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The Use of Acrylic Compounds in Organic Synthesis. Part-1

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The previously reported reactions using acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide are reviewed. The present article involves the reaction with the compounds having labile hydrogen atoms, the reaction with enamines, the Oxo reaction, the formation of phosphorus ylides, the reaction with sulfur ylides, the Ritter reaction as well as the transesterification.

KEY WORDS: Reaction of acrylonitrile/ Reaction of methyl acrylate/
Reaction of ethyl acrylate/ Reaction of acrylamide/

I. INTRODUCTION

One of the major objectives of modern organic synthesis is the finding of techniques for synthesizing useful and exciting compounds from easily available and relatively cheap starting materials. Some acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide, which appear to be the parent compounds of a variety of acrylic compounds previously reported, may be included among these starting materials in organic synthesis. Owing to the widespread use of these acrylic monomers for the manufacture of synthetic rubber, adhesives, textile and paper coatings, leather finish resins, water emulsion paint vehicles, etc., many efforts have been devoted to the industrial preparation of these unsaturated compounds. The industrial preparation of acrylonitrile by the ammoxidation of propylene in the presence of suitable catalysts is well known as SOHIO process. There are two industrially important methods by which methyl and ethyl acrylate can be prepared, though many other processes have been reported. The first method is based on the reaction of acetylene and nickel carbonyl to give the hypothetical cyclopropenone, which, in the presence of methyl and ethyl alcohol, gives methyl and ethyl acrylate, respectively. Another, and generally preferred, production method for these acrylates starts from propylene, which is converted to acrolein and further to acrylic acid by air oxidation using suitable catalysts. The latter acid can then be converted to the acrylic esters by esterification. Thus, these acrylic monomers are readily made from very cheap raw materials, viz., propylene, acetylene, ammonia, carbon monoxide, and methyl and ethyl alcohol. The emphasis of the reaction using them has been mostly on the preparation and development of useful high-polymers. On the contrary, little is recognized regarding

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the role of these acrylic compounds in organic synthesis and related industry. The synthetic method for the preparation of monosodium \( L \)-glutamate involves the conversion of acrylonitrile to \( \beta \)-formypropionitrile in a variation of the Oxo synthesis and the Strecker reaction with the resulting nitrile to provide \( \alpha \)-aminoglutaronitrile followed by hydrolysis. However, the half part of the monosodium slat is even now manufactured by hydrolysis of protein or by fermentation. Accordingly, the finding of a novel reaction using these acrylic compounds as well as the making use of them in a variation of the known reaction may be a significant objective of organic synthesis. A better understanding of the previously reported reactions with these acrylic compounds will serve to attain the objective. Thus, in this and the continued reviews a survey is given of experimental results and some pertaining rationalization in the area of organic reactions in which acrylonitrile, methyl and ethyl acrylate or acrylamide participate. The classification used is based on the type of reaction and on the kind of reaction partner. The present paper deals with reactions of the acrylic compounds which seem to belong to the following sections; the reaction with the compounds possessing labile hydrogen atoms, the reaction with enamines, the hydroformylation with carbon monoxide and hydrogen, the reaction of phosphorus ylides derived from acrylic compounds and the reaction with sulfur ylides as well as the Ritter reaction and the transesterification. These are schematically outlined below.

II. THE REACTION WITH THE COMPOUNDS POSSESSING LABILE HYDROGEN ATOMS

The utility of acrylonitrile, methyl and ethyl acrylate, and acrylamide as acceptors in the Michael reaction is well known. The literature is summarized in an earlier review\(^1\) of this reaction. Under the influence of alkaline reagents, typically alkali metal alkoxides, the acrylic compounds react with a variety of compounds containing

\[ \begin{align*}
\text{CH}_2=\text{CHCONHR} & \quad \text{ROH} \\
\text{Y}=\text{CO}_2\text{CH}_3, \text{CO}_2\text{C}_2\text{H}_5 & \quad \text{Z-CH}_2\text{CH}_2\text{Y} \\
\text{R}^+, \text{H}_2\text{O} & \quad \text{ZH} \\
\text{Y}=\text{CN} & \quad \text{N-C}=\text{C}^=\text{C}^=\text{YCH-CH}_2 \\
\text{Y}=\text{CO}_2\text{CH}_3, \text{CO}_2\text{C}_2\text{H}_5, \text{CONH}_2 & \quad \text{CH}_2=\text{CHY} \\
\text{R}_3\text{P} & \quad \text{HCOCH}_2\text{CH}_2\text{Y} \\
\text{CH}_2=\text{CHCH}(\text{CHO})\text{Y} & \quad \text{CH}_3\text{CH}(\text{CHO})\text{Y} \\
\text{R}_3\text{PCH}_2\text{CH}_2\text{Y} & \quad \text{R}_3\text{PCH}_2\text{CH}_2\text{Y} \\
\end{align*} \]
active hydrogen atoms such as malonates, cyano esters, keto esters, carboxylic acid esters, aldehydes, ketones, nitriles, nitro compounds, sulfones, to form the corresponding adducts. The Michael reaction using acrylonitrile as an acceptor results in the formation of molecules containing a \(\beta\)-cyanoethyl group at the location of the reactive hydrogen atom contained in a donor, and the reaction is commonly known as cyanoethylation. The scope, limitations, and experimental conditions as well as experimental procedures of cyanoethylation reactions have also been presented in an earlier review by Bruson.\(^2\) Although it is impossible to introduce directly a cyanoethyl group into benzene itself, phenol, anisole and their certain derivatives undergo cyanoethylation by acrylonitrile on the benzene nucleus when the reaction is conducted in the presence of AlCl\(_3\) plus HCl. Simple phenol, for example, forms \(\beta\)-(\(p\)-hydroxyphenyl)propionitrile in good yield.\(^3\) Also, \(p\)-substituted phenols react with acrylonitrile to furnish dihydrocoumarin (1) and its derivatives 2, 3, and 4.\(^4\) This cyanoethylation is also possible with anisole (5)\(^5\) and its derivatives such as 6\(^5\), 7\(^5\), and 8.\(^6\) The method has been further extended\(^7\) to some derivatives of phenetole as well as methyl and ethyl ether of resorcinol as the starting materials. However, in the presence of alkaline catalysts such as alkali metals and alkoxides, phenol, resorcinol, and many of their derivatives are cyanoethylated on the hydroxyl groups to form the corresponding cyanoethyl ethers, indicating that the reactions occur in a manner similar to those of aliphatic alcohols with acrylonitrile.\(^2\)

\[
\begin{align*}
\text{R-OH} & \quad \text{+ CH}_2\text{=CHCN} \quad \text{AlCl}_3, \text{HCl} \quad \text{R-O-C=O} \\
\text{R} & \quad \text{R} = \text{H} \quad \text{R} = \text{OCH}_3 \\
\text{CH}_3\text{O} & \quad \text{R} \quad \text{CH}_2\text{=CHCN} \quad \text{AlCl}_3, \text{HCl} \quad \text{CH}_3\text{O} \quad \text{R} \quad \text{CH}_2\text{CHCH}_2\text{CN} \\
\text{R} & \quad \text{R} = \text{H} \quad \text{R} = \text{CH}_3 \\
\text{CH}_3\text{O} & \quad \text{OCH}_3 \quad \text{R} \quad \text{CH}_2\text{=CHCN} \quad \text{AlCl}_3, \text{HCl} \quad \text{OCH}_3 \quad \text{R} \quad \text{CH}_2\text{CHCH}_2\text{CN} \\
\text{R} & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{OCH}_3 \quad \text{R} \quad \text{CH}_2\text{=CHCN} \quad \text{AlCl}_3, \text{HCl} \quad \text{OCH}_3 \quad \text{R} \quad \text{CH}_2\text{CHCH}_2\text{CN} \\
\text{R} & \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]
Although the addition of the acidic compounds such as HCN, HCl, HBr, NaHSO₃ to acrylonitrile in the presence or absence of alkaline catalysts has been known for a long time it was only in 1968 that Javaid and his co-workers found that free carboxylic acids also add to excess acrylonitrile at elevated temperature. In this and similar cases studied by Fujita and his co-woaker, metallic Cu—Cu(OH)₂ has been found to act as a useful catalyst in the process. Best results are obtained with Cu[P(C₆H₅)₃]₂Cl₂ as a catalyst than with the other Cu salts in the cyanoethylation of several carboxylic acids to afford the corresponding β-cyanoethyl carboxylates as shown.

\[
\begin{align*}
R \text{CO}_2\text{CH}_2\text{CH}_2\text{CN} & \quad \text{NCCCH}_2\text{CH}_2\text{O}_2\text{C(CH}_3)_n\text{CO}_2\text{CH}_2\text{CH}_2\text{CN} \\
R = \text{CH}_3, \text{C}_2\text{H}_5, n-\text{C}_3\text{H}_7, n-\text{C}_7\text{H}_{15}, \text{CH}_2=\text{C(})\text{CH}_3) & \quad n=0-4
\end{align*}
\]

The compounds having one or more –NH– groups such as primary and secondary amines, lactams, imides, and amides add to acrylonitrile with or without the aid of a catalyst. Many instances are listed in the review above mentioned. Recently, the cyanoethylation reaction has been extended to many more complex primary and especially secondary amines. For example, the compounds 9 have been prepared by reacting the corresponding alkylamines with acrylonitrile in the presence of acetic acid at 110–150°C. An aliphatic polyamine 10 is synthesized by cyanoethylation of hexamethylenediamine followed by hydrogenation. Bis[3-dimethylaminopropyl]-amine and acrylonitrile, when refluxed in isopropyl alcohol, react to give a cyanoethylated triamine 11. The former 10 is useful as corrosion inhibitor, and the latter 11 is a good catalyst for manufacture of urethane polymer foams.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_n\text{N(CH}_2\text{CH}_2\text{CN})_2 & \quad (\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{N(CH}_2)_6\text{N(CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2} \\
n = 3-26 & \quad (10) \\
[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{CH}_2]_2\text{NCH}_2\text{CH}_2\text{CN} & \quad (11)
\end{align*}
\]

A convenient procedure has been developed for the synthesis of some macrocyclic lactams by Kramer and his co-workers. Cyanoethylation of 12 with acrylonitrile, followed by hydrogenation over Raney Ni, affords 13, and repetition of this process once and twice gives 14 and 15. When 13, 14, and 15 are treated with potassium 3-aminopropylamide (16) in 1, 3-diaminopropane at room temperature, ring expansion take place to afford 17, 18, and 19, respectively. The probable path is indicated in the accompanying equations. This procedure is also applicable to 7-heptanelactam (20) as a starting lactam. However, when 2-pyrolidone (21) and ε-caprolactam (22) are submitted to this series of transformations, dehydration of the intermediate 23 to form 24 is observed. The dehydration may be also brought about by heating 23 with p-toluenesulfonic acid in xylene. Very often, the compounds 24 are used for removal of hydrogen halide from halides. Di-cyanoethylation takes place in the reaction between acrylamide and a large excess of acrylonitrile in the presence of sodium methoxide. When the resultant 25 is heated under reduced pressure, it undergoes decomposition to afford 26 and acrylonitrile.
Aldehydes and ketones in which the α-carbon atom has one or more hydrogen atoms add to acrylonitrile in the presence of alkaline catalysts. Thus, one, two, three, or more cyanoethyl groups are introduced into the methinyl, methylene, and methyl groups adjacent to the carbonyl group. The reaction has been considered in detail by Bruson\textsuperscript{2} and later by Bergmann and his co-workers.\textsuperscript{1} The behavior of acrylonitrile with some aromatic aldehydes in which an α-hydrogen is lacking in the presence of alkaline catalysts such as sodium methoxide, Triton B, and piperidine has also been reported.\textsuperscript{19} However, the behavior of acrylonitrile with some aromatic and heterocyclic aldehydes in the presence of NaCN is rather interesting. For example, several γ-keto cyanides such as 27 are prepared\textsuperscript{20} from the reaction of the corresponding aromatic and heterocyclic aldehydes with acrylonitrile using NaCN catalyst. In a similar manner, these aldehydes are reacted with ethyl acrylate in N, N-dimethylformamide to give the corresponding γ-keto esters 28.\textsuperscript{21} Stetter and his co-worker have examined the possibility of substituting another catalyst, 3-
benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (29), for NaCN employed in the above procedure and found\(^{22}\) that both aromatic and heterocyclic as well as aliphatic aldehydes add similarly to acrylonitrile and to ethyl acrylate under the catalytic influence of 29 in the presence of triethylamine. When silver acetate is used to catalyze the reaction of butyraldehyde and methyl acrylate, methyl \(\beta\)-butyrylpropiionate can be formed.\(^{23}\) However, the mechanism of this reaction may be entirely different, involving attack by butyryl radical.

\[
\text{RCHO} + \text{CH}_2=\text{CHCN} \xrightarrow{\text{NaCN}} \text{RCOCH}_2\text{CH}_2\text{CN} \\
(27)
\]

\[
\text{R}=\text{C}_6\text{H}_5, \ p-\text{ClC}_6\text{H}_4, \ p-\text{BrC}_6\text{H}_4, \ 2-\text{C}_10\text{H}_7, \ \\ 3-\text{pyridyl}, \ 4-\text{pyridyl}, \ 2-\text{furyl}, \ 2-\text{thienyl}
\]

\[
\text{RCHO} + \text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{NaCN}} \text{RCOCH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5 \\
(28)
\]

\[
\text{R}=\text{C}_6\text{H}_5, \ p-\text{ClC}_6\text{H}_4, \ 3-\text{pyridyl}, \ 2-\text{thienyl}
\]

Like acrylonitrile, methyl and ethyl acrylate also react with free carboxylic acids at elevated temperature. For example, these acrylates containing small amounts of hydroquinone monomethyl ether react with acetic acid at 190\(^{\circ}\)C in the presence of CuO to form \(\beta\)-(methoxy- and ethoxycarbonyl)ethyl acetate (30, \(\text{R}=\text{CH}_3\) and 30, \(\text{R}=\text{C}_2\text{H}_5\)). Further work involving conversion of propionic and butyric acid to the corresponding \(\beta\)-(methoxy- and ethoxycarbonyl)ethyl carboxylate is also patented.\(^{24}\) Methyl acrylate reacts with ethyl fluorocarbamate in sulfuric acid to give methyl \(N\)-ethoxycarbonyl-\(N\)-fluoro-\(\beta\)-aminopropanoate (31), the product of alkylation by the terminal position of the resonance-stabilized protonated ester.\(^{25}\) The reaction of ethyl acetoacetate with ethyl acrylate in the presence of Triton B produce the adduct 32 after a NaOH-catalyzed hydrolysis. Grob and his co-worker\(^{26}\) have found that heating 32 with potassium acetate leads to the cyclic compound 33, which can be converted into 34 by the action of sodium ethylate.

\[
\text{CH}_3\text{CO}_2\text{H} + \text{CH}_2=\text{CHCO}_2\text{R} \xrightarrow{\text{CuO, 190\(^{\circ}\)C}} \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{R} \\
(30)
\]

\[
\text{R}=\text{CH}_3, \ \text{C}_2\text{H}_5
\]

\[
\text{NHFCO}_2\text{C}_2\text{H}_5 + \text{CH}_2=\text{CHCO}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{O}_2\text{CCH}_2\text{CH}_2\text{NFCO}_2\text{C}_2\text{H}_5 \\
(31)
\]

\[
\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{Triton B}} \text{CH}_3\text{CO} \xrightarrow{\text{NaOH}} \text{C}_2\text{H}_5\text{O}_2\text{C} \xrightarrow{\text{C}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2} \\
(32)
\]

\[
\text{CH}_3\text{CO}_2\text{K} \xrightarrow{\text{C}_2\text{H}_5\text{O}_2\text{C} \xrightarrow{\text{COCH}_3} \text{C}_2\text{H}_5\text{O}_2\text{C} \xrightarrow{\text{NaO}_2\text{C}_2\text{H}_5} \text{C}_2\text{H}_5\text{O}_2\text{C} \xrightarrow{\text{O}} \\
(33) \quad (34)
\]
At 40–50°C, ethyl acrylate reacts with ethanolamine and diethanolamine to give the adducts 35 and 36, respectively. These adducts are treated with stearylamine at elevated temperature, reacted with ethylene oxide, and then quaternized with dimethyl sulfate for the production of revelling agents for dyeing. 27) The preparation of 3-dimethylamino-N, N-dimethylpropionamide is accomplished 28) by heating ethyl acrylate, dimethylamine, and small amounts of so-called inhibitors in an autoclave. This amide together with bis[2-(N, N-dimethylamino)ethyl]ether and triethylenediamine is used as a catalyst in the manufacture of flexible or highly resilient polyurethane foams. Ethylenimine can react with one or two moles of methyl acrylate. 29, 30) Low temperatures favor the addition of one molecule of ethylenimine with formation of N, N-ethylene-β-alanine methyl ester (37); higher temperatures result in the addition of the initially formed 37 to a second molecule of methyl acrylate with formation of 38. The reaction of 2-(aminomethyl)ethylenimine with acrylic compounds such as acrylonitril, methyl and ethyl acrylate proceeds smoothly at room temperature to afford both the corresponding 1:1 adducts 39 and 1:2 adducts 40. Among these adducts only one of 39, in which Y = CN, is converted into diazabicyclohexanes 41 by treatment with aldehydes. 31) The reaction of 2-aminopyridine with alkyl acrylates gives not only a noncyclic product, an alkyl ester of N-(2-pyridyl)-β-alanine (42) but also a cyclic product 43. 32) The latter compound is formed by the attack of alkyl acrylates at the ring nitrogen of the imino form of 2-aminopyridine.
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The carbamoylthelylation of aliphatic alcohols having two or more hydroxyl groups is accomplished\(^{33}\) by heating them with acrylamide in the presence of an alkaline catalyst. For example, diethylene glycol and acrylamide react in the presence of Triton B to yield 44, which is further reacted with 1-butanol to afford the compound 45 that has found use as a plasticizer.\(^{33}\) Some \(\alpha\)-amino acids add in aqueous solution to acrylamide in the presence of KOH to give the 1:1 adducts 46 or 1:2 adducts 47, depending upon the proportion of reagents.\(^{34}\) Analogous behavior is also observed\(^{35}\) in the reaction of \(\beta\)-alanine with acrylamide in aqueous solution under the catalytic action of triethylamine. The carbamoylthelylation reaction of primary and secondary amines is also known. The literature is summarized in an earlier review.\(^{36}\)

III. THE REACTION WITH ENAMINES

The addition of enamines to electrophilic olefins such as acrylonitrile or methyl acrylate has been shown to give the Stork alkylation products 49 and/or cycloaddition products 50 depending on choice of reactants and reaction conditions.

When the piperidine enamine of cyclopentanone (51, \(n=1\)) or of cyclohexanone (51, \(n=2\)) and methyl acrylate are allowed to react in acetonitrile without controlling the temperature, only the Stork alkylation product 52 is obtained.\(^{37}\) When, however, the reaction mixture is maintained below 30°C, both 52 and the cycloaddition product 53 are produced.\(^{37}\) Similar reactions have been found to occur when the dimethyl-
amine enamines of cyclopentanone and of cyclohexanone were used as the enamine component. Fleming and his co-worker have found that some enamines such as 54, 55, and 56 derived from pyrrolidine and alicyclic ketones react with acrylonitrile at room temperature to afford exclusively the corresponding cyclobutane derivatives (57, 58, and 59), respectively. Also, when the reaction of β-hydrogen-containing enamines derived from aldehydes or the only acyclic ketone studied, 3-pentanone, with acrylonitrile or with methyl acrylate is carried out under properly mild conditions, the occurrence of the Stock alkylation is prevented and only the cycloaddition product is produced. For example, the piperidine enamine (60) of butyraldehyde give, with methyl acrylate, the cyclobutane derivative 61 when the reaction is carried out in acetonitrile for 2 days at room temperature. Enamines containing no β-hydrogen are incapable of undergoing the Stork alkylation; they react with electrophilic olefins such as acrylonitrile or methyl acrylate to give only the cyclobutane derivatives on heating the reactants at elevated temperature in an autoclave or, better, by refluxing in acetonitrile. However, it is very difficult to determine which course the reaction of these electrophilic olefins with enamines having β-hydrogens would take. Yamada and his co-workers have found that L-proline alkyl ester enamines (62) of cyclohexanone react with methyl acrylate and with acrylonitrile to give, after hydrolysis, S-2-(2-methoxycarbonyl- and 2-cyanoethyl)cyclohexanones (63, Y=CO2CH3 and 63, Y=CN), respectively. This is a rare case in which the reaction course may be easily determinable although the employed enamines possess β-hydrogens. Presumably, steric hindrance in 62 may operate which tend to depress the occurrence of cycloaddition reaction. The Stork alkylation above described involves nucleophilic attack by the enamine carbon on the electrophilic carbon of acrylonitrile or of methyl acrylate, with the generation of a zwitterionic intermediate 48, and it was developed largely by Stork and his co-workers whose extensive paper describes the technique and range of the reaction. On the other hand, the cycloaddition reaction, leading to a cyclobutane derivative, could proceed either from a zwitterionic intermediate similar to 48 by intramolecular attack, or by direct cycloaddition of the enamine to the acrylic compounds, and it offers a very simple and frequently high-yield route to the cyclobutane derivatives. No cycloaddition product is obtained from the reaction of 1-ethoxy-N, N-dimethylvinylamine with methyl acrylate. Instead, the Stork alkylation product 64 is obtained. 1-Ethoxy-N, N, 2-trimethylpropenylamine react with methyl acrylate to give the cyclobutene derivative 65, but in poor yield, presumably by loss of alcohol from the initially formed cyclobutane derivative. In general, secondary enamines such as 66 are thermodynamically unstable since they exist in equilibrium with the tautomeric imines 67. Recently, Jeso and his co-worker have obtained pure secondary enamines by partial methanolysis of organo-tin or magnesium salts of imines. The secondary enamines thus obtained are quite stable at −80°C, and undergo the attack of acrylonitrile at 0°C, leading, besides some polymerization, to the adducts 68.
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\[ (\text{CH}_3)_2N\text{C}2\text{H}_5 - \text{N}\left(\text{CH}_3\right)_2 + \text{CH}_2=\text{CHO}_2\text{C}_2\text{H}_3 \xrightarrow{20-60^\circ\text{C}} \text{CH}_3\text{O}_2\text{CCH}_2\text{CH}_2\text{CH} = \]

\( \text{C(OC}_2\text{H}_5)\text{N} - \text{N}(\text{CH}_3)_2 \) 

\[ (\text{CH}_3)_2\text{C} = \text{C(OC}_2\text{H}_5)\text{N} - \text{N}(\text{CH}_3)_2 + \text{CH}_2=\text{CHO}_2\text{C}_2\text{H}_3 \xrightarrow{\text{reflux}} \]

\( \left(\text{CH}_3\right)_2\text{N}\text{OC}_2\text{H}_5 \text{CO}_2\text{CH}_3 \)

\[ -\text{C}_2\text{H}_5\text{OH} \]

\[ (\text{CH}_3)_2\text{N}\text{CO}_2\text{CH}_3 \]
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\[
\begin{align*}
\text{R'\text{C=CH-NHR} + CH}_2=CHCN & \rightarrow \text{NCCH}_2\text{CH}_2\text{C-CH=NR} \\
\text{R''} & \\
\text{R'\text{CH-CH=NR}} & \\
\text{R''}
\end{align*}
\]

\[(66) \quad \text{R'=CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7, \text{iso-C}_4\text{H}_9\]

\[(67) \quad \text{R'=CH}_3, \text{R''=H, CH}_3\]

IV. THE HYDROFORMYLATION WITH CARBON MONOXIDE AND HYDROGEN

\[
\text{CH}_2=\text{CHY} + \text{CO} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{HCOCH}_2\text{CH}_2\text{Y} + \text{CH}_3\text{CH} (\text{CHO})\text{Y}
\]

\[Y=\text{CO}_2\text{CH}_3, \text{CO}_2\text{C}_2\text{H}_5, \text{CN}\]

The Oxo reaction originally consisted of the treatment of an olefin with water gas or synthesis gas in the presence of a cobalt catalyst to produce aldehydes containing 1 carbon atom more than the starting olefin. The reaction was also carried out with some acrylic compounds instead of the olefins. The reaction results in the addition of the units of formaldehyde, \(\text{H-CHO}\), across the double bond of the applied acrylic compounds. It is apparent that the addition can lead to one or the other of two compounds or to a mixture of both, depending on which carbon atom of the acrylic compound adds the formyl group. For example, the product from ethyl acrylate in the Oxo reaction is usually a mixture of ethyl \(\alpha\)- and \(\beta\)-formylpropionate. The proportion of them is affected by various reaction conditions as is well illustrated by Takegami and his co-workers\(^{45}\) who studied in detail the effects of reaction conditions on the distribution of the products in the \(\text{Co}_2(\text{CO})_8\)-catalyzed hydroformylation of ethyl acrylate in toluene. Cobalt tricarbonyl modified by \(\text{PR}_3\) (\(\text{R}=\text{C}_6\text{H}_5\), cyclohexyl, \(n\text{-C}_4\text{H}_9\)), \([\text{Co}(\text{CO})_3\text{PR}_3]_2\)^{46} and \(\text{Rh}_2\text{O}_3\)^{47} are also known to be active catalysts for the hydroformylation of methyl and ethyl acrylate. Tanaka and his co-workers\(^{48}\) studied the \(\text{Rh}_2\text{Cl}_2(\text{CO})_4\)-catalyzed hydroformylation of ethyl acrylate at \(150^\circ\text{C}\) under 100 atm of synthesis gas in the absence or presence of various additional phosphorus ligands, and found that in order to attain a high selectivity of \(\alpha\)-formylation (\(>95\%)\) leading to ethyl \(\alpha\)-formylpropionate, the addition of shorter methylene-chained diphosphines \([\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2], \text{R}=\text{C}_6\text{H}_5\) or cyclohexyl, \(n=2-4\) to the reaction system was essential, while the use of \(\text{Rh}_2\text{Cl}_2(\text{CO})_4\) alone or in combination with triphenylphosphine or a diphosphine having a longer methylene chain, \((\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_5\text{P}(\text{C}_6\text{H}_5)_2\), resulted in a very low yield of ethyl \(\alpha\)-formylpropionate. Besides, it has been noted in a patent claim\(^{49}\) that the highest \(\alpha\)-selectivity (\(>99\%\)) in the hydroformylation of methyl acrylate in cyclohexane could be accomplished by the use of \(\text{HRh}(\text{CO})(\text{PR}_3)_3\), in which \(\text{R}=\text{C}_6\text{H}_5\), together with triphenylphosphine. If the Oxo reaction of methyl and ethyl acrylate in benzene was performed at \(250^\circ\text{C}\) and at about 300 atm by using a catalytic amount of \(\text{Co}_2(\text{CO})_8\), the main product was \(\gamma\)-
butyrolactone (69). Presumably, the initially formed methyl and ethyl β-formylpropionate were reduced to the corresponding alcohols under the reaction conditions, which were further converted into 69, suggesting that Co\(_2\)(CO)\(_8\) also favors β-formylation under the above reaction conditions.

\[
\text{CH}_2=\text{CHCO}_2\text{R} + \text{CO} + \text{H}_2 \xrightarrow{\text{Co}_2\text{(CO)}_8, 250^\circ\text{C}, 300\ \text{atm}} \text{R} = \text{CH}_3, \text{C}_2\text{H}_5
\]

The product from acrylonitrile in the Co\(_2\)(CO)\(_8\)-catalyzed Oxo reaction is usually a mixture of α- and β-formylpropionitrile, but the former is in relatively small amounts. As described in the preface of this review, β-formylpropionitrile has found a particularly important use in the preparation of monosodium L-glutamate. Thus, many efforts have been devoted to the industrial preparation of this nitrile. Many chemists of Ajinomoto Co., Inc. in Japan have also carried out considerable experiments and presumably pooled their knowledge concerning the preparation of β-formylpropionitrile from acrylonitrile. We cannot reveal here the pooled knowledge, and hence only the published literature of the hydroformylation of acrylonitrile will be summarized below.

If the Co\(_2\)(CO)\(_8\)-catalyzed reaction was run in a polar solvent such as methyl alcohol or acetone, a higher selectivity of β-formylation leading to β-formylpropionitrile could be accomplished than that obtained in the reaction with a nonpolar solvent such as benzene. Further, Kashina and his co-workers have found that the Co\(_2\)(CO)\(_8\)-catalyzed hydroformylation of acrylonitrile in methyl alcohol gave a 1:10 mixture of α- and β-formylpropionitrile together with a small amount of methyl α-cyanopropionate. The addition of a small amount of diethylamine, N, N-dimethylaniline or pyridine also facilitates the formation of β-formylpropionitrile in the Co\(_2\)(CO)\(_8\)-catalyzed hydroformylation of acrylonitrile in benzene. Noyori and his co-workers have proposed two unique methods by which the isolation of the desired β-formylpropionitrile is easily achieved. When a solution of acrylonitrile and a small amount of Co\(_2\)(CO)\(_8\) in benzene was heated with a 1:2 mixture of carbon monoxide and hydrogen at 120°C and at pressures over 240 atm and further at 200°C, β-hydroxy-a-methylpropionitrile (70), γ-hydroxybutyronitrile (71), and ethyl cyanide were obtained in yields of 12, 56, and 16%, respectively. The former two of them are the compounds which were formed by subsequent reduction of the initially produced α- and β-formylpropionitrile. Other catalysts such as Rh\(_3\)O\(_8\), [Co(CO)\(_3\)P-(n-C\(_4\)H\(_9\))]\(_2\) and Co\(_2\)(CO)\(_8\) in combination with porphyrins can also be used for the reaction of acrylonitrile with carbon monoxide and hydrogen. When acrylamide was submitted to the reaction with carbon monoxide at 200°C and at 300 atm under
the catalytic action of Co$_2$(CO)$_6$, it was easily converted to succinimide.$^{61}$

V. THE REACTION OF PHOSPHORUS YLIDES DERIVED FROM ACRYLIC COMPOUNDS AND THE REACTION WITH SULFUR YLIDES

In the presence of several alcohols, triphenylphosphine catalyze the conversion of acrylonitrile to a high-melting, insoluble hexamer 74.$^{62}$ As shown in the following equations, this reaction is believed to proceed by the initial formation of a betaine intermediate 72 which gives rise to the corresponding phosphorus ylide 73. Presumably, this is the first information concerning the formation of a phosphorus ylide from a trivalent phosphorus compound and an acrylic compound such as acrylonitrile. In later report, Oda and his co-workers$^{63}$ have described that triphenylphosphine adds to activated olefins such as acrylonitrile, ethyl acrylate and acrylamide to give the betaines and further that the betaines give rise to the corresponding ylides 75 which can be captured by benzaldehyde in Wittig olefin syntheses. If the phosphorus ylide 75 ($Y=\text{CN}$) was trapped with propionaldehyde, the product was an olefinic cyanide 76 ($Y=\text{CN}, R=C_6\text{H}_5$) with the cis-isomer predominating, and in the case with benzaldehyde the trans-isomer in the product 76 ($Y=\text{CN}, R=C_6\text{H}_5$) was found to be predominant.$^{64}$ Further, Trippett$^{65}$ has shown that when the phosphines such as 77, 78, and 79, where $R''$ is a group capable of stabilizing an adjacent carbanion, are treated with the activated olefins the intermediate betaines transfer a proton forming the more stable ylides 80 which can be used in situ in Wittig olefin syntheses. The betaine 82 formed from diphenyl-1-phenylvinylphosphine (81) and acrylonitrile cyclize to a five-membered ylide 83, which is further reacted with benzaldehyde and with $p$-tolualdehyde to afford 84 and 85 respectively.$^{66}$ No product of a Wittig reaction was isolated from a mixture of tricyclohexylphosphine, an acrylic compound such as acrylonitrile or methyl acrylate, and an aldehyde kept under conditions which seem to be suitable for yielding the product of the Wittig reaction. Instead, a secondary alcohol formulated as 88 was isolated.$^{67}$ The result of this reaction is consistent with the reaction process which does not involve the conversion of the initially formed betaine 86 to the corresponding ylide 87. Recently, Fauduet and his co-worker$^{68}$ have described a unique method for the preparation of substituted cyclopropanes 90 by condensing acrylonitrile or methyl acrylate with the betaines 89, derived from hexamethylphosphorous triamide and some 1, 2-dicarbonyl compounds. They have further described that the reaction proceeds by a nucleophilic attack of the initially formed betaine 89 on the electrophilic carbon atom of the acrylonitrile or methyl acrylate followed by a cyclization accompanying the release of hexamethylphosphoric triamide.

\[
\begin{align*}
\text{(C}_6\text{H}_5)_3\text{P} + \text{CH}_2=\text{CHCN} & \rightarrow (\text{C}_6\text{H}_5)_3\text{PCH}_2{\text{CHCH}}_2\text{CN} & \text{CHCH}_2\text{CN} \\
\text{CH}_2=\text{CHCN} & \rightarrow (\text{C}_6\text{H}_5)_3\text{PCHCH}_2\text{CN} & \text{CH}_2\text{CHCN} \\
& \text{CH}_2\text{CHCN} & \text{CH}_2\text{CHCN}
\end{align*}
\]
The Use of Acrylic Compounds in Organic Synthesis. Part-1

\[
(CN)_{2}CH_{2}CH_{3}CN = \text{CH}C\left(CH_{2}CH_{2}CN\right)_{2}
\]

(74)

\[
(C_{6}H_{5})_{3}P + CH_{2}=CHY \rightarrow (C_{6}H_{5})_{3}PCH_{2}=CHY \rightarrow (C_{6}H_{5})_{3}PCHCH_{2}Y
\]

(75)

\[
Y = \text{CN, CO}_{2}C_{2}H_{5}, \text{CONH}_{2}
\]

R = C_{2}H_{5}, C_{6}H_{5}

\[
R(R')PCH_{2}R'' + CH_{2}=CHY \rightarrow R(R')PCH_{2}CH_{2}Y + (C_{6}H_{5})_{3}PO
\]

(76)

\[
Y = \text{CN, CO}_{2}C_{2}H_{5}, \text{CONH}_{2}
\]

R = C_{2}H_{5}, C_{6}H_{5}

\[
(C_{6}H_{5})_{2}PC=CH_{2} + CH_{2}=CHCN \rightarrow (C_{6}H_{5})_{2}PCH_{2}CH_{2}C=CHR
\]

(81)

RCHO \rightarrow (C_{6}H_{5})_{2}P(O)CH_{2}CHCH_{2}C=CHR

(84) R = C_{6}H_{5}

(85) R = p-CH_{3}C_{6}H_{4}

\[
\left(\begin{array}{c}
B \\
C
\end{array}\right) \cdot CH_{2}=CHY \rightarrow \left(\begin{array}{c}
B \\
C
\end{array}\right) \cdot PCH_{2}=CHY \rightarrow \left(\begin{array}{c}
B \\
C
\end{array}\right) \cdot PCHCH_{2}Y
\]

(86)

\[
Y = \text{CN, CO}_{2}CH_{3}
\]

R = C_{6}H_{5}, C_{6}H_{4}CO

\[
\left[\left(CH_{n}\right)_{n}P \cdot R\cdot CO\cdot CO\cdot R'\right] \rightarrow \left[\left(CH_{n}\right)_{n}P \cdot R\cdot CH_{2}=CHY \rightarrow Y \cdot R'\right]
\]

(89)

R = C_{6}H_{5}, CO_{2}C_{2}H_{5}

R' = C_{6}H_{5}, OCH_{3}, OC_{2}H_{5}

Y = \text{CN, CO}_{2}CH_{3}
Sulfonium salts and oxosulfonium salts have alpha C–H bonds which are sufficiently acidic that they may be converted to the corresponding sulfur ylides by treatment with strong bases. There have been several reports concerning the reaction of such the sulfur ylides with acrylic compounds. Corey and his co-worker\(^5^9\) reported a direct approach to the gem-dimethylcyclopropane derivative \(92\) using the reaction of diphenylsulfonium isopropylide \((91)\) with methyl acrylate. The reaction of dimethylsulfonium methylide and ethyl acrylate in dimethyl sulfoxide to afford ethyl cyclopropanecarboxylate has also been reported.\(^7^0\) If substituents that can delocalize negative charge are present at the alpha carbon atom then the sulfur ylides become more stable and can often be isolated. The formation of diethyl 1, 2-cyclopropanedicarboxylate \((94, Y=CO_2C_2H_3)\) or ethyl 2-cyanocyclopropanecarboxylate \((94, Y=CN)\) was achieved\(^7^1\) by allowing equimolar amounts of ethyl (dimethylsulfuranylidene)-acetate \((93)\) and ethyl acrylate or acrylonitrile to react in an aprotic solvent such as dichloromethane at ambient temperature. In both cases the trans-isomer predominated. However, the analogous reaction of \(93\) which was conducted in ethanol solution led not to cyclopropanes but rather to open-chain products of varying complexity.\(^7^2\) For example, the reaction of \(93\) with an excess of ethyl acrylate in ethanol at 30–35°C afforded triethyl 2-pentene-1, 3, 5-tricarboxylate \((95)\) along with triethyl 3-(2-ethoxycarbonylethyl)-1-pentene-1, 3, 5-tricarboxylate \((96)\) with the former predominating. Recently, this kind of reaction has been extended so as to include the case of structurally complex systems containing sulfur ylide moiety. In 1973, Marino and his co-worker\(^7^3\) described that a carbonyl-stabilized allyloxosulfonium ylide \((97)\) react with acrylonitrile to afford a complex cyclopropane derivative \((98)\). Dimethylsulfonium 3-methoxycarbonylallylide \((99)\), prepared from the corresponding sulfonium bromide and NaH, reacted with methyl acrylate to afford cis-\((100)\) and trans-1-(trans-2-methoxycarbonyl)vinyl-2-methoxycarbonylcyclopropane \((101)\) with the latter predominating.\(^7^4\) Also, a sulfur ylide \((102)\) stabilized by a phosphinyl substituent was reacted with ethyl acrylate at room temperature to give a phosphono-substituted cyclopropane \((103)\).\(^7^5\) It should be noted that a optically active ylide \((104)\) was generated and reacted with methyl acrylate to afford, after hydrolysis, \((+)-(1S, 2S)-trans-2-methylcyclopropanecarboxylic acid \((105)\) with an optical purity of 43\%.\(^7^6\) Hercouet and his co-worker\(^7^7\) have found that a diylide such as \((106)\) also react with methyl acrylate to give a cyclopropane derivative \((107)\) having phosphorus ylide structure. Brule and his co-worker\(^7^8\) studied the reaction of an oxosulfonium ylide \((108)\) with methyl acrylate in dimethyl sulfoxide, where three products, \((109), (110),\) and \((111)\) were isolated. However, when tetrahydrofuran was used as the solvent instead of dimethyl sulfoxide, \((109)\) was the only product isolated.

\[
\begin{align*}
\text{[(C}_6\text{H}_5)_2\text{S}^+\text{C(CH}_3)_2] & + \text{CH}_2=\text{CHCO}_2\text{CH}_3 & \rightarrow & \begin{array}{c}
\text{CO}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_3
\end{array} \\
\text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{CH}_3
\end{align*}
\]

\((91)\)

\[
\begin{align*}
\text{(CH}_3)_2\text{S}^+\text{CHCO}_2\text{C}_2\text{H}_5 & + \text{CH}_2=\text{CHY} & \rightarrow & \text{C}_2\text{H}_5\text{O}_2\text{C} & \begin{array}{c}
\text{Y} \\
\text{CH}_2\text{CH}_2\text{Cl}_2
\end{array} \\
\text{Y} & = \text{CN, CO}_2\text{C}_2\text{H}_5
\end{align*}
\]

\((94)\)
VI. THE RITTER REACTION AND THE TRANSESTERIFICATION

The well known Ritter reaction has been extended to the addition of acrylonitrile to a variety of compounds capable of forming a carbonium ion such as olefinic compounds, hydroxy compounds and, less commonly, aliphatic aldehydes. These reactions are conducted in concentrated sulfuric acid with or without glacial acetic acid as a diluent, and generally the reaction temperature are mild. Tables I and II summarize data in the literature, but some publications are undoubtedly missed.

Numerous acrylic higher esters can be prepared by heating an appropriate higher alcohol with methyl or ethyl acrylate in the presence of a suitable catalyst, followed by drawing off the produced methyl or ethyl alcohol by azeotropic distillation with the starting acrylate or with reaction solvent, if it was used.

\[
\begin{align*}
\text{catalyst} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\text{or} & \\
\end{align*}
\]

\[\text{Table I. The Ritter Reaction of Acrylonitrile with Olefinic Compounds}\]

<table>
<thead>
<tr>
<th>Olefinic compound</th>
<th>Reaction medium</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2=\text{CHCO}_2\text{CH}_3) + ROH</td>
<td>(\text{H}_2\text{SO}_4)</td>
<td>(\text{CH}_2=\text{CHCO}_2\text{R} + \text{CH}_3\text{OH})</td>
</tr>
<tr>
<td>(\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(136)
### Table II. The Ritter Reaction of Acrylonitrile with Hydroxy Compounds and Aldehydes

<table>
<thead>
<tr>
<th>Hydroxy compound or aldehyde</th>
<th>Reaction medium</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₂OH</td>
<td>H₂SO₄</td>
<td>C₆H₅CH₂NHCOCH=CH₂⁸⁹⁷</td>
</tr>
<tr>
<td>(CH₃)₂CHO</td>
<td>H₂SO₄</td>
<td>(CH₃)₂CHNHCOCH=CH₂⁸⁴⁰</td>
</tr>
<tr>
<td>(C₆H₅)₂CHO</td>
<td>H₂SO₄</td>
<td>(C₆H₅)₂CHNHCOCH=CH₂⁸⁸⁸</td>
</tr>
<tr>
<td>(CH₃)₃COH</td>
<td>H₂SO₄+CH₃CO₂H</td>
<td>(CH₃)₃CNHCOCH=CH₂⁸⁰⁸</td>
</tr>
<tr>
<td>C₆H₅C(CH₃)(OH)CH₂CO₂C₂H₅</td>
<td>H₂SO₄</td>
<td>C₆H₅C(CH₃)CH₂CO₂C₂H₅⁹³⁹</td>
</tr>
<tr>
<td>CH₃COCH₂C(CH₃)₂OH</td>
<td>H₂SO₄</td>
<td>CH₃COCH₂C(CH₃)₂NHCOCH=CH₂⁹⁸</td>
</tr>
<tr>
<td>CH₃COCH₂C(CH₃)₂OH³¹</td>
<td>H₂SO₄</td>
<td>CH₃COCH₂C(CH₃)₂NHCOCH=CH₂⁹₈</td>
</tr>
<tr>
<td>C₆H₅COCH₃</td>
<td>H₂SO₄</td>
<td>C₆H₅COCH₂C(CH₃)₂NHCOCH=CH₂⁹₅</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>H₂SO₄</td>
<td>CH₃COCH₂C(CH₃)₂NHCOCH=CH₂⁹₵</td>
</tr>
<tr>
<td>(C₆H₅CH₂OH)Cr(CO)₃</td>
<td>H₂SO₄</td>
<td>(C₆H₅CH₂NHCOCH=CH₂)Cr(CO)₉³⁴</td>
</tr>
<tr>
<td>C₆H₅COCH₃</td>
<td>H₂SO₄</td>
<td>C₆H₅COCH₂C(CH₃)₂(C₆H₅)NHCOCH=CH₂⁹₄</td>
</tr>
<tr>
<td>CH₂O</td>
<td>H₂SO₄</td>
<td>(CH₃=CHCONH)₂CH₃⁹₴</td>
</tr>
<tr>
<td>CCl₃CHO</td>
<td>H₂SO₄</td>
<td>(CH₃=CHCONH)₂CH₂CCl₃⁹₴</td>
</tr>
</tbody>
</table>

a) Acetone can be also used instead of diacetone alcohol.⁹³¹

As shown in Tables III and IV, a variety of catalysts have been employed in this transesterification.

### VII. SUMMARY

From the foregoing review of the use of acrylic compounds in organic synthesis, it will be seen that the main emphasis has lain in synthetic work, both in the preparation of the useful compounds and in their use as intermediates for further synthesis. There remains, however, large areas of the synthetic chemistry of these compounds, particularly regarding their cycloaddition and dimerization etc., which will latter be described in this bulletin.
Table III. The Reaction of Methyl or Ethyl Acrylate with Some Amino Alcohols

<table>
<thead>
<tr>
<th>R in ROH and CH₂=CHCO₂R</th>
<th>Catalyst used</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂N(CH₂)₄CH(R⁺)⁻</td>
<td>ZnCl₂, Zn(O₂CCH₃)₂, Zn(C₂H₅)₂</td>
</tr>
<tr>
<td>R⁺=CH₃, C₂H₅, n-C₆H₁₃</td>
<td></td>
</tr>
<tr>
<td>n=1, 2</td>
<td></td>
</tr>
<tr>
<td>(CH₂)₂N(CH₂)₃⁻</td>
<td>CaO, Ca(OH)₂</td>
</tr>
<tr>
<td>R⁺=CH₃, C₂H₅, n-C₆H₁₃</td>
<td></td>
</tr>
<tr>
<td>R⁺=CH₃, C₂H₅</td>
<td></td>
</tr>
<tr>
<td>(CH₂)₂NCH₂CH₂-(n-C₄H₉)₂Sn(O₂CCH₃)₂</td>
<td>Al(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>R⁺=CH₃, C₂H₅</td>
<td></td>
</tr>
<tr>
<td>(CH₂)₃CNHCH₂CH₂-</td>
<td></td>
</tr>
<tr>
<td>(CH₂)₃CNHCH₂CH₂CH(CH₃)-</td>
<td></td>
</tr>
<tr>
<td>CH₅CH₂CH₂C(CH₃)₂NHCH₂CH₂-</td>
<td></td>
</tr>
<tr>
<td>CH₅CH₂CH₂C(CH₂)₂NHCH₂CH₂CH(CH₃)-</td>
<td></td>
</tr>
</tbody>
</table>

Table IV. The Reaction of Methyl or Ethyl Acrylate with Numerous Hydroxy Compounds other than Amino Alcohols

<table>
<thead>
<tr>
<th>R in ROH and CH₂=CHCO₂R</th>
<th>Catalyst used</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₃CH(C₂H₅)CH₂-</td>
<td>TiOCH₂C₅H₅NO₃</td>
</tr>
<tr>
<td>(CH₂)₄C(OCH₂)₄CH₂CH(CH₃)-</td>
<td>p-CH₃C₆H₄SO₂H</td>
</tr>
<tr>
<td>n-C₆H₁₃⁻</td>
<td>p-CH₃C₆H₄SO₂H, BaO, TiO₂, (\text{KU} \frac{2}{8} \text{cation exchanger})</td>
</tr>
<tr>
<td>Straight and branched</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>higher alkyl ((C₃-2₅))</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>Straight and branched</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>higher alkyl ((≥C₆))</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>Straight and branched</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>higher alkyl</td>
<td>Ti(O-iso-C₃H₇)₄</td>
</tr>
<tr>
<td>([\text{CH₃CHO}]_{2p}(O)\text{CH}_2-)</td>
<td>Ca (β)-diketone-chelated catalyst</td>
</tr>
<tr>
<td>CH₂=C(CH₃)₂-</td>
<td>Fe acetylacetonate</td>
</tr>
<tr>
<td>R⁺CO₂CH₂CH₂C₈F₂ₙ₊₁ + CH₂=CHCO₂CH₃</td>
<td>p-CH₃C₆H₄SO₂H</td>
</tr>
<tr>
<td>CH₂=CHCO₂CH₂CH₂C₈F₂ₙ₊₁</td>
<td></td>
</tr>
<tr>
<td>R⁺=H, CH₃</td>
<td></td>
</tr>
<tr>
<td>n=1 - 2₃</td>
<td></td>
</tr>
</tbody>
</table>
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