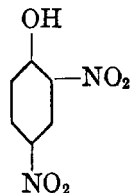
2,4-Dinitrophenol

This behavior of o- and p-dinitrobenzene is general (53).   Thus Kuhn, Reinemund, and Weygand (47) carried out the following replacement:
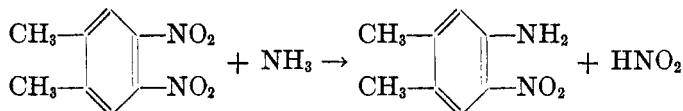
SIDE-CHAIN ACTIVATION IN THE PYRIDINE SERIES AND IN RELATED COMPOUNDS

The imino group ($-C=N-$), which forms a part of many heterobenzenoid rings, may fulfill the function of $E_1 = E_2$.   This is demonstrated by the fact that the methyl groups in quinaldine (77, 39), 2-methylquinoxaline (10), 1-methylisoquinoline (57), 2-methyl-4-phenylthiazole (57), and similar substances containing the structural unit $CH_3-C=N-$, are much more reactive than in such compounds as 3-methylquinoline and 2-phenyl-4-methylthiazole in which this structural unit is not present:
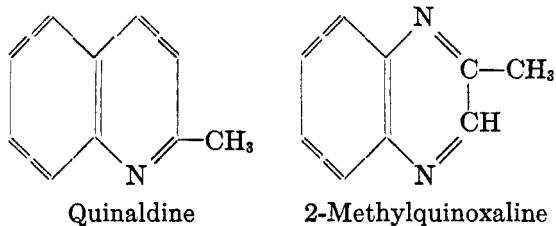
Quinaldine   2-Methylquinoxaline
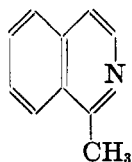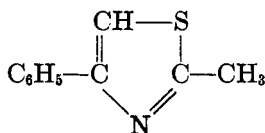
1-Methylisoquinoline   2-Methyl-4-phenylthiazole
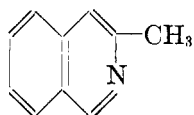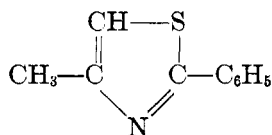
$$\text{3-Methylisoquinoline} \qquad \text{2-Phenyl-4-methylthiazole}$$

Perhaps the most characteristic reaction of active methyl groups in such compounds is the formation of benzal derivatives by interaction with aromatic aldehydes in the presence of a suitable catalyst such as zinc chloride. It has been found that in 2,3-dimethylquinoxaline (10) and α, α'-dimethylpyridine (67) both methyl groups are active; in each case a dibenzal derivative may be prepared:

$$+ \; 2C_6H_5CHO \rightarrow$$
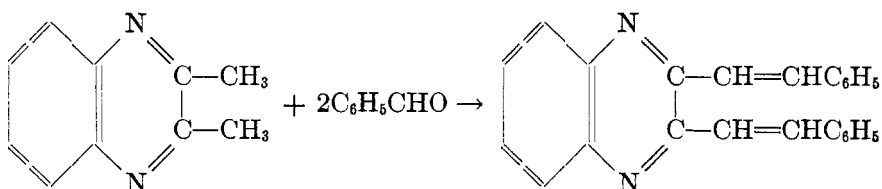
2,3-Dimethylquinoxaline

In the case of α,α'-dimethylpyridine the condensation may be assumed to proceed in two steps and to involve a shift of the double bonds in the benzenoid nucleus:
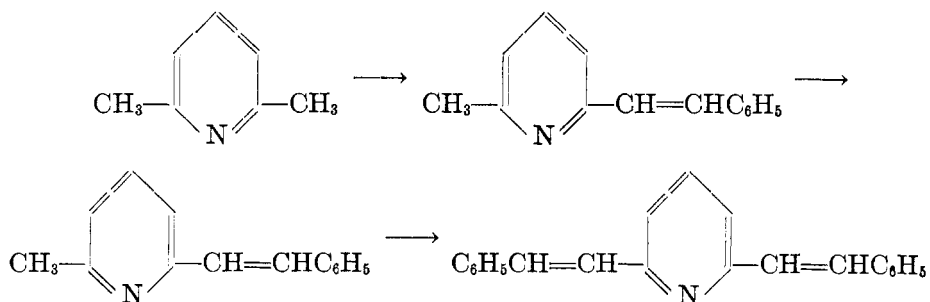
It is interesting to note, however, that according to the principle of vinylogy both methyl groups may be active without any shift of double bonds.

In all of these compounds $A = CH_3$, $E_1 = C$, $E_2 = N$, and $n = 0$. Examples of the next higher vinylog ($n = 1$) are γ-picoline and lepidine. In accordance with the implications of the fact that these compounds are vinylogous with α-picoline and quinaldine, the methyl groups are found to

show the same type of reactivity. γ-Picoline (29) yields a benzal derivative when treated with benzaldehyde. Lepidine behaves similarly (23).

γ-Picoline
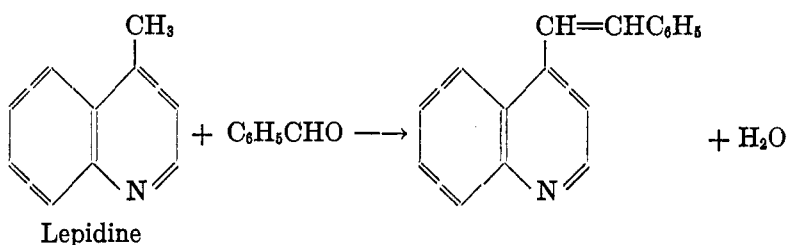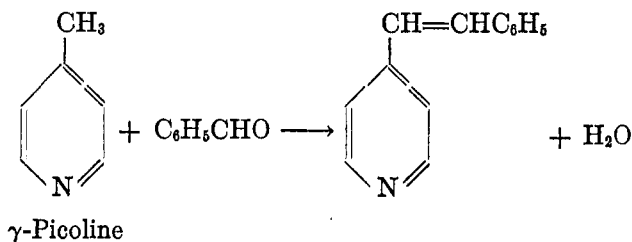
Lepidine

With p-chlorobenzaldehyde lepidine gives a 70 per cent yield of p-chloro-benzallepidine (30). When treated with benzaldehyde 2-phenyllepidine gives a 54 per cent yield of the corresponding benzal derivative (40).

The fact that a methyl group will be reactive if located in the α- or γ-positions of the pyridine ring and inactive if situated in the corresponding β-position was early recognized by Koenigs (44) and is frequently spoken of as Koenigs rule. It is evident that, so far as concerns compounds of this type, this rule is equivalent to the principle under discussion.

An interesting observation, which illustrates this rule, has recently been made by Henze (35). Henze found that in the oxidation of 2-ethyl-3-methylquinoline with selenium dioxide the ethyl group is attacked preferentially:
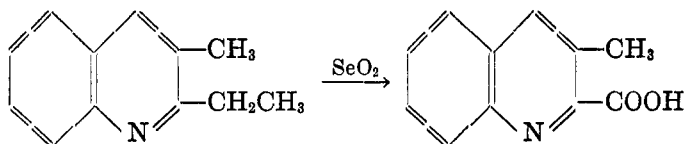
Similarly, it was found by Wislicenus and Kleisinger (80) that quinaldine and lepidine react with oxalic ester to give the corresponding α-keto esters. β-Methylquinoline, on the other hand, is unreactive toward oxalic ester (79). Another example is furnished by α, m-dimethylbenzimidazole in which only the α-methyl group condenses with benzaldehyde (6):
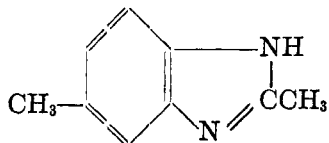
α, m-Dimethylbenzimidazole

CYCLOPENTADIENES

Cyclopentadiene, indene, and fluorene may be regarded as the initial (n = 0) members of a vinylogous series in which the corresponding dimethylfulvenes exemplify the next higher member (n = 1):
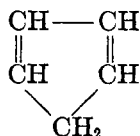
Cyclopentadiene
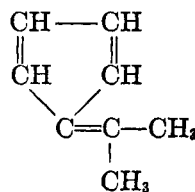
Dimethylfulvene
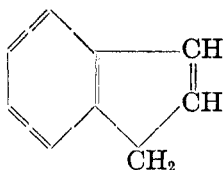
Indene
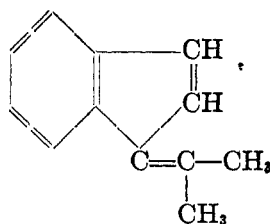
Dimethylbenzofulvene
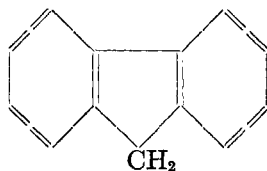
Fluorene
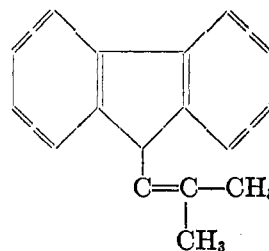
Biphenylenedimethylethylene

Schlenk and Bergmann (66) have shown that the peculiar activity of the hydrogen atoms of the methylene group characteristic of the first members of this series is present also in the higher vinylogs. These act upon sodium triphenylmethyl to convert it to triphenylmethane, thus behaving as compounds possessing active hydrogen atoms.

More recently Ziegler and Crössmann (83) have been able to confirm this viewpoint by effecting a condensation between biphenylenemethylethylene and anisaldehyde:

Biphenylenemethyl-
    ethylene
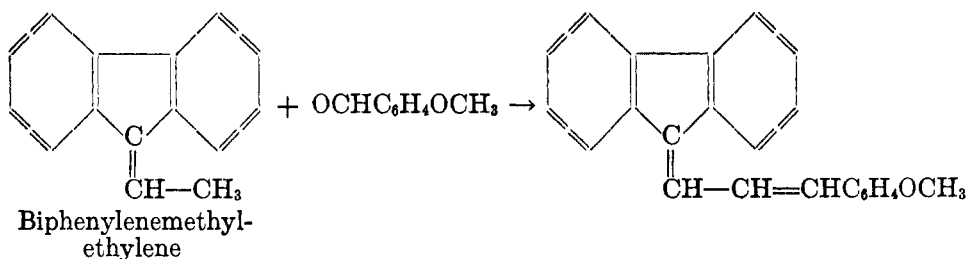
The analogous reaction was also effected in the indene system:
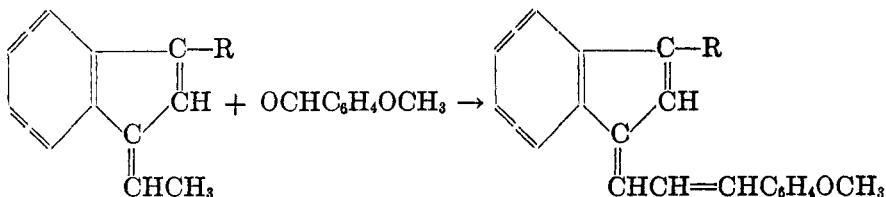
THE INTRODUCTION OF GROUPS INTO THE META POSITION IN MONOSUBSTITUTED BENZENE DERIVATIVES

In view of the fact that such groups as $-NO_2$, $-COR$, and $-C\equiv N$ when present as substituents on a benzene ring direct entering substituents preferentially to the meta position, it is interesting to note that such benzene derivatives may be regarded as vinylogs, respectively, of nitromethane, methyl ketones, and acetonitrile:
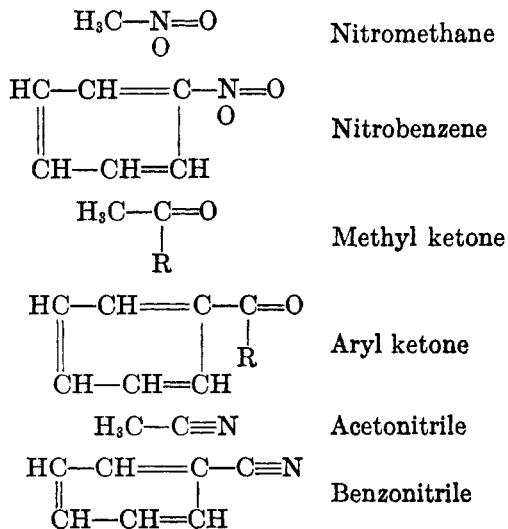
From this point of view one might expect the hydrogen atoms in the meta positions to be more active than those in ortho and para positions. In fact, Lapworth was led to his discovery of the activity of the gamma hydrogen atoms of crotonic ester through a consideration of the structural similarity of this ester to benzoic ester (50).

ACTIVATION OF HALOGENS IN VINYLOGOUS SYSTEMS

In vinyl halogen compounds such as chlorobenzene and chloroethylene the halogen atom is relatively unreactive, and this sluggishness in entering into reaction has come to be regarded as normal for compounds having the

structural unit $\begin{matrix} C{=}C{-}X \\ | \\ R \end{matrix}$. However, there are notable exceptions and

these have, of course, been looked upon as anomalous. Perhaps the simplest example is ethyl β-chlorocrotonate. Ruhemann and Wragg have shown that with sodium phenoxide this ester suffers replacement of its halogen atom by the phenoxy group (64):

$$\underset{\underset{Cl}{|}}{CH_3{-}C{=}CHCOOC_2H_5} + C_6H_5ONa \rightarrow \underset{\underset{OC_6H_5}{|}}{CH_3C{=}CHCOOC_2H_5}$$
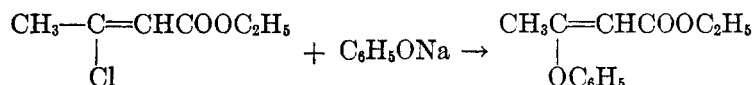
Similarly, Fichter and Schwab (27) were able to condense the chloroester with malonic ester:

$$\underset{\underset{CHCOOC_2H_5}{\|}}{CH_3CCl} + CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} \underset{\underset{CHCOOC_2H_5}{\|}}{CH_3{-}C{-}CH(COOC_2H_5)_2}$$
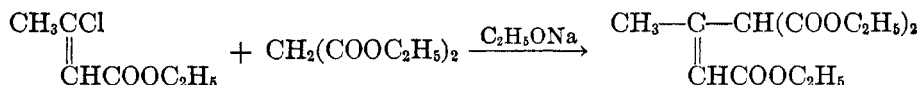
The unexpected reactivity of the chlorine atom is, however, readily explained on the basis of the vinylogous relationship between ethyl β-chlorocrotonate and ethyl chlorocarbonate:

$$\underset{\underset{OC_2H_5}{|}}{Cl{-}C{=}O} \qquad \text{Ethyl chlorocarbonate}$$

$$\underset{\underset{CH_3}{|}\qquad\underset{OC_2H_5}{|}}{Cl{\div}C{=}CH{\div}C{=}O} \qquad \text{Ethyl } \beta\text{-chlorocrotonate}$$
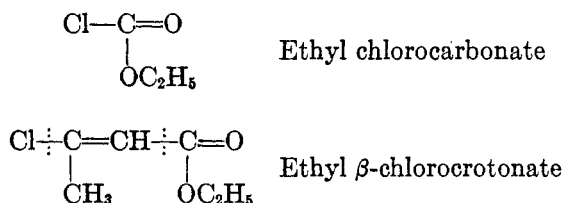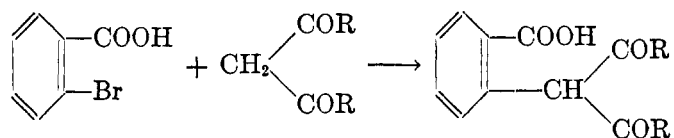
The foregoing example is only one of a wide variety of halogen derivatives in which an active halogen atom is attached to the vinyl grouping. This group of substances can be conveniently related to the numerous active methyl derivatives already considered by reference to the rule that when an active methyl group is replaced by a halogen atom the halogen atom will be active.
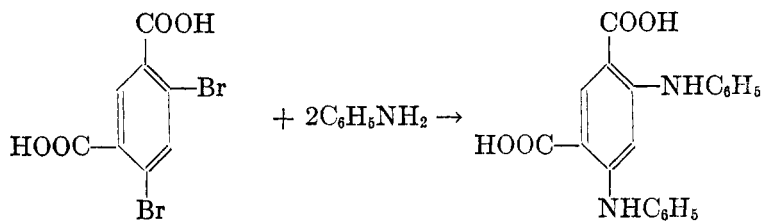
Another example of the same sort is the replacement of the halogen atom in *o*-bromo- and *o*-chloro-benzoic acids. Thus Ullmann and Zlokasoff showed that when sodium *o*-chlorobenzoate is treated with sodium phenoxides in the presence of copper it gives the corresponding aryl ethers of salicylic acid (76):
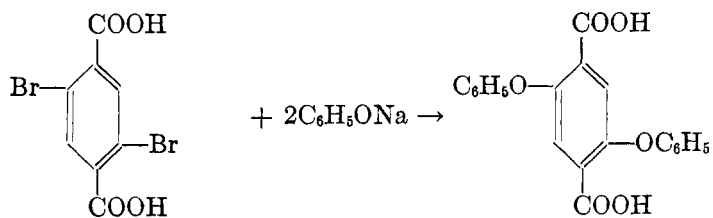
$$\text{(ring)}\begin{matrix}\text{—COONa}\\\text{—Cl}\end{matrix} + \text{NaOAr} \xrightarrow{\text{Cu}} \text{(ring)}\begin{matrix}\text{—COOH}\\\text{—OAr}\end{matrix}$$
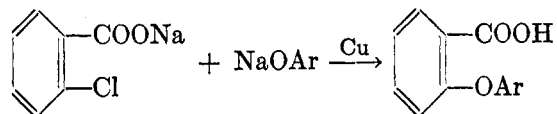
Similarly, *o*-bromobenzoic acid reacts with active methylene compounds in the following fashion (36):

$$\text{(ring)}\begin{matrix}\text{—COOH}\\\text{—Br}\end{matrix} + \text{CH}_2\begin{matrix}\text{COR}\\\text{COR}\end{matrix} \longrightarrow \text{(ring)}\begin{matrix}\text{—COOH}\\\text{—CH}\end{matrix}\begin{matrix}\text{COR}\\\text{COR}\end{matrix}$$

Eckert and Seidel (24) studied the replaceability of the bromine atoms in 4,6-dibromoisophthalic acid and 2,5-dibromoterephthalic acid. In both instances the halogen atoms are readily replaceable by anilino and phenoxy residues:

$\text{(structure)} + 2\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{(structure)}$

, -Dibromoisophthalic
acid

$\text{(structure)} + 2\text{C}_6\text{H}_5\text{ONa} \rightarrow \text{(structure)}$

2,5-Dibromoterephthalic
acid

The replacement of the halogen atoms in the anils is a similar reaction (38):
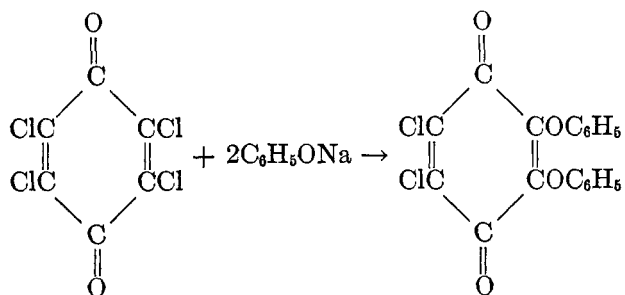
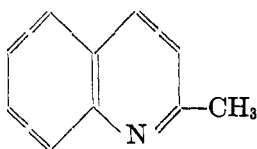The following list of pairs will make clear the application of the rule:

$$CH_3C{=}O \quad\quad CH_3C{=}O$$
$$|\qquad\qquad\quad |$$
$$CH_3 \qquad\qquad\quad Cl$$
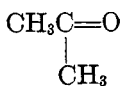
Acetone   Acetyl chloride
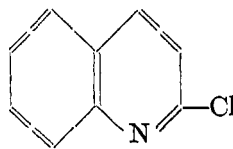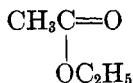
$$CH_3CN \qquad\qquad BrCN$$
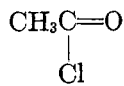
Acetonitrile   Cyanogen bromide
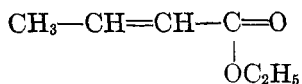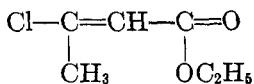

Quinaldine   2-Chloroquinoline

$$CH_3C{=}O \qquad\qquad Cl{-}C{=}O$$
$$|\qquad\qquad\qquad\quad |$$
$$OC_2H_5 \qquad\qquad\quad OC_2H_5$$
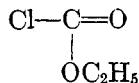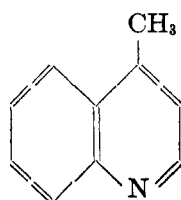
Ethyl acetate   Ethyl chlorocarbonate

The rule holds equally well for compounds vinylogous with the above types.

$$CH_3{-}CH{=}CH{-}C{=}O \qquad\quad Cl{-}C{=}CH{-}C{=}O$$
$$|\qquad\qquad\qquad\qquad\quad |\qquad\quad |$$
$$OC_2H_5 \qquad\qquad\qquad\quad CH_3 \quad\; OC_2H_5$$
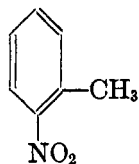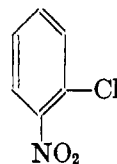
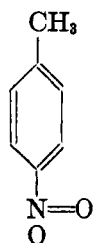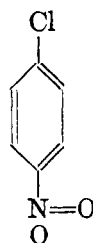Ethyl crotonate   Ethyl β-chlorocrotonate
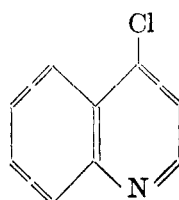
Lepidine   γ-Chloroquinoline

o-Nitrotoluene   o-Chloronitrobenzene

An example of the next higher vinylog is p-nitrotoluene; in accordance with prediction, the chlorine atom in p-chloronitrobenzene is active.

p-Nitrotoluene   p-Chloronitrobenzene

ADDITION REACTIONS OF VINYLOGOUS COMPOUNDS

That the 1,2-addition which is characteristic of compounds of the type $A—E_1=E_2$ is frequently supplanted by 1,4-addition in the next higher vinylog, $A—C=C—E_1=E_2$, is another example of a way in which the carbon atom joined to A may usurp the function of E_1. Examples of 1,6, 1,8, 1,10 and similar types of addition reactions illustrate the behavior of the higher vinylogs.

The diphenylpolyenes prepared by Kuhn and Winterstein (49) are of especial interest. They constitute a vinylogous series in which $A = C_6H_5$, $E_1 = C$, and $E_2 = C$:

$$A—(C=C)_n—E_1=E_2$$

$$C_6H_5—(CH=CH)_n—CH=CHC_6H_5$$
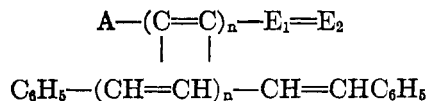
It is to be noted that when the vinylogs in which n is greater than 1 are condensed with maleic anhydride the reaction is always of the 1,4 type, even when the formation of a larger ring is possible (26, 22, 48):
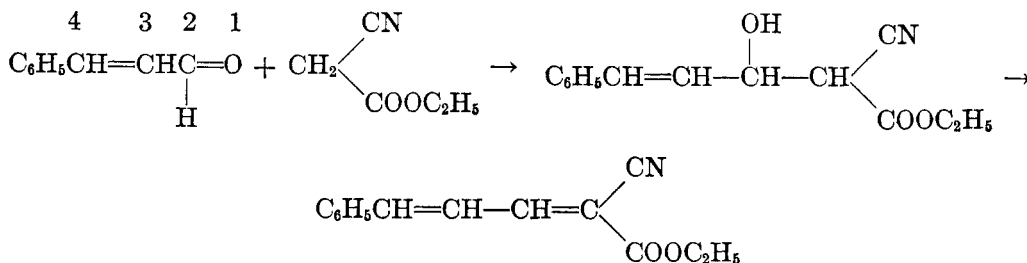
$$C_6H_5CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}C_6H_5 + \begin{array}{c} CH{-}CO \\ \| \qquad\quad\ \rangle O \\ CH{-}CO \end{array} \rightarrow$$

$$C_6H_5CH{=}CH{-}CH{-}CH{=}CH{-}CHC_6H_5$$
$$\diagdown \qquad\qquad \diagup$$
$$CH{-}CH$$
$$| \qquad |$$
$$CO \quad CO$$
$$\diagdown \ \diagup$$
$$O$$
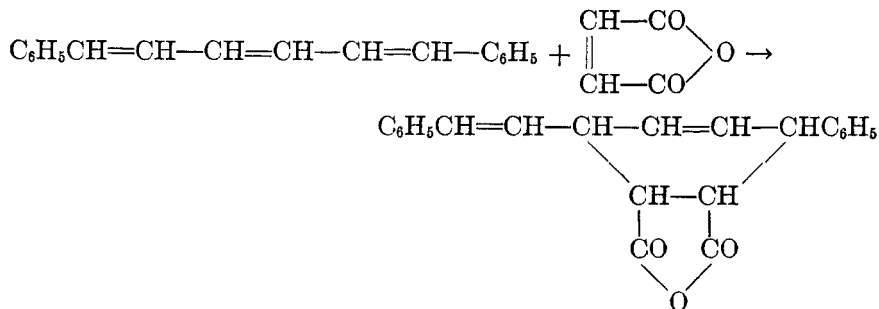
In order to interpret this result according to the principle of vinylogy we must set A equal to $C_6H_5CH{=}CH{-}$, E_1 and E_2 both being carbon atoms:

$$C_6H_5CH{=}CH{-}CH{=}CH{-}CH{=}CHC_6H_5$$
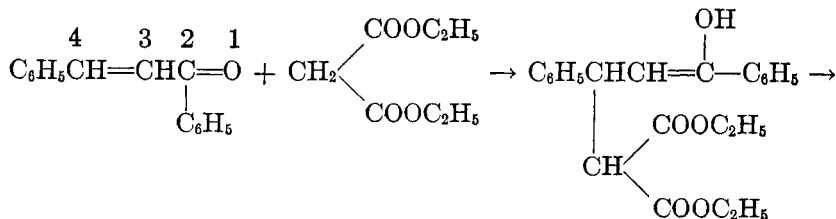$$A{-}C{=}C{-}E_1{=}E_2$$
$$\quad\ | \quad |$$
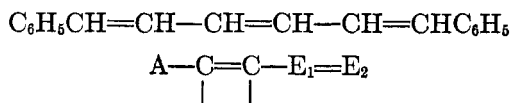
THE ALDOL AND MICHAEL CONDENSATIONS

The condensation reactions of α, β-unsaturated carbonyl compounds may be either of the 1,2 or aldol type, or of the 1,4 or Michael type. Cinnamaldehyde and ethyl cyanoacetate, for example, react in the 1,2 manner (9):

$$\overset{4}{C_6H_5}\overset{3}{CH}{=}\overset{2}{CH}\underset{|}{\overset{1}{C}}{=}O + CH_2\overset{CN}{\diagdown COOC_2H_5} \rightarrow C_6H_5CH{=}CH{-}\underset{|}{\overset{OH}{C}}H{-}CH\overset{CN}{\diagdown COOC_2H_5} \rightarrow$$
$$\quad\ \overset{|}{H}$$

$$C_6H_5CH{=}CH{-}CH{=}C\overset{CN}{\diagdown COOC_2H_5}$$

On the other hand, malonic ester adds to benzalacetophenone in the 1,4 fashion (46):

$$\overset{4}{C_6H_5}\overset{3}{CH}{=}\overset{2}{CH}\underset{|}{\overset{1}{C}}{=}O + CH_2\overset{COOC_2H_5}{\diagdown COOC_2H_5} \rightarrow C_6H_5CHCH{=}\underset{|}{\overset{OH}{C}}{-}C_6H_5 \rightarrow$$
$$\qquad\ \overset{|}{C_6H_5}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH\overset{COOC_2H_5}{\diagdown COOC_2H_5}$$

$$C_6H_5CHCH_2C=O$$
$$\diagdown C_6H_5$$
$$|$$
$$\diagup COOC_2H_5$$
$$CH\diagdown$$
$$\diagdown COOC_2H_5$$
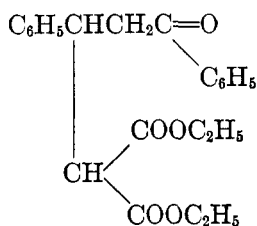
It is evident from these examples that the aldol condensation becomes the Michael condensation when, in the vinylogs of the simple carbonyl compounds, the function of the carbon atom in position 2 is usurped by that in position 4.

The Michael condensation occurs in a 1,6 manner with the next higher vinylog. Thus β-vinylacrylic ester condenses with malonic ester in this way (12):
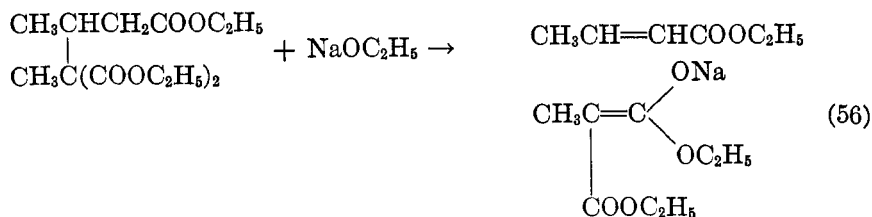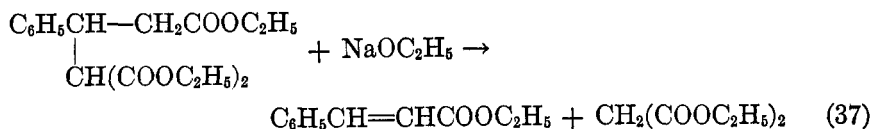
$$\overset{6}{C}H_2=\overset{5}{C}H-\overset{4}{C}H=\overset{3}{C}H\overset{2}{C}\overset{1}{=}O + CH_2\diagup^{COOC_2H_5}_{\diagdown COOC_2H_5} \rightarrow$$
$$\diagdown OC_2H_5$$

$$CH_2-CH=CH-CH=C-OH \qquad CH_2CH=CH-CH_2C=O$$
$$| \qquad\qquad\qquad | \qquad\qquad | \qquad\qquad\qquad\qquad |$$
$$| \qquad\qquad\qquad OC_2H_5 \rightarrow \quad | \qquad\qquad\qquad\qquad OC_2H_5$$
$$\diagup COOC_2H_5 \qquad\qquad\qquad \diagup COOC_2H_5$$
$$CH\diagdown \qquad\qquad\qquad\qquad CH\diagdown$$
$$\diagdown COOC_2H_5 \qquad\qquad\qquad \diagdown COOC_2H_5$$
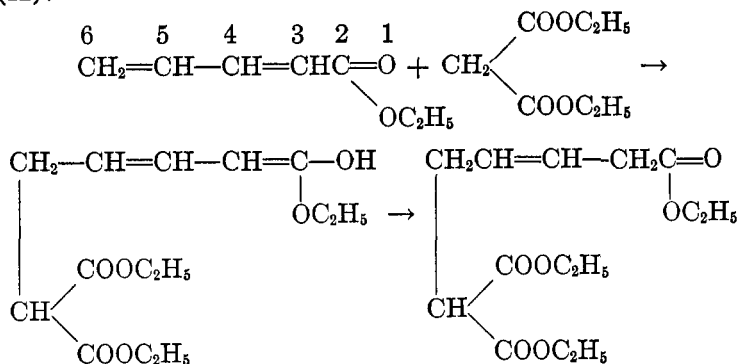
In view of this close relationship between the aldol and the Michael types of condensation it is interesting to note that the reversibility of the aldol type of reaction is characteristic, likewise, of the Michael condensation. The following are illustrative examples of fissions of this type:

$$C_6H_5CH-CH_2COOC_2H_5$$
$$| \qquad\qquad\qquad\qquad + NaOC_2H_5 \rightarrow$$
$$CH(COOC_2H_5)_2$$

$$C_6H_5CH=CHCOOC_2H_5 + CH_2(COOC_2H_5)_2 \quad (37)$$

$$CH_3CHCH_2COOC_2H_5 \qquad\qquad\qquad CH_3CH=CHCOOC_2H_5$$
$$| \qquad\qquad\qquad\qquad + NaOC_2H_5 \rightarrow \qquad\qquad\qquad ONa$$
$$CH_3C(COOC_2H_5)_2 \qquad\qquad\qquad\qquad\qquad CH_3C=C\diagup$$
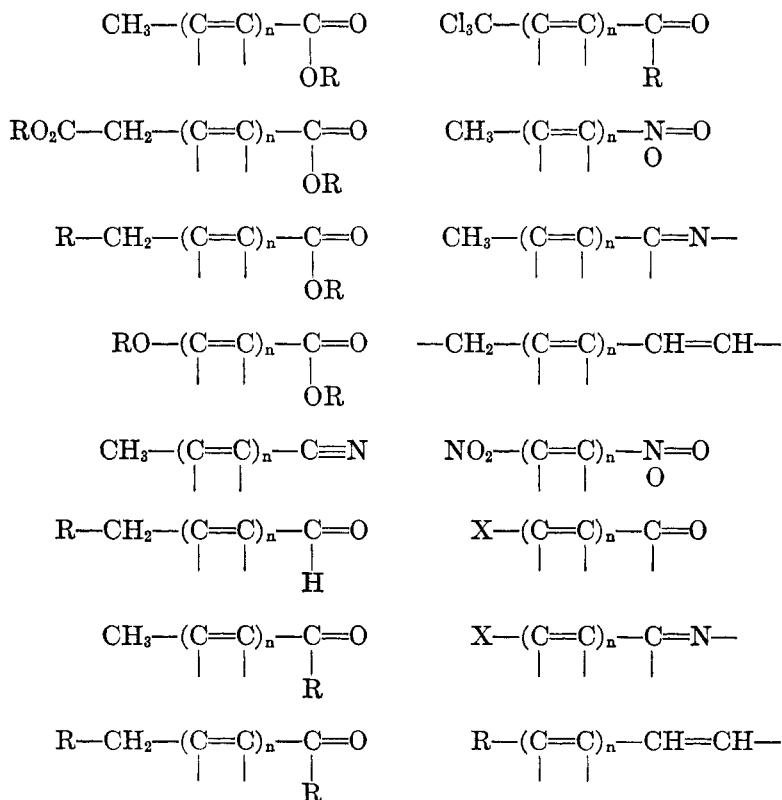$$\diagdown OC_2H_5 \quad (56)$$
$$|$$
$$COOC_2H_5$$

SUMMARY AND DISCUSSION

The principle of vinylogy states that when, in a compound of the type $A—E_1=E_2$ or $A—E_1\equiv E_2$ (in which E_1 and E_2 represent non-metallic elements), a structural unit of the type $—(C=C)_n—$ is interposed between A and E_1, the function of E_2 remains qualitatively unchanged but that of E_1 may be usurped by the carbon atom attached to A.

The resulting compound has the form $A—(C=C)_n—E_1=E_2$ or $A—(C=C)_n—E_1\equiv E_2$, and in any given series of this type the members differ from each other by one or more vinylene residues. Such a group of compounds has been termed a *vinylogous series*. The members of such a series are *vinylogs* of one another.

Examples of the following vinylogous series have been mentioned, and in each case it is shown that the principle of vinylogy is applicable:

$$CH_3—(C=C)_n—C=O \qquad\qquad Cl_3C—(C=C)_n—C=O$$
$$\text{OR} \qquad\qquad\qquad\qquad\qquad \text{R}$$

$$RO_2C—CH_2—(C=C)_n—C=O \qquad CH_3—(C=C)_n—N=O$$
$$\text{OR} \qquad\qquad\qquad\qquad\qquad \text{O}$$

$$R—CH_2—(C=C)_n—C=O \qquad\qquad CH_3—(C=C)_n—C=N—$$
$$\text{OR}$$

$$RO—(C=C)_n—C=O \qquad\qquad —CH_2—(C=C)_n—CH=CH—$$
$$\text{OR}$$

$$CH_3—(C=C)_n—C\equiv N \qquad\qquad NO_2—(C=C)_n—N=O$$
$$\text{O}$$

$$R—CH_2—(C=C)_n—C=O \qquad\qquad X—(C=C)_n—C=O$$
$$\text{H}$$

$$CH_3—(C=C)_n—C=O \qquad\qquad X—(C=C)_n—C=N—$$
$$\text{R}$$

$$R—CH_2—(C=C)_n—C=O \qquad\qquad R—(C=C)_n—CH=CH—$$
$$\text{R}$$

It is generally recognized that the behavior of any class of organic compounds represents a resultant of several tendencies, and that usually no one of these tendencies will predominate throughout the whole range of the series.   Hence, it is to be expected that any generalization which predicts uniform behavior for all the members of the series will be subject to exceptions.   In view of this situation, it is recognized that the principle of vinylogy is not to be regarded as a rule.   It states, not that the function of E_1 *will* be usurped by the carbon atom joined to A, but that it *may* be usurped.   Further, it is not implied that effects of the types discussed will not be encountered with structures which lie outside the general category covered by the principle.

The principle of vinology has been used in this review to correlate in a helpful manner many types of reactions which are ordinarily regarded as somewhat anomalous in nature.   Also, it is made apparent that this principle may serve to direct attention to possible reactions which might otherwise appear unlikely.

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