Bull. Inst. Chem. Res., Kyoto Univ., Vol. 62, No. 2, 1984

REVIEW

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

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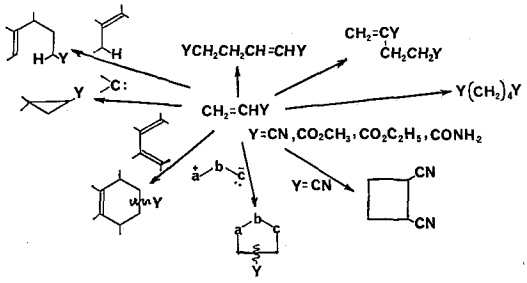
Received April 9, 1984

Almost all reactions using acrylic compounds described in this review belong to either one of the following sections: the formation of linear dimers, the formation of branched dimers, the formation of hydrogenated linear dimers, the formation of cyclic dimer, the reaction with 1, 3-dipoles, the reaction with 1, 3-butadienes and with related compounds, the thermal addition to olefins having an allylic hydrogen, and the miscellaneous reactions. This review together with the preceding review[1] will cover the greater part of the previously reported reaction using acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide.

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

I. INTRODUCTION

As described in the preface of the preceding review,[1] some acrylic compounds such as acrylonitrile, methy and ethyl acrylate, and acrylamide are easily made from very cheap raw materials, *viz.*, propylene, acetylene, ammonia, carbon monoxide, and methyl and ethyl alcohol. Accordingly, it seems worthwhile idea to make use of these cheap acrylic compounds as the starting substrates in organic synthesis. A better understanding of the previously reported organic reactions in which these acrylic compounds participate will serve to realize this idea. Thus, the prime objective of the preceding and this reviews is the presentation of a survey of synthetic methods used in converting these acrylic compounds into useful, or at least usable products other than high-polymers. The preceding review dealt with reaction of the acrylic compounds which seem to belong to the following sections: the reaction with the compounds pos-



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sessing 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. This review involves the remaining area of the synthetic chemistry of the acrylic compounds, which are schematically outlined above.

II. THE FORMATION OF LINEAR DIMERS

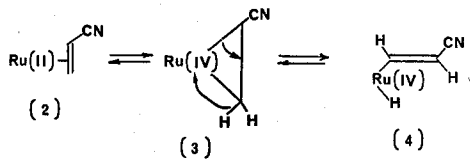
Misono and his co-workers[2,3] have reported that a ruthenium complex, $RuCl_2 \cdot (CH_2=CHCN)_3$, prepared by interaction of an ethanolic solution of $RuCl_3 \cdot 3H_2O$ with excess acrylonitrile, catalyzes the conversion of acrylonitrile under an elevated pressure of hydrogen to a mixture of propionitrile, *cis*- and *trans*-1, 4-dicyano-1-butene (**1**), and adiponitrile, where the former two of them are the main products.

$$2CH_2=CHCN \xrightarrow{RuCl_2(CH_2=CHCN)_3,\ H_2} \begin{cases} \textit{cis}\text{- and } \textit{trans}\text{-}NCCH_2CH_2CH=CHCN \quad (\mathbf{1}) \\ C_2H_5CN \\ NC(CH_2)_4CN \end{cases}$$

Subsequently, it was observed by McClure and his co-workers[4] that an analogous ruthenium complex, $RuCl_2(CH_2=CHCN)_4$ also catalyze the dimerization of acrylonitrile in the presence of hydrogen and that the reaction is affected significantly by tertiary amines such as *N*-methylpyrrolidine. Thus, the presence of the amine produces a 2 to 3-fold increase in the yield of **1**. Besides $RuCl_2(CH_2=CHCN)_4$, various other catalysts for this reaction have been recommended; $RuCl_3 \cdot 3H_2O$, $RuCl_2 \cdot [P(C_6H_5)_3]_3$, $RuCl_2[P(C_6H_5)_3]_2(CH_2=CHCN)_2$, $RuCl_3[As(C_6H_5)_3]_2(CH_3OH)$, $RuCl_2 \cdot [Sb(C_6H_5)_3]_4$, and $Ru(OCOCH_3)_2[P(C_6H_5)_3]$.[4] However, the highest yield of **1** is obtained with $RuCl_2(CH_2=CHCN)_3$ or with $RuCl_2(CH_2=CHCN)_4$ in which three or four bonded acrylonitrile molecules are contained. In those days, several patents on the dimerization of acrylonitrile using analogous ruthenium complexes were obtained independently by some other chemists.[5] In recent years, a wide variety of catalysts including the above ruthenium complexes have been employed for the dimerization. For example, the reaction under a hydrogen atmosphere is conducted in *N, N*-dimethylformamide in the presence of one of the catalysts such as $Ru_2(OCOR)_4Cl$ ($R=CH_3$, n-C_3H_7, C_6H_5),[6] $RuCl_3$ plus *p*-nitrobenzonitrile,[7] $RuCl_3$ plus $Bi(C_6H_6)_3$,[8] and $RuCl_3$ plus $Zn(OCOCH_3)_2$,[9] or in an aqueous solution of $Ru(OCOCH_3)_2OH \cdot H_2O$,[10] $RuCl_3[P(C_6H_5)_3]$,[10] or $Ru(OH)_3$.[11] The reaction is also performed in the gas phase over the following catalysts on Al_2O_3: Bi_2O_3,[12] ruthenium metal,[13] a complex which is prepared by treating RuX_3 ($X=Cl$, Br) (or their hydrates) with triarylphosphine such as $P(C_6H_5)_3$, $P(o\text{-}ClC_6H_4)_3$, $P(m\text{-}CH_3C_6H_4)_3$, $P(p\text{-}CH_3OC_6H_4)_3$, or $P(p\text{-}C_6H_5OC_6H_4)_3$, and by blowing O_2 into the reaction product in benzene,[14] a mixture comprising $RuCl_3$, $HAuCl_4$, $As(C_6H_5)_3$, and complexes among them,[15] a mixture of $Au[As(C_6H_5)_3]Cl$, $Mo[As(C_6H_5)_3](CO)_3$, and $AsCl_3$.[16] Besides, the use of trivalent phosphorus compounds such as $RP(OR')(R'')$,[17] $R_2P \cdot$

(OR'),[17,19~22] or $RP(OR')_2$[17,18,20,21] (R=aromatic nucleus substituted by an electron-donating substituent or, in rare cases, unsubstituted aromatic nucleus; R′=alkyl or cycloalkyl; R″=unsubstituted aromatic nucleus) as the catalyst for the dimerization is described, where the reaction is mostly performed in a mixture of an alcohol capable of donating protons and an inert hydrocarbon.[17,19~22] The acrylonitrile in such the solvents is pretreated with a scavenging reagent[17,22] [for example, $C_6H_5P(O)(OR)_2$, R=alkyl or cycloalkyl] before being contacted with the catalyst, resulting in the formation of the objective dimer **1** in a better yield. The dimerization can also be achieved by the employment of trialkyl phosphite such as $P(OC_2H_5)_3$ in toluene containing a small amount of ethyl alcohol.[23]

As described[4] in the beginning of this section, the dimerization of acrylonitrile under an elevated pressure of hydrogen and under a catalytic action of the ruthenium complex such as $RuCl_2(CH_2=CHCN)_4$ leading to **1** together with propionitrile and adiponitrile is affected significantly by such additives as *N*-methylpyrrolidine. Further, Billig and his co-workers[24] reported the effect on a $RuCl_3\cdot 3H_2O$-catalyzed reaction of adding $(C_2H_5)_4NSnCl_3$ (or $SnCl_2$) together with bifunctional amines such as *N*-methylmorpholine, and/or bifunctional alcohols such as Methylcellosolve. The result of inclusion of these compounds is a lowering of the minimum hydrogen pressure requirement by a factor of *ca.* 4 (under the same temperature conditions as the analogous high-pressure dimerization). They also suggested[24] that, in this low-pressure reaction, the solvent is functioning as a bridging ligand and a possible inner-sphere oxidative addition mechanism may be operative. A path that is consistent with the accumulated data obtained in the low-pressure reaction under a deuterium atmosphere is presented.[24] The path involves the formation of a catalytic species (**4**) by transition-metal insertion into a vinylic carbon-hydrogen bond of acrylonitrile, the reaction of **4** with acrylonitrile affording **5**, and that of **5** with acrylonitrile giving **1** and **2**.



(2) (3) (4)

$$4 + CH_2=CHCN \longrightarrow \underset{(5)}{NCCH_2CH_2-Ru(IV)-CH=CHCN} \xrightarrow{CH_2=CHCN} \mathbf{1} + \mathbf{2}$$

The research upon the dimerization of methyl and ethyl acrylate leading to dimethyl and diethyl 2-hexanedioate has been initiated prior to the analogous research using acrylonitrile above-mentioned. The linear dimerization of methyl acrylate has been accomplished[25] for the first time by the use of $RhCl_3\cdot 3H_2O$ and $RuCl_3\cdot 3H_2O$. Thus, a high yield of dimethyl 2-hexenedioate (**6**) was obtained by heating a solution

$$2CH_2=CHCO_2CH_3 \xrightarrow[CH_3OH]{RhCl_3\cdot 3H_2O \text{ or } RuCl_3\cdot 3H_2O} CH_3O_2CCH_2CH_2CH=CHCO_2CH_3 \quad (\mathbf{6})$$

of methyl acrylate in methyl alcohol in the presence of $RhCl_3 \cdot 3H_2O$ or $RuCl_3 \cdot 3H_2O$ in a pressure vessel. A mixture of $AgBF_4$ and either one of such palladium complexes as L_2PdCl_2 and $[LPdCl_2]_2$, in which $L=P(C_6H_5)_3$ or $P(n\text{-}C_4H_9)_3$, also catalyze the dimerization of methyl acrylate, where **6** and dimethyl 3-hexenedioate (**7**) are produced in yields of 96–99 and 1–4%, respectively.[26] However, the employment of $(C_6H_5CN)_2 \cdot PdCl_2$ along with $AgBF_4$ instead of the above palladium complex containing $AgBF_4$ gave, in addition to **6** (48–88%), substantial amounts of the latter olefinic diester **7** (12–52%).[26] In the case with $(C_6H_5CN)_2PdCl_2$ alone, the formation of **7** is found[27] to be predominant with decreasing yield of the desired **6**.

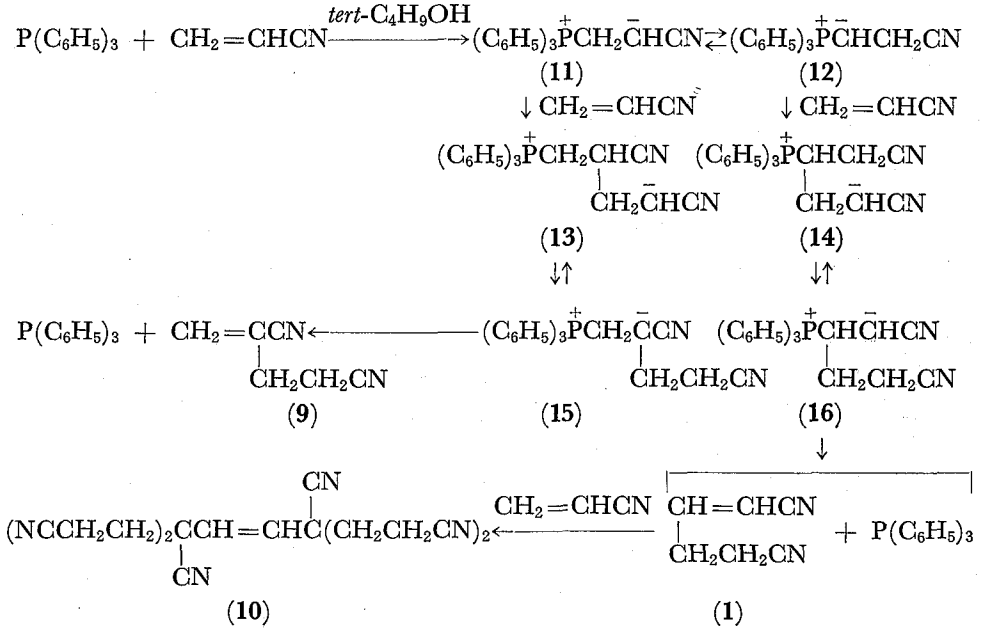
$$2CH_2=CHCO_2CH_3 \xrightarrow{(C_6H_5CN)_2PdCl_2} \left[\begin{array}{l} \mathbf{6} \\ CH_3O_2CCH_2CH=CHCH_2CO_2CH_3 \\ \quad\quad (\mathbf{7}) \end{array}\right.$$

The preparation of *trans*-2-hexenediamide (**8**) by dimerization of acrylamide is effected[28] smoothly by heating acrylamide in an alcoholic solution in the presence of $RhCl_3 \cdot 3H_2O$.

$$2CH_2=CHCONH_2 \xrightarrow[n\text{-}C_4H_9OH]{RhCl_3 \cdot 3H_2O} \underset{(\mathbf{8})}{H_2NCOCH_2CH_2\diagdown CH=CH\diagup CONH_2}$$

III. THE FORMATION OF BRANCHED DIMERS

The branched dimer of acrylonitrile, 2-methyleneglutaronitrile (**9**), is produced by α to β coupling of the monomer. In the course of years, the compound **9** has acquired a wide technical use for the preparation of chemicals, drugs, heat resistant varnishes, polyesters, and polyamides.[5] Among these the most important use is in the



preparation of a solvent having useful characteristics, 2-methylglutaronitrile, *via* hydrogenation of **9**.[5] In the process developed and used by U.S. Industrial Chemical Co., Inc., a trivalent phosphorus compound is used as the catalyst for technical production of **9** from acrylonitrile.[5] In 1965, Baizer and Anderson[29] have found that the triphenylphosphine-catalyzed reaction of acrylonitrile in the presence of *tert*-butyl alcohol as a proton donor give **9** and *cis*- and *trans*-1, 4-dicyano-1-butene (**1**) together with a small amount of a hexamer of acrylonitrile (**10**). They also proposed[29] such a mechanism as is shown in the above equations in which acrylonitrile reacts with triphenylphosphine in two ways; one way reveals that the intermediate betaine **13**, produced by the addition of acrylonitrile to the initially formed betaine **11**, transfer a proton forming **15** which can be converted to **9** with the release of triphenylphosphine, and the other way involves the addition of acrylonitrile to the intermediate phosphorus ylide **12** arising from proton-transfer of **11** giving **14**, the formation of **16** by a further proton-transfer, and that of **1** with the release of triphenylphosphine, as well as the further conversion of **1** into **10**.

The proposed mechanism is in apparent contradiction to the earlier mechanistic interpretation[30] that under specified conditions triphenylphosphine (with ethy lalcohol) converts acrylonitrile to **10** presumably *via* the intermediate 1, 4-dicyano-2-butene. Thus, they further presented[29] an unambiguous evidence supporting that the mechanism proposed by them is correct and **10** is formed *via* **1**. The dimerization which takes place when tributylphosphine or tricyclohexylphosphine is used instead of triphenylphosphine yields preferentially **9** together with a small amount of or none of **1**. Presumably, the initially formed betaines in these reactions do not undergo ready conversion to the corresponding ylides. When a solution of triphenylphosphine, ethyl acrylate, and *tert*-butyl alcohol kept at 40°C over a 2-week period, a preponderant amount of diethyl 2-methyleneglutarate was formed together with a very small quantity of diethyl *trans*-2-hexenedioate.[29] According to their opinion,[29] these results, when considered in conjunction with those described above for acrylonitrile, suggest that in the equilibrium $(C_6H_5)_3\overset{+}{P}CH_2\overset{-}{C}HR \leftrightarrows (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2R$ carbethoxy ($R=CO_2C_2H_5$) in competition with triphenylphosphonium is much more able to stabilize an α-carbanion than is cyano($R=CN$) in competition with triphenylphosphonium. In addition to triphenyl-, tributyl-, and tricyclohexylphosphine above mentioned, a variety of trivalent phosphorus compounds such as PR_3 [$R=C_2H_5$,[31] OCH_3,[31] $N(C_2H_5)_2$,[31] cyclopentyl,[32] cycloheptyl,[32] or cyclooctyl[32]], $C_6H_5PR_2$[33] [$R=n$-C_4H_9, $CH_3(CH_2)_7$, or cyclohexyl], $P[N(CH_2CH=CHR)_2]_n(NR'_2)_{3-n}$[34] ($R=H$, CH_3; $R'=C_{1-12}$ straight-chain alkyl or alkenyl or R'_2N=polymethyleneamino; $n=1$–3), $P[N(CH_2CH=CHR)R']_3$[34] (R, R′ have almost same significance), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$,[31] and cross-linked polystyrenes[35] containing $-(CH_2)_nPR_2$ moiety ($R=C_6H_5$, C_2H_5, or cyclohexyl; $n=0$ or 3) as a pendant group are used for the dimerization of acrylonitrile affording **9** or its mixture with **1**. Catalysts prepared by depositing either triphenylphosphine oxide or $(C_6H_5)_2P(OCH_3)$ on SiO_2 are also used,[36] but the use of the latter one results in the formation of considerable amounts of **1** in addition to the objective **9**. Watanabe and Takeda[37,38] have initially found that acrylonitrile is easily converted to **9** together with a small amount of 2, 4, 6–

$$2CH_2{=}CHCN \xrightarrow{\text{Metal halide + Tertiary amine}} \underset{\textbf{(17)}}{\overset{\textbf{9}}{CH_2{=}CCN\,|\,CH_2CHCN\,|\,CH_2CH_2CN}}$$

tricyano-1-hexene (**17**) by a binary catalyst comprising a metal halide such as $CoCl_2$, $ZnCl_2$, $ZnBr_2$, ZnI_2, $FeCl_2$, $AlCl_3$, $CdCl_2$, or $TiCl_4$ and a trialkylamine such as triethylamine or tripropylamine. It has also been proposed[38] that catalytic activities of the metal halides in the reaction decrease in the series the meatl=Co (II)≥Zn (II) >Fe (II)>Al (III)>Cd (II)>Ti (IV) and in the series the halogen=I>Br>Cl and that triethylamine is most effective among trialkylamines. In such the process, the employment of $Co(OSO_2CF_3)_2$,[39] $Zn(OSO_2CF_3)_2$,[39] $Co(OCOCF_3)_2$,[40] $Zn(OCOCF_3)_2$,[40] or $Zn[OSO_2C_6H_4CH_3(\text{-}p)]_2$[40] instead of the above metal halide and that of *N*, *N*-diethylaniline[40,41] or *N*-methylpiperidine[41] as the tertiary amine are also recommended. The other method[42] of dimerizing acrylonitrile to **9** involves the use of a binary catalyst system of copper (II) acetylacetonate and *tert*-butyl isocyanide or cyclohexyl isocyanide in the presence of a mixture of *tert*-butyl alcohol and acetonitrile. Besides copper (II) acetylacetonate, the acetylacetonates of Fe (II and III) and Co (II and III) in combination with such the isocyanide and the alcohol are also active in the acrylonitrile dimerization. It was further observed[42] that, in the presence of *tert*-butyl alcohol and acetonitrile, a binary catalyst system consisting of Cu_2O and cyclohexyl isocyanide catalyze the dimerization of methyl acrylate leading to dimethyl 2-methyleneglutarate (**18**, R=CH_3), but the yield is low. Also, such the binary catalyst comprising Cu_2O and cyclohexyl isocyanide accelerate the codimerization of methyl *trans*-2-butenoate (**20**) with methyl acrylate and that of 2-butenenitrile (a mixture of *cis*- and *trans*-isomer) (**22**) with acrylonitrile leading to the formation of dimethyl 3-pentene-1, 3-dicarboxylate (**21**) and 1, 3-dicyano-3-pentene (**23**), respectively.[43]

$$\underset{\textbf{(20)}}{\textit{trans}\text{-}CH_3CH{=}CHCO_2CH_3} + CH_2{=}CHCO_2CH_3 \longrightarrow \underset{\textbf{(21)}}{CH_3CH{=}CCO_2CH_3\,|\,CH_2CH_2CO_2CH_3}$$

$$\underset{\textbf{(22)}}{\textit{cis}\text{- and }\textit{trans}\text{-}CH_3CH{=}CHCN} + CH_2{=}CHCN \longrightarrow \underset{\textbf{(23)}}{CH_3CH{=}CCN\,|\,CH_2CH_2CN}$$

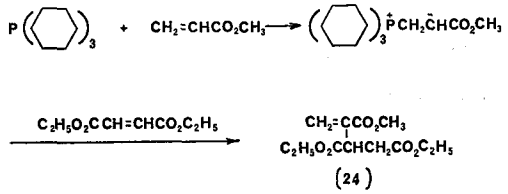
Based on the experience of Baizer and Anderson[29] with the dimerization of ethyl acrylate utilizing triphenylphosphine and *tert*-butyl aclohol, a patent is obtained by McClure[44] in which tributylphosphine in combination with *tret*-butyl alcohol is adopted. The cross-linked polystyrenes[35] containing -$(CH_2)_nPR_2$ moiety (R=C_6H_5, C_2H_5, or cyclohexyl; n=0 or 3) as a pendant group, as well as the binary catalysts[41] consisting

of $AlCl_3$ or $ZnCl_2$ and *N*, *N*-dimethylaniline or *N*-methylpiperidine, both of which have already been described in the case of dimerization of acrylonitrile, also seem to serve as the catalyst for the dimerization of methyl and ethyl acrylate. However, the following compounds appear to be more effective catalysts for the dimerization: $P[N(iso\text{-}C_3H_7)CH_3]_3$,[45] $P[N(CH_2CH=CHR)_2]_n(NR'_2)_{3-n}$[46] (R=H, CH_3; R′=C_{1-12} alkyl or NR'_2=piperidino; n=1–3), $P[N(CH_2CH=CHR)R']_3$[46] (R=H, CH_3; R′=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9), zinc (II) acetylacetonate in combination with tricyclohexylphosphine, $P[N(C_2H_5)_2]_3$, or n-$C_4H_9P[N(C_2H_5)_2]_2$,[47] $(C_2H_5)_2NP(R)R'$[48] [R=$N(C_2H_5)_2$, C_2H_5, C_2H_5O; R′=$N(C_2H_5)_2$, C_2H_5, C_2H_5O, $C(CH_3)_3$, NCO, CN, $Si(CH_3)_3$], an adduct of tricyclohexylphosphine and CS_2 in the presence of $ZnCl_2$,[49] tris(hexahydro-1*H*-azepin-1-yl)phosphine,[50] $RP[N(R')R'']_2$[51] (R=C_{1-18} alkyl or phenyl group which is optionally substituted with C_{1-8} alkyl group; R′ and R″ are each C_{1-18} alkyl groups or form together with the adjacent N atom a saturated cyclic amino group containing optionally C_{1-6} alkyl substituents, but both R′ and R″ are bonded to the N atom by a primary C atom), $R_2PN(R')R''$[51] (R, R′, and R″ have same significance), and $P[N(n\text{-}C_3H_7)_2]_3$.[52] In most experimental examples using these catalysts, the formation of trimer of methyl acrylate and that of ethyl acrylate, dimethyl 2-methylene-4-carbomethoxypimelate (**19**, R=CH_3) and diethyl 2-methylene-4-carbethoxypimelate (**19**, R=C_2H_5) respectively, is recognized as a minor product.

$$2CH_2=CHCO_2R \xrightarrow{\text{Trivalent phosphorus compound}} \begin{array}{l} CH_2=C(CH_2CH_2CO_2R)CO_2R \quad (\mathbf{18}) \\ CH_2=C(CH_2CH(CH_2CH_2CO_2R)CO_2R)CO_2R \quad (\mathbf{19}) \end{array}$$

R=CH_3, C_2H_5

When diethyl fumarate was added to a reaction system comprising tricyclohexylphosphine and methyl acrylate, the main product was not dimethyl 2-methyleneglutarate (**18**, R=CH_3) but methyl diethyl 1-butene-2,3,4-tricarboxylate (**24**),[53] proving that diethyl fumarate is more electrophilic than methyl acrylate. The formation of such a codimer, triethyl 1-butene-2,3,4-tricarboxylate, by the reaction of diethyl maleate with ethyl acrylate in the presence of tributylphosphine was found independently by Ito and Kimura.[54] They have described that several trivalent and



pentavalent phosphorus compounds such as triethylphosphine, trihexylphosphine, hexaethylphosphoric triamide, *N,N,N′,N′*-tetrabutyl-*P*-ethylphosphoric diamide, etc. are also effective for such the codimerization.[54]

IV. THE FORMATION OF HYDROGENATED LINEAR DIMERS

For a long time many experimentations were done on the preparation of adiponitrile (**25**) by the hydrodimerization of acrylonitrile. However, none of the high-yielding procedures was found. In 1954, an important new development in this field was made by Knunyants and Vyazankin.[55] They demonstrated that, when acrylonitrile in 20% HCl was contacted with a K amalgam, **25** is produced in 60% yield and also that the reaction proceeds *via* coupling of initially formed cyanoethyl radicals.[5]

$$CH_2{=}CHCN + e + H^+ \longrightarrow [\cdot CH_2CH_2CN] \longrightarrow NC(CH_2)_4CN$$
(**25**)

This original idea has been worthy of remark among many chemists and chemical engineers because it may be applicable for industrial production of **25**. Subsequently, many informations concerning the preparation of **25** have been published describing a modified method capable of increasing the yield of **25**, and most such data are contained in the patent literatures. Instead of 20% HCl, an aqueous solution of quaternary ammonium hydroxide (such as benzyltrimethyl-, tetrabutyl-, phenyltrimethyl-, or cetyltrimethylammonium hydroxide) plus diglyme,[56] an aqueous solution containing tetraethylammonium *p*-toluenesulfonate,[57] a *N, N*-dimethylformamide-water mixture with benzyltriethylammonium chloride,[58] a mixture of water and *N, N*-dimethylacetamide with dimethylpropylphenylphosphonium chloride,[59] and any one of polar organic solvents such as *N, N*-dimethylformamide, formamide, *N, N*-dimethylacetamide, and *N*-methyl-2-pyrrolidone containing a small proportion of water and tetraethylammonium *p*-toluenesulfonate[60] have been found to be available. Thus, **25** was produced in 80-90% or more yield, where a Na amalgam was mainly employed in place of the K amalgam.[56,58~60] The mechanistic aspects of the hydrodimerization in the presence of the above-quoted onium salts are different from those of the hydrodimerization in 20% HCl. The mechanism of the former reaction using onium salts is believed to be analogous[61] to that of electrohydrodimerization of acrylonitrile which will be subsequently described. The electrohydrodimerization of acrylonitrile giving **25** was initially found by Baizer.[62] He has described[62] that the

$$CH_2{=}CHCN \longleftrightarrow [\overset{+}{C}H_2{-}\overset{-}{C}H{-}C{\equiv}N \longleftrightarrow \overset{+}{C}H_2{-}CH{=}C{=}\overset{-}{N}]$$
(**26**)
$$\downarrow e$$
$$[:CH_2{-}\underset{\cdot\cdot}{C}H{-}CN]^{--} \xleftarrow{e} [\cdot CH_2{-}\underset{\cdot\cdot}{C}H{-}CN]^{-}[R_4N]^{+}$$
(**28**) (**27**)
$$\downarrow H_2O$$
$$[:CH_2{-}CH_2{-}CN]^{-} \xleftarrow{e} [\cdot CH_2{-}CH_2{-}CN] + OH^- \quad R{=}C_2H_5, \text{ etc.}$$
(**30**) (**29**)

$$\left[\begin{array}{l} \mathbf{28} + 2H_2O \longrightarrow C_2H_5CN + 2OH^- \\ \mathbf{28} + CH_2{=}CHCN \longrightarrow [NC\ddot{C}HCH_2CH_2\ddot{C}HCN]^- \xrightarrow{2H_2O} \mathbf{25} + 2OH^- \end{array}\right.$$

$$\left[\begin{array}{l} \mathbf{30} + H_2O \longrightarrow C_2H_5CN + OH^- \\ \mathbf{30} + CH_2{=}CHCN \longrightarrow [NC\ddot{C}HCH_2CH_2CH_2CN]^- \xrightarrow{H_2O} \mathbf{25} + OH^- \end{array}\right.$$

electrolysis of acrylonitrile in aqueous tetraethylammonium *p*-toluenesulfonate at Pb or Hg cathode and at controlled pH yield **25** in a virtually quantitative yield. This method has been already industrialized by Monsanto Co., Inc. and is now employed satisfactorily for technical production.[5] The probable path proposed by Baizer[62] is indicated in the accompanying equations. However, none of distinctions was given as to whether the actual intermediate is **28** or **30**. Although several investigations were undertaken in order to obtain some mechanistic informations,[61,63] the actual intermediate in the electrohydrodimerization of acrylonitrile is still uncertain. There have been several literatures including patents on recent improvement in the electrohydrodimerization of acrylonitrile. Regarding some additives other than quaternary ammonium salts in the cathodic section or anodic section,[64,65] some effective quaternary ammonium salts other than the initially employed tetraethylammonium *p*-toluenesulfonate,[64~66] a phosphonium salt which can be employed instead of quaternary ammonium salts,[64] some alkali earth metal hydroxides capable of removing inhibitors of electrode reaction,[67] and the utilization of ion-exchange membranes,[66,68] as well as the practical methods for the pretreatment of cathodes,[69,70] many informations are given in literature.

For larger amounts of **25** these methods as mentioned above are used. Small laboratory preparation are, of course, described in the literature. Agnes and his coworkers[71] reported a novel stoichiometric procedure for dimerizing acrylonitrile to **25**, based on the use of powdered Mn and $CoCl_2$ in *N*, *N*-dimethylformamide. The reaction can be represented by the following equation. The employment of powdered

$$2CH_2{=}CHCN + Mn + CoCl_2 + 2H_2O \longrightarrow \mathbf{25} + MnCl_2 + Co(OH)_2$$

Zn or Mg instead of powdered Mn and that of $FeCl_2$, $CoBr_2$, CoI_2, $Co_3(PO_4)_2$, $Co(OCOCH_3)_2$, or CoC_2O_4 in place of $CoCl_2$ are claimed in some patent literatures.[72~74] Another procedure[75] for the hydrodimerization is also proposed, in which a solution of acrylonitrile in isopropyl alcohol containing CuCl is treated with hydrazine hydrate at low temperature.

The hydrodimerization of methyl and ethyl acrylate leading to dimethyl and diethyl adipate (**31**, R=CH_3 and R=C_2H_5) was accomplished[76] by the reaction of these acrylates with a complex derived from CoX_2 (X=Cl, Br, or I) and triphenylphosphine along with powdered Zn in ethyl alcohol plus tetrahydrofuran. The further addition of KI to the reaction mixture resulted in an increase in the yields of these adipates **31**.[76] According to a patent literature,[77] acrylic esters and acrylamide may be similarly converted to the corresponding adipates and adipamide (**32**), respectively, by the hydrodimerization utilizing a K amalgam in formamide containing proper amounts of water and acetic acid. The procedure here may be in a similar

manner as was discussed previously in the hydrodimerization of acrylonitrile with an alkali metal amalgam. The electrohydrodimerization of acrylamide giving **32** is also accomplished[78] by using Hg as the cathode in a aqueous solution of tetraethylammonium *p*-toluenesulfonate.

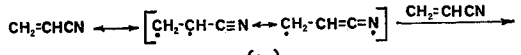
$$2CH_2{=}CHCO_2R \longrightarrow RO_2C(CH_2)_4CO_2R$$
$$R{=}CH_3,\ C_2H_5 \qquad (31)$$
$$2CH_2{=}CHCONH_2 \longrightarrow H_2NCO(CH_2)_4CONH_2 \qquad (32)$$

Recently, the electrochemical hydrodimerization of acrylonitrile or acrylamide giving **25** or **32** has found a useful application[79~82]. Thus, several γ-hydroxynitriles (**33**) were prepared by reductive coupling of acrylonitrile with an aliphatic aldehyde such as formaldehyde, acetaldehyde, or propionaldehyde. In this procedure, an aqueous solution of KH_2PO_4 or of $[(C_2H_5)_4N]_2SO_4$ is used as catholyte and 5% H_2SO_4 or 50% H_3PO_4 as anolyte.

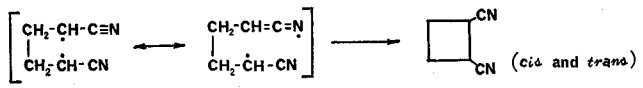
$$RCHO + CH_2{=}CHCN \longrightarrow RCH(OH)CH_2CH_2CN$$
$$R{=}H,\ CH_3,\ C_2H_5,\ n\text{-}C_3H_7 \qquad (33)$$

V. THE FORMATION OF CYCLIC DIMER

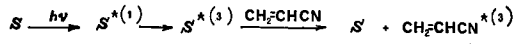
Among the presumable cyclic dimers of acrylic compounds described here, only that of acrylonitrile has been synthesized directly from the monomer. The first synthesis of *cis*- and *trans*-1,2-dicyanocyclobutane (**34**) was accomplished[83] by treating acrylonitrile with or without benzene in a autoclave at temperature over 200°C, but the yield was very low. The reaction is believed to proceed *via* biradical intermediates such as **35** and **36**, as the accompanying equation demonstrates. In 1968, Hosaka and Wakamatsu[84] have found that acrylonitrile dimerize into **34** photochemically in the presence of sensitizers. In a typical example, a solution of acrylonitrile in acetonitrile containing small amounts of benzophenone and aqueous ammonia was irradiated by a high pressure mercury lamp at room temperature. The yield of **34** was approxi-

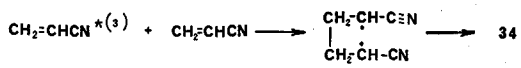


(35)

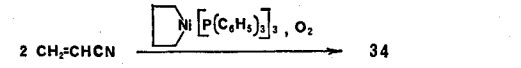


(36) (34) (*cis* and *trans*)

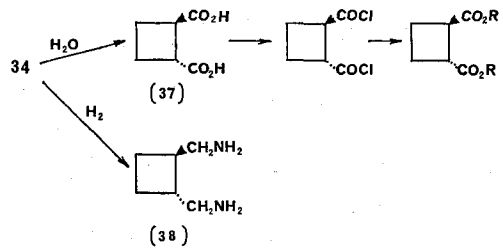




34



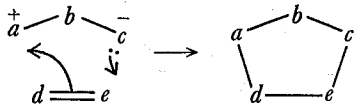
34



mately 10%. In addition to benzophenone, propiophenone, xanthone, acetophenone, benzaldehyde, carbazole, thioxanthone, and 4-phenylbenzophenone are found to be effective as sensitizers. The reaction mode can be represented by the above equation, where the sensitizer is indicated by *S*. Recently, **34** has been prepared[85] in 45% yield by allowing acrylonitrile containing tris(triphenylphosphene)-tetramethylenenickel (II) to warm from −20°C to room temperature over a 48 hr period and treating subsequently the reaction mixture with oxygen. Both hydrolysis and hydrogenation of **34** are accompanied with isomerization to the *trans* form yielding the *trans*-diacid (**37**) and *trans*-diamine (**38**), respectively.[86] These bifunctional compounds have been used for the preparation of a variety of linear condensation polymers containing recurring cyclobutane rings in the backbone.[86]

VI. THE REACTION WITH 1, 3-DIPOLES

As is described by Huisgen,[87] a 1,3-dipole, $\overset{+}{a}$-b-$\overset{-}{\underset{\cdot\cdot}{c}}$ must be defined, such that atom *a* possesses an electron sextet, *i.e.* an incomplete valence shell combined with a positive formal charge, and that atom *c*, the negatively charged center, has an unshared electron pair. Combination of such a 1,3-dipole with a multiple bond system, for example such as $d=c$, termed the dipolarophile, is referred to as a 1,3-dipolar cycloaddition which proceeds in concerted fashion. The two components coalesce by means of a cyclic electron displacement with extinction of the formal charges to give a five-membered ring. Numerous individual examples of such the reaction, in which the double bond of the acrylic compounds described in this review participates, are known. In most cases, the atoms, *a*,*b*, and *c* are restricted to carbon, nitrogen, and oxygen.[87]



$d=e$: $CH_2=CHCN$, $CH_2=CHCO_2CH_3$, $CH_2=CHCO_2C_2H_5$

In rare cases, the reaction of such 1,3-dipoles as contain sulfur as the middle atom, *b*, with the acrylic compounds has been reported (see Table I). Thus, a variety of 1,3-dipoles such as nitrile ylides, nitrile imines, nitrile oxides, diazoalkanes, azides, azomethine ylides, azomethine imines, and nitrones, in which the middle atom, *b*, is nitrogen, have been reported to react with acrylonitrile or methyl and ethyl acrylate to form five-membered heterocycles. Except the heavily substituted derivatives, many of them are short lived *in situ* intermediates which are not stable enough to be isolated. Such

Table I. The Reaction of Acrylic Compounds (Acrylonitrile, Methyl and Ethyl Acrylate) with 1, 3-Dipoles

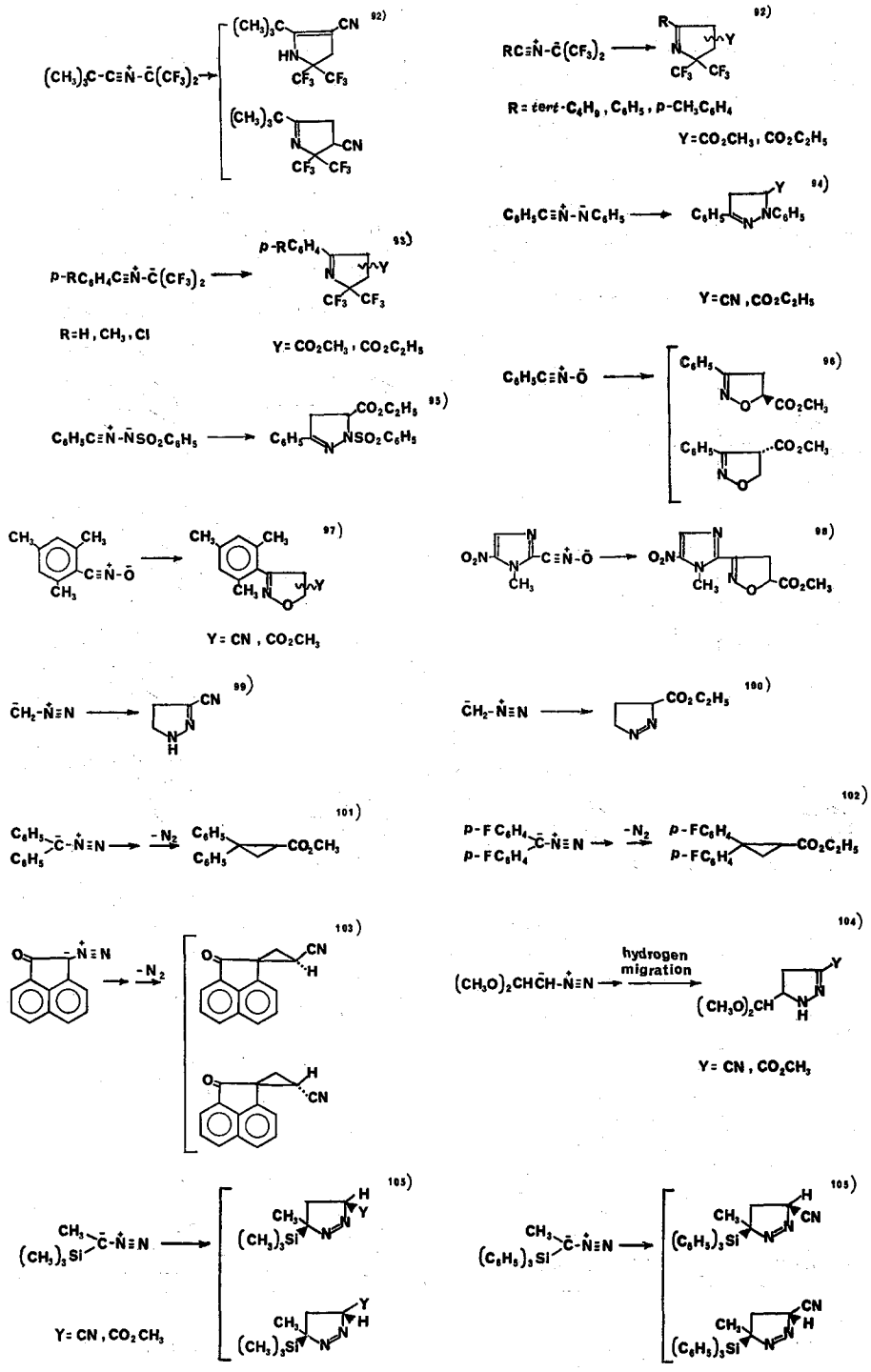


Table I. Continued

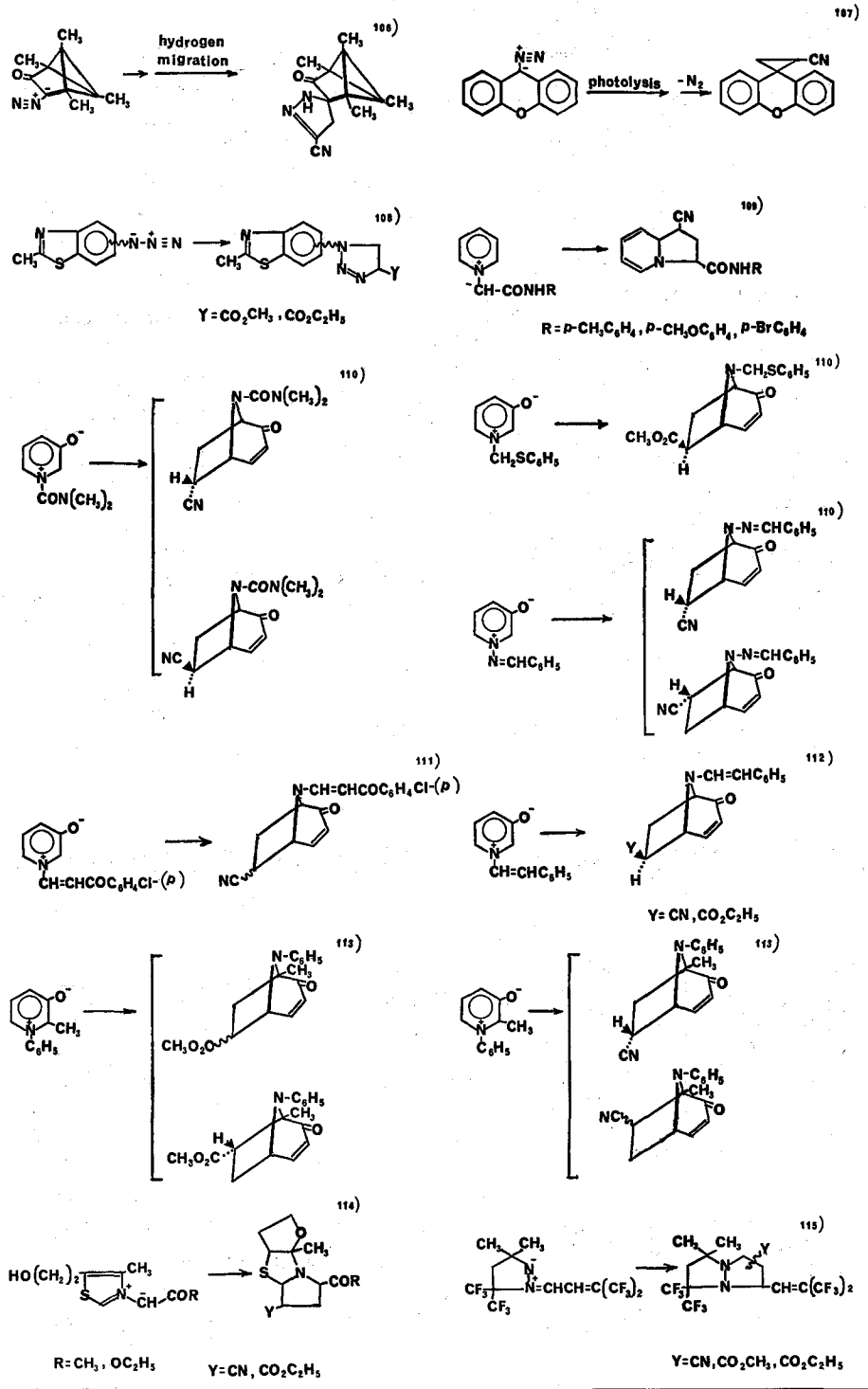
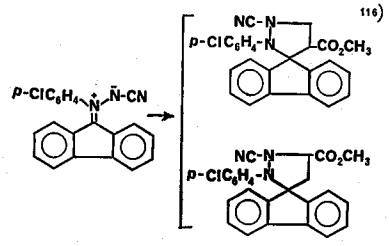
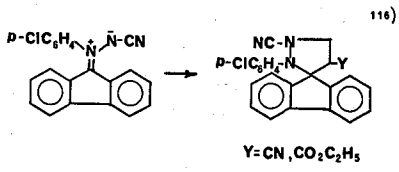
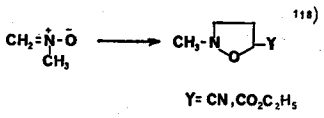
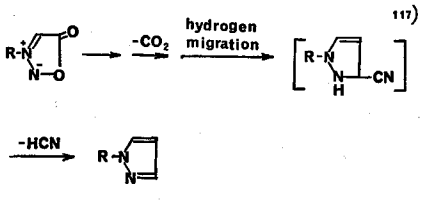


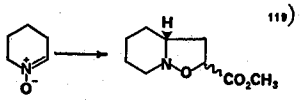
Table I. Continued

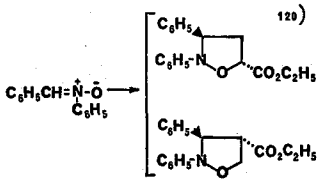


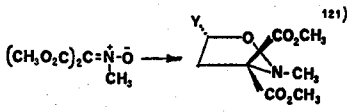


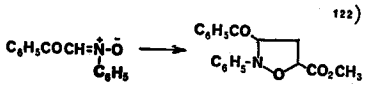


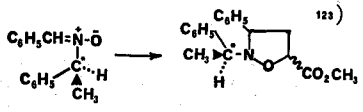


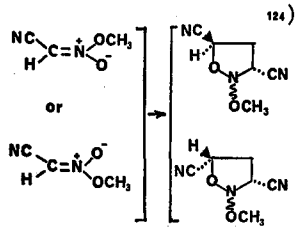


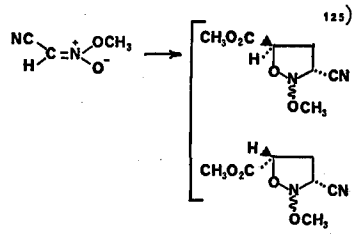


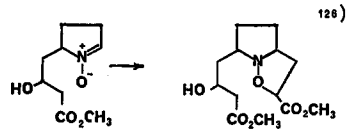


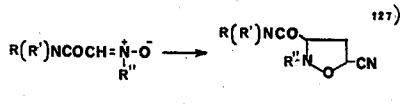








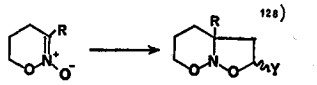




R = H, C_6H_5

R' = C_6H_5, p-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$CH_3COC_6H_4$

R'' = C_6H_5, p-$(CH_3)_2NC_6H_4$



R=CH_3, $COCH_3$, CN, CO_2CH_3, C_6H_5 Y=CN, CO_2CH_3

Table I. *Continued*

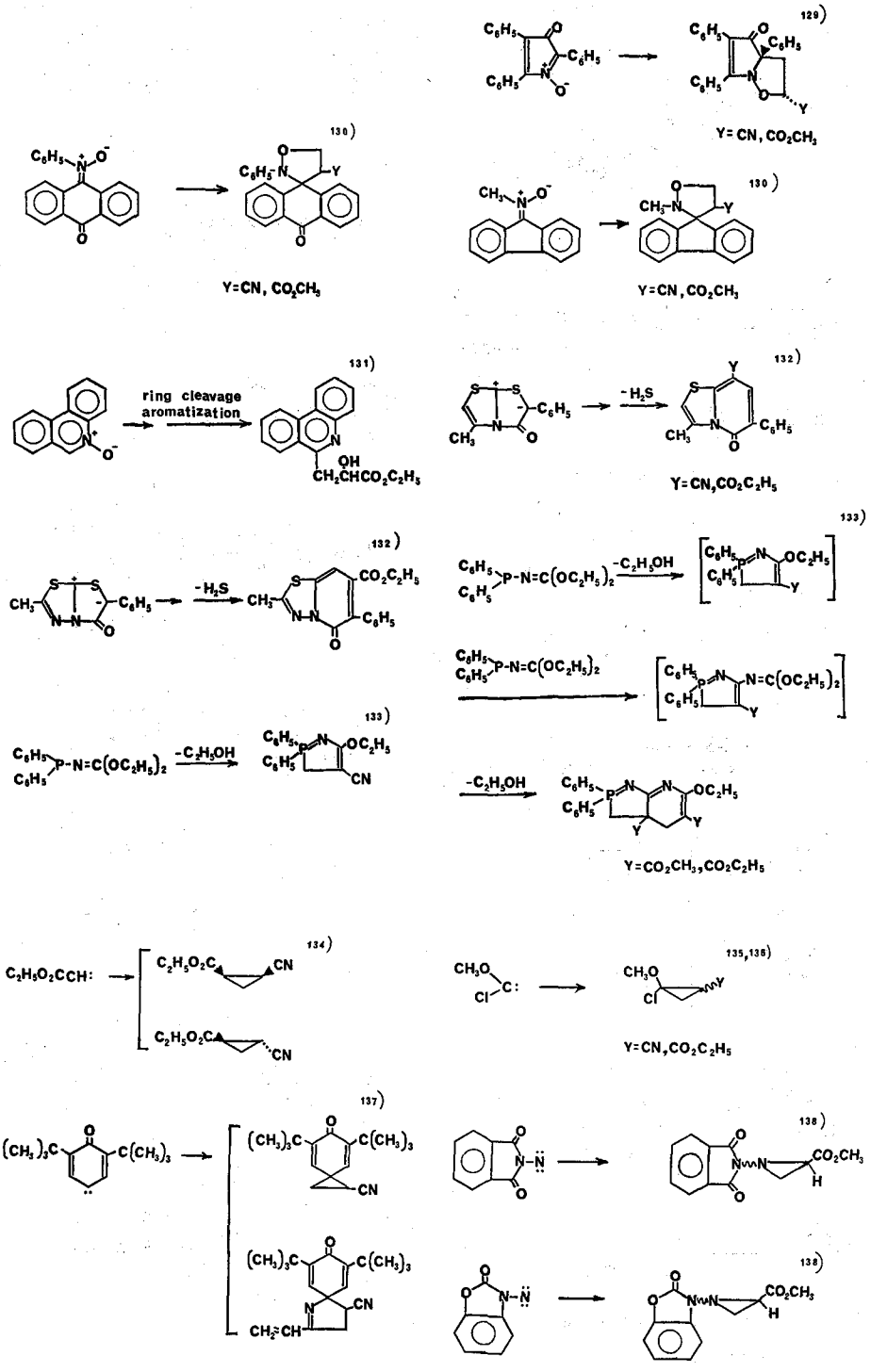
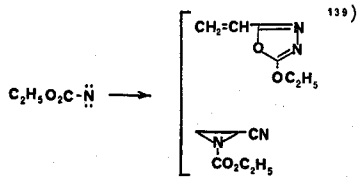


Table I. Continued



[139]

systems must therefore be treated with the acrylic compounds *in situ*. The number of cycloadditions carried out with such the type of 1,3-dipoles together with the acrylic compounds is still modest and hence any attempt at their classification appears to be unjustified. Table I summarized the data in the literature, but some publications are omitted in moderation. The left-hand side of the equations in Table I shows the used 1, 3-dipole without any distinction whether it is an *in situ* prepared intermediate or it were capable of isolation. The right-hand side of the equations gives the obtained products. The comparison of the structure of products with that of the starting 1, 3–dipole will provide the understanding of the used acrylic compound and its role as dipolarophile in the reaction. The description concerning the reaction conditions, which is seen in the cited literatures, is all omitted. In the most frequent cases, the product is a mixture of regio- and/or stereoisomers. In a few example, however, only one product with a single structure is produced, suggesting that the 1, 3-dipolar cycloaddition occurs regio- and stereospecifically due to an appropriate selection of 1, 3–dipole and dipolarophile, as well as reaction conditions. In cases where the initial product is unstable under the given reaction conditions and hence it undergoes transformation leading to any other compound, only the structure of the finally obtained product is shown. For example, the intial products of addition of diazoalkanes are 1-pyrazolines, which often isomerize rapidly to the crorresponding 2-pyrazolines.[87] The evolution of nitrogen giving cyclopropane derivatives also occurs depending on choice of 1, 3-dipole as well as reaction conditions. Frequently the rate of evolution of nitrogen exceeds even that of the addition. As is described by Huisgen,[87] however, there is no reason to postulate a change in mechanism, as long as the rate of addition is greater than that of the decomposition of the diazoalkane. The mechanism of this synthetic route to cyclopropane derivatives *via* pyrazolines must be distinguished from that of the addition of carbenes onto olefinic compounds such as the acrylic compounds[87]; the latter reactions involving the attack of carbenes onto the acrylic compounds are joined to this section and are summarized together in Table I. The experimentally observed regio- and stereoselectivity of these 1, 3-dipolar cycloadditions have been the most difficult phenomena to explain and have remained essentially as an unsolved problem.[87~91] Thus, the role of substituents of 1, 3-dipoles in determining the reaction products is by no means established. However, the small effect of solvent polarity on the ratio of regio- and/or stereoisomeric adducts is generally accepted.

VII. THE REACTION WITH 1, 3-BUTADIENES AND WITH RELATED COMPOUNDS

Table II. The Diels-Alder Reaction of Acrylic Compounds (Acrylonitrile, Methyl and Ethyl Acrylate, and Acrylamide) with 1, 3-Butadienes and with Related Compounds

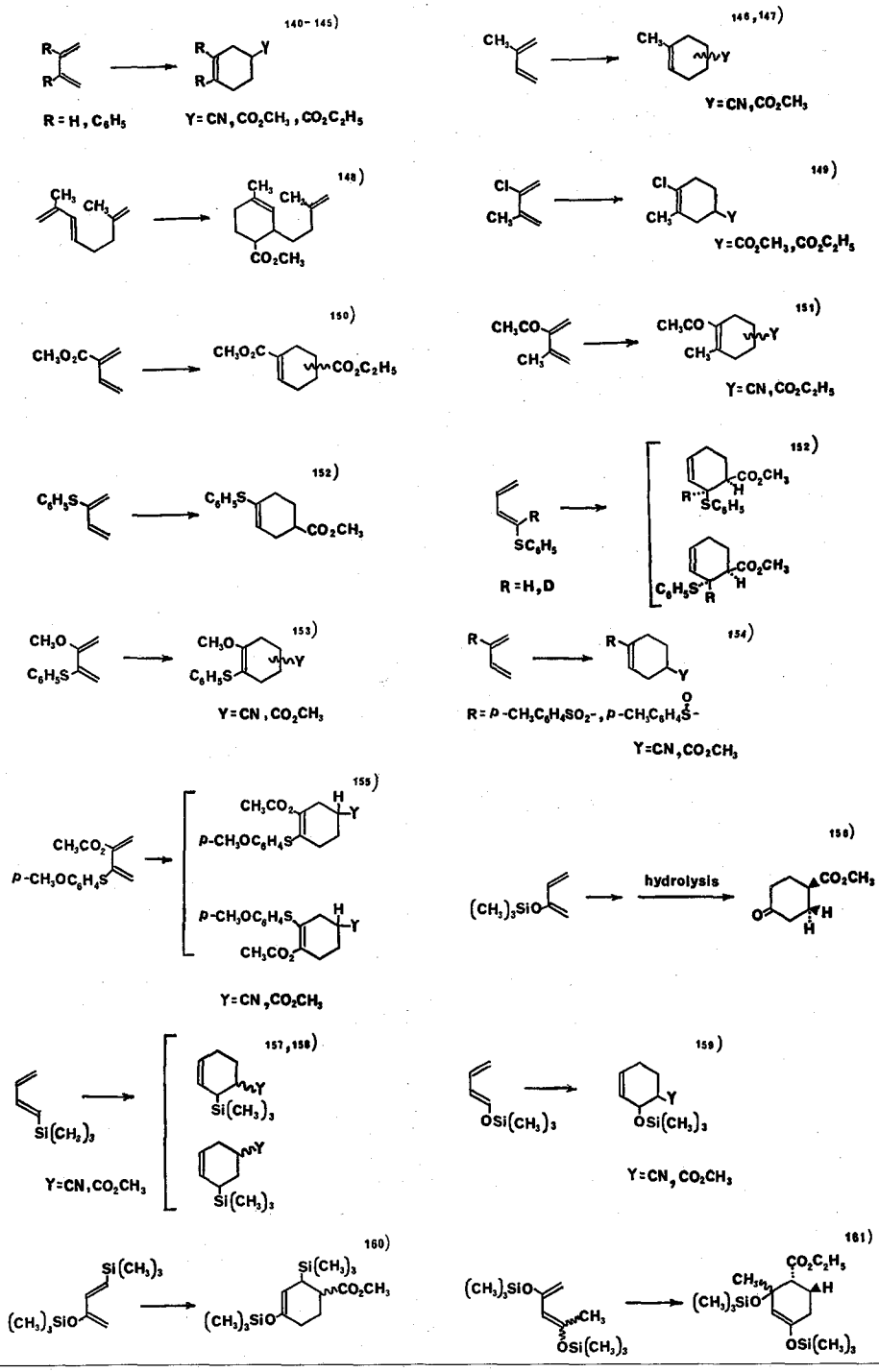


Table II. Continued

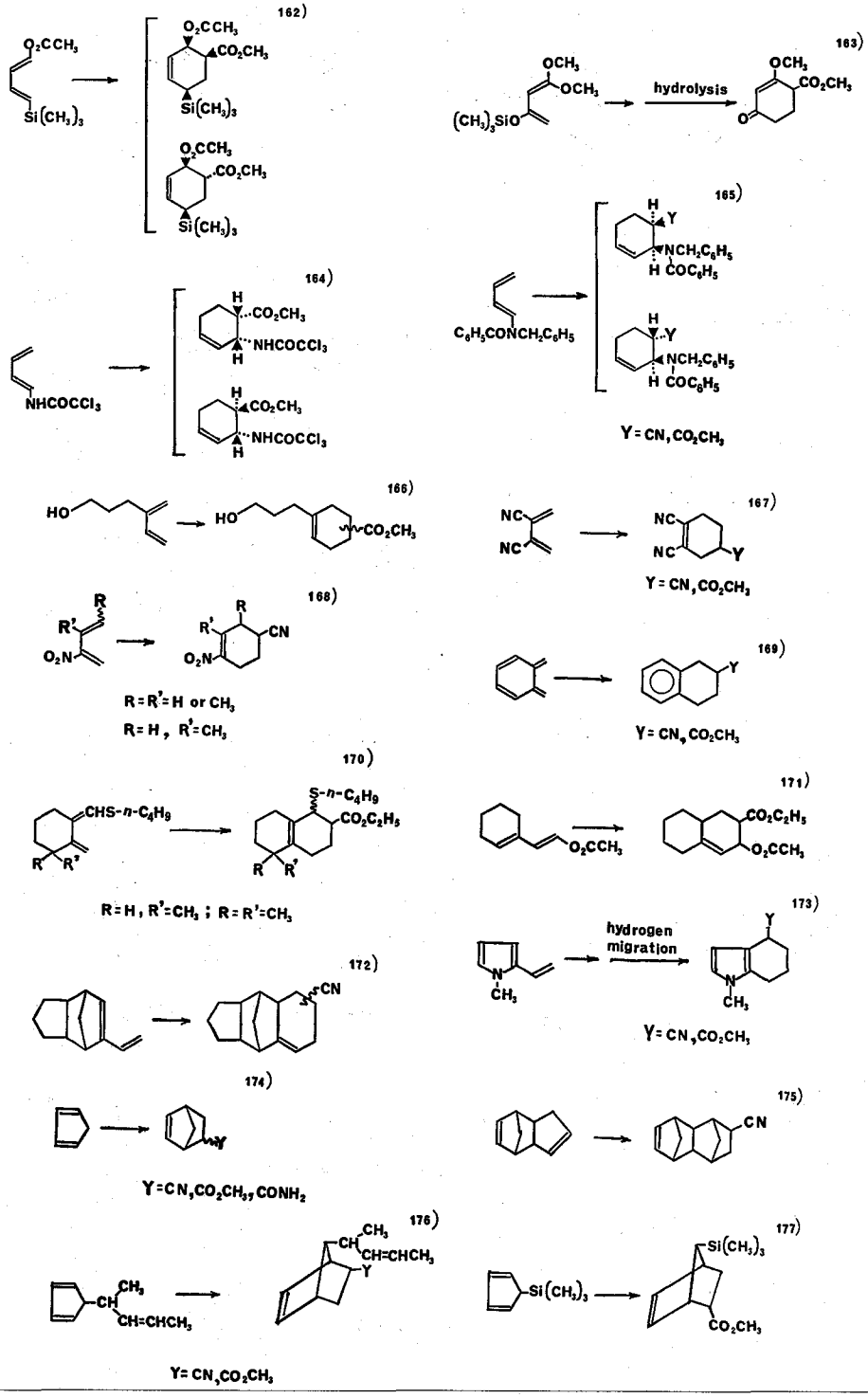


Table II. *Continued*

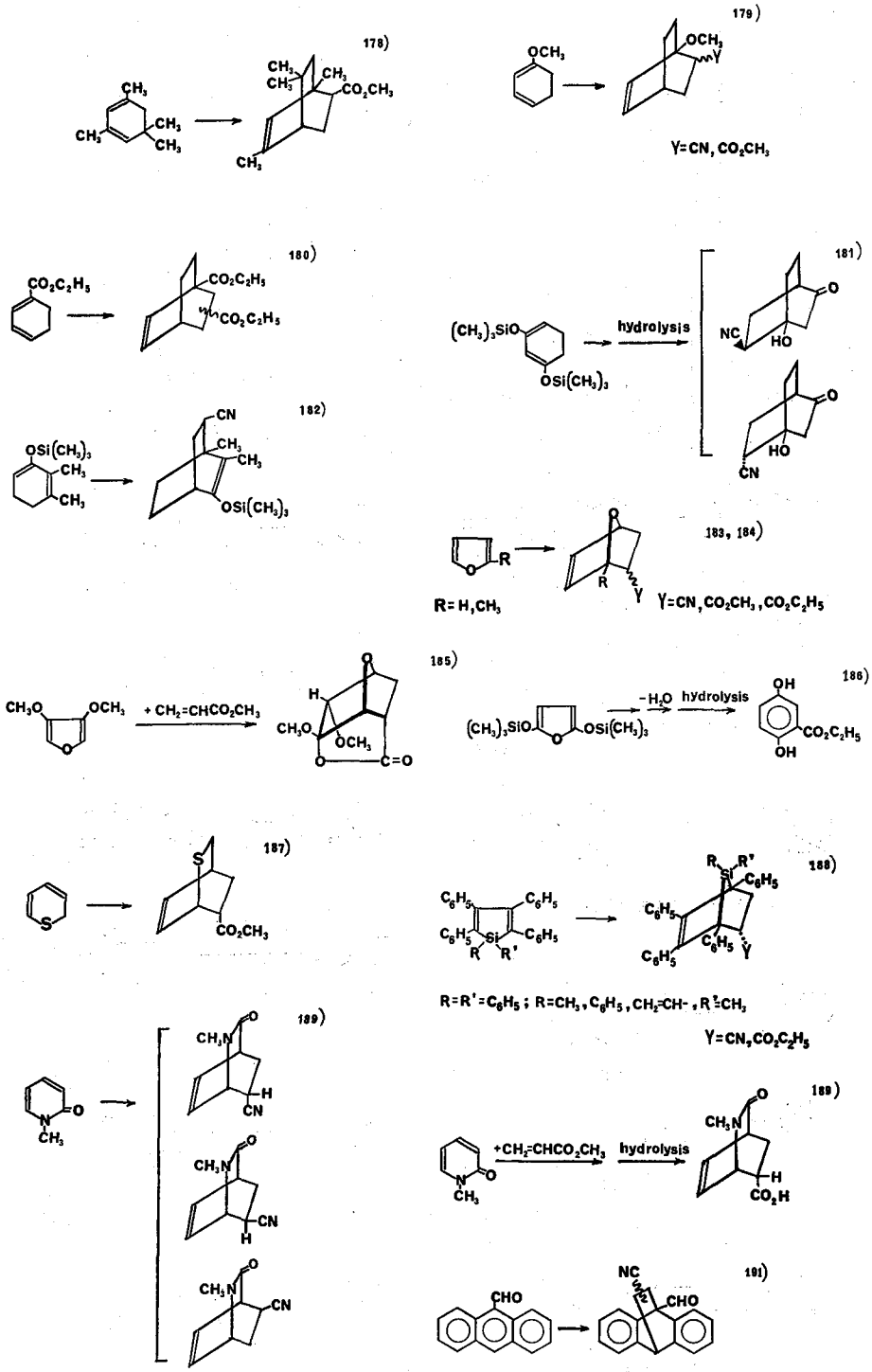
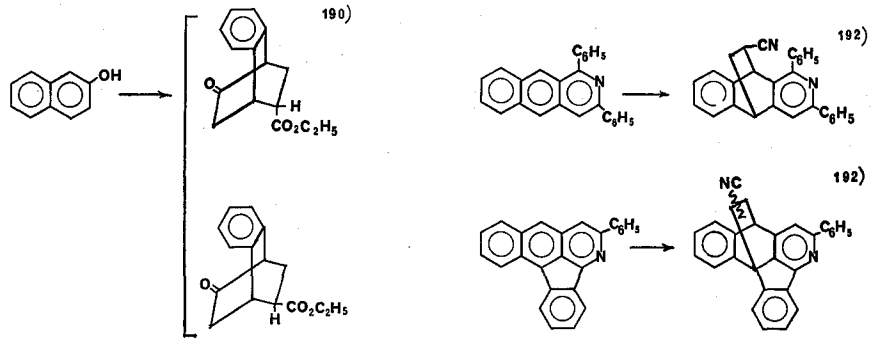


Table II. Continued

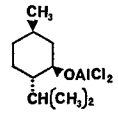


The greater part of the reactions involved in this section falls into the Diels-Alder reaction (diene synthesis). When one considers that the mechanism of the Diels-Alder reaction and of the 1, 3-dipolar cycloaddition reaction are closely related, it is easily understandable that the acrylic compounds such as acrylonitrile, methyl and ethyl acrylate, and acrylamide, which are active dipolarophile, shoud also be good dienophiles. The Diels-Alder reaction consists in the *cis*-addition of the acrylic compounds to the 1, 4-positions of a conjugated diene system, mainly with the formation of cyclohexene derivatives. There have been hundreds of examples of such the reaction, in which the acrylic compounds described in this review participate. Table II summarizes the data in the literature, but only the typical examples are collected in the table. In the same manner as that described in the case of Table I, the left-hand side of the equations in Table II shows the used 1, 3-butadienes and related compounds and the right-hand side of the equations gives the obtained products. By comparison of the structure of products with that of the starting 1, 3-butadienes and related compounds, it is possible to differentiating between the used acrylic compounds in the reaction. The description concerning the reaction conditions, which is seen in the cited literatures, is all omitted.

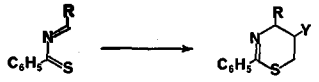
Unlike the 1,3-dipoles, many of 1,3-butadienes and related compounds are stable enough to be isolated. In some cases, the appropriate precursors giving 1,3-butadienes and related compounds are used with the idea of giving the least trouble. As is illustrated[173] by the reaction of 1-methyl-2-vinylpyrrole with acrylonitrile or with methyl acrylate, when a certain 1,3-butadiene or related compound carrying a unsaturated substituent is employed in the Diels-Alder reaction, stabilization of the adduct may occur through spontaneous migration of the double bond to afford a conjugated system. As is also illustrated in Table II, some aromatic systems such as the furan ring[183~186] and the central ring of anthracene and similar compounds[191,192] can furnish the 1,3-butadiene unit out of their more complex construction. Another examples in which 2-naphthol[190] and 1-methyl-2(1*H*)-pyridone[189] do so are also collected in Table II. The catalytic activity of acidic compounds such as Lewis acids to enhance reaction rate, regioselectivity, and stereoselectivity in the Diels-Alder reaction is frequently documented. However, the stereochemistry of the adducts has

not yet been rigidly established except several instances. It is easily understandable that two regioisomeric adducts are possible when an unsymmetrical 1,3-butadienic compound and either one of the acrylic compounds interact. However, as can be seen from the results summarized in Table II, only one of these regioisomeric adducts is recognized in many instances, suggesting that the Diels-Alder reaction proceeded regioselectively. Presumably, the employment of an acidic compound such as Lewis acid may also serve the appearance of such the regioselectivity.

It is reported by Hashimoto and his co-workers[193] that considerable asymmetric induction can occur when the Diels-Alder reaction of cyclopentadiene with methyl acrylate is conducted under the catalytic action of chiral alkoxyaluminium dichloride such as menthoxyaluminium dichloride (**39**). Also, it has been found that some thioketone derivatives such as **40**, **42**, and **44** involving a conjugated diene system undergo the Diels-Alder reaction with the acrylic compounds to afford the corresponding adducts **41**, **43**, and **45**, respectively.[194~196] An interesting report concerning the Diels-Alder reaction of a "pull-push" activated isoprene derivative **46** with acrylonitrile

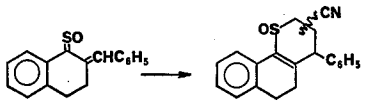


(39)

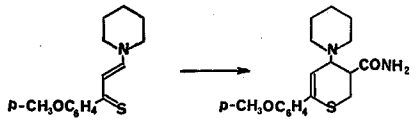


(40) (41)

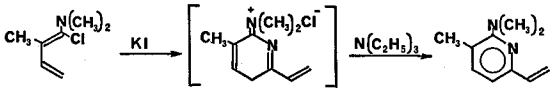
R=N(CH3)2, piperidino, morpholino
Y=CN, CO2CH3, CO2C2H5



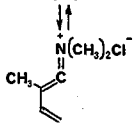
(42) (43)



(44) (45)

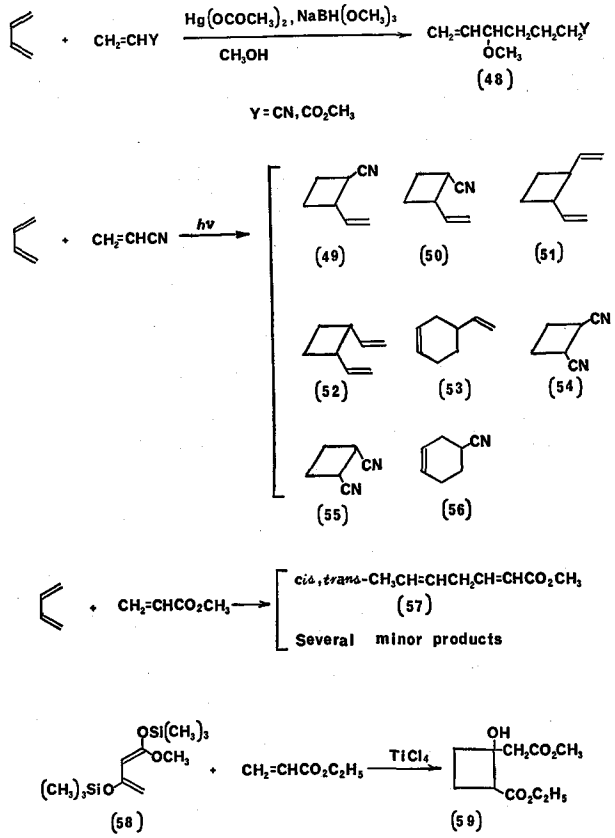


(46) (47)



has been published by Gillard and his co-workers.[197] Thus, the reaction of **46** with acrylonitrile in the presence of KI, followed by addition of triethylamine, gives a pyridine derivative **47** in 62% yield. It is clearly indicated that the reaction consists in the addition of the C≡N bond of acrylonitrile to the 1,4-positions of **46**.

In the next place, we will describe the examples of the reaction of acrylic compounds with 1,3-butadienes and with related compounds other than those of the Diels-Alder reaction. Giese and his co-workers[198] have shown that 1,3-butadiene can be coupled with acrylonitrile or with methyl acrylate to give products **48** in one pot syntheses. In practice, the reaction is carried out by the following steps of procedure: a 1 : 1 mixture of HgO and $Hg(OCOCH_3)_2$ is combined with a excess of 1,3-butadiene in methanol and, after decolouration of HgO, methanol is distilled off, and further the acrylic compound is added, and finally the reaction mixture is reduced by $NaBH(OCH_3)_3$. Dilling and Kroening[199] have carried out the photosensitized addition of 1,3-butadiene to acrylonitrile using acetophenone as the sensitizer. In addition to the cyclobutyl cross-adducts **49** and **50**, the diene dimers **51**, **52**, and **53**, the nitrile dimers **54** and **55**, and a small amount of the Diels-Alder adduct **56** were formed. The reaction of 1,3-butadiene with methyl acrylate in benzene or dichloromethane containing $Co[CH(COCH_3)_2]_3$-$Al(C_2H_5)_3$ give methyl *cis, trans*-2, 5-heptadienoate (**57**) as a major product along with methyl 3, 5-heptadienoate, methyl 1-cyclohexene-1-



carboxylate, 3-vinyl-1-cyclohexene, 1, 5-cyclooctadiene, and 3-methylheptatriene.[200] It is found[201] that heating a 1, 3-butadiene derivative such as **58** with ethyl acrylate leads to the product **59** of Michael addition at the 4-position of **58** followed by cyclization. The yield of **59** is improved by performing the reaction at −78°C in the presence of $TiCl_4$.[201] It is very interesting that the occurrence of the Diels-Alder addition is not recognized.

VIII. THE THERMAL ADDITION TO OLEFINS HAVING AN ALLYLIC HYDROGEN

The ene reaction (ene synthesis) is defined as the indirect substituting addition of a compound with a double bond (enophile) to an olefin with an allylic hydrogen (ene).[202] The reaction is also carried out with some acrylic compounds as the enophile. In 1956, Albisetti and his co-workers[203] have treated several simple olefins **60** such as propylene, 1-butene, 2-butene, isobutylene, and 2-methyl-1-butene with acrylonitrile or with methyl acrylate under high temperature (200–300°C) and identified the resulting thermal adducts **61** by converting them into the appropriate derivatives. In the similar manner, thermal adducts with acrylonitrile or with methyl acrylate have also been obtained[203] from some alicyclic olefins such as cyclohexene, vinylcyclohexane, and (−)-β-pinene. Several years later, it has been found[204] that, in the ene reaction of some simple olefins with methyl acrylate, the reaction leads to

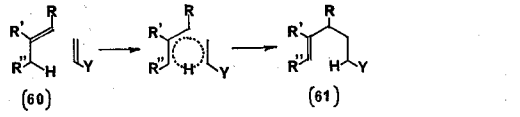
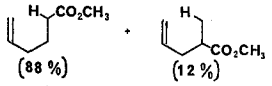
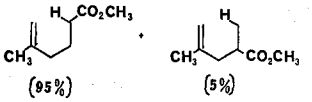
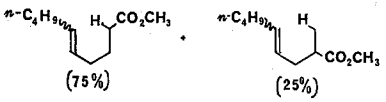
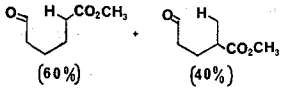
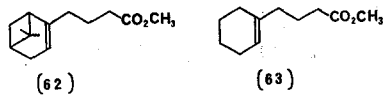


Table III. The Products in the Ene Reaction of Some Simple Olefins with Methyl Acrylate

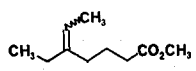
Ene	Products (yield)
	 (88 %) (12 %)
	 (95%) (5%)
	 (75%) (25%)
	 (60%) (40%)

a mixture of two isomers rather than a simple product as is compiled in Table III. This reveals that the ene reaction is formally related to the Diels-Alder addition described in Section VII. However, the linear isomer always predominates over the branched isomer.[204] Since the Diels-Alder reaction often proceeds in much higher yield and with greater stereospecificity in the presence of Lewis acid catalysts, it was proposed[205] as an idea to study the ene reaction of olefins with moderately reactive enophiles such as the acrylic compounds in the presence of these catalysts. Thus, the reaction of (−)-β-pinene with methyl acrylate in the presence of $AlCl_3$ at room temperature gave the ene adduct **62** in 70% yield. In the similar manner, methylenecyclohexane was converted to **63** in 70% yield. Also, the reaction of 2-

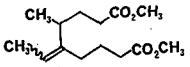


(62)

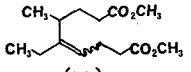
(63)



(64)



(65)



(66)

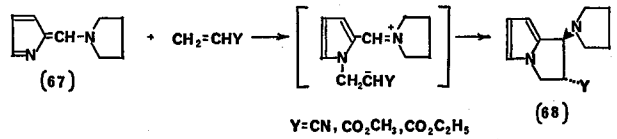
ethyl-1-butene with methyl acrylate under similar conditions afforded a mixture from which the ene adduct **64** and the 1:2 adducts **65** and **66** were isolated in 59 and 9% yield, respectively. From these data it is clear that Lewis acid catalysts greatly accelerate the ene reaction so that such the reaction is possible even under room temperature. Moreover, the employment of $AlCl_3$ in the ene reaction often bring about the exclusive formation of the linear isomer above mentioned.[205,206] This is also illustrated by the $AlCl_3$-catalyzed reaction of 1-hexene with methyl acrylate at 150°C, in which only one product, methyl 4-octene-1-carboxylate is isolated.[207] A patent literature[208] claims that the reaction of isobutylene with methyl acrylate in a autoclave in the presence of $AlCl_3$ catalyst affords the corresponding 1:2 adduct, dimethyl 4-methyl-3-heptene-1, 7-dicarboxylate. Eutectic potassium-sodium-aluminum chloride[209] is used as a mild catalyst for the ene reaction of 1-octene with methyl acrylate.

Since the pioneering work by Albisetti and his co-workers[203] concerning the ene reaction with acrylonitrile, there has not been any detailed report in this limited area. Only a limited number of patents are found in the literature. Thus, Drake[210] has found that B_2O_3 promote the reaction of isobutylene with acrylonitrile and that adiponitrite is a useful reaction diluent to reduce the formation of polymeric compounds in the same reaction. In another patent literature,[211] Drake has proposed the employment of sulfolane or of sulfolane-H_2O to enhance the selectivity for objective unsaturated nitriles in the reaction of isobutylene with acrylonitrile. Besides, two patent literatures[212,213] which describe the techniques of suppressing the formation of by-products in the same ene reaction are also found.

IX. THE MISCELLANEOUS REACTIONS

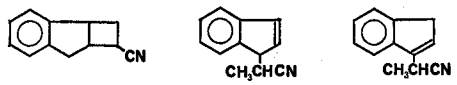
Mori and his co-workers[214] have reported that the acrylic compounds such as acrylonitrile, methyl and ethyl acrylate add in a [6+2] fashion to a 1-azafulvene derivative such as **67**. It has been suggested that the acrylic compounds react across the 1- and 6-position of **67** to give **68**. Irradiation under nitrogen at 10–15°C of a 1 : 1 mixture of benzene and acrylonitrile give the 1 : 1 adduct, 7-cyanobicyclo[4,2,0]octa-2, 4-diene (**69**).[215] Similar irradiation at reflux temperature give mainly a higher boiling product **70**, identified as the 2 : 1 adduct of acrylonitrile and benzene.[215] Photolysis of indene and acrylonitrile in ethanol, using a mercury lamp and a Vycor filter, leads to the formation of the adducts such as **71**, **72**, and **73**.[216] In a similar manner, naphthalene was converted to **74** and **75**.[216] Analogous photoaddition of acrylonitrile to a 2(1*H*)-pyridone derivative such as **76** leading to a mixture of **77**, **78**, and **79** is also performed by Kaneko.[217] Both the former two of these products are a mixture of *syn*- and *anti*-isomer.

Cripps and his co-workers[218] have found initially that cycloaddition of

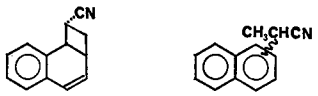


(67) (68)

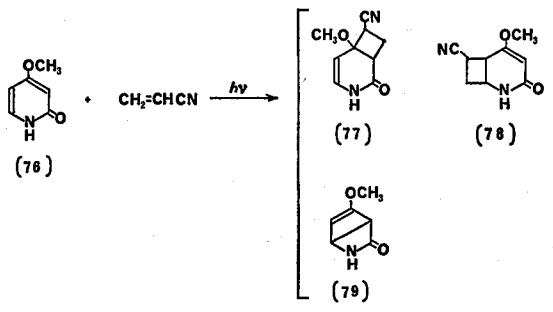
(69) (70)



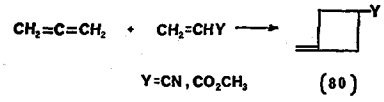
(71) (72) (73)

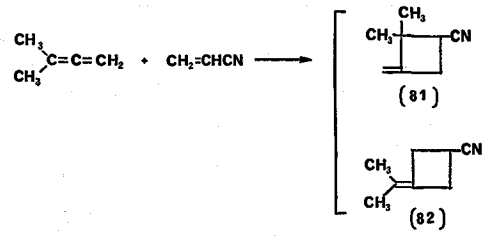


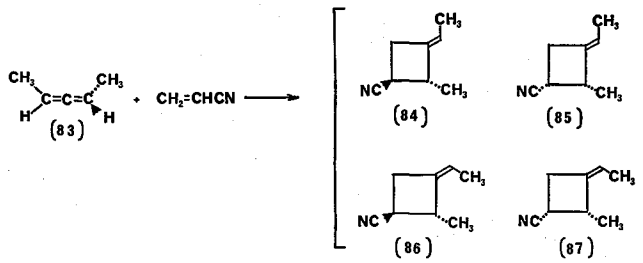
(74) (75)



(76) (77) (78) (79)

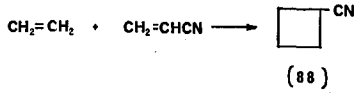


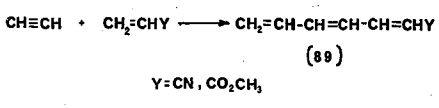




acrylonitrile or of methyl acrylate to allene under autogenous high pressure affords a general route to substituted 3-methylenecyclobutanes **80**. When acrylonitrile is treated with 1, 1-dimethylallene instead of allene under the similar conditions, two isomeric cyclobutanes **81** and **82** are obtained.[218] The four isomeric ethylidenecyclobutanes **84**, **85**, **86**, and **87** from *R*-(—)-1, 3-dimethylallene (**83**) and acrylonitrile are all optically active. These results require that the intermediate in this cycloaddition should be dissymmetric.[219]

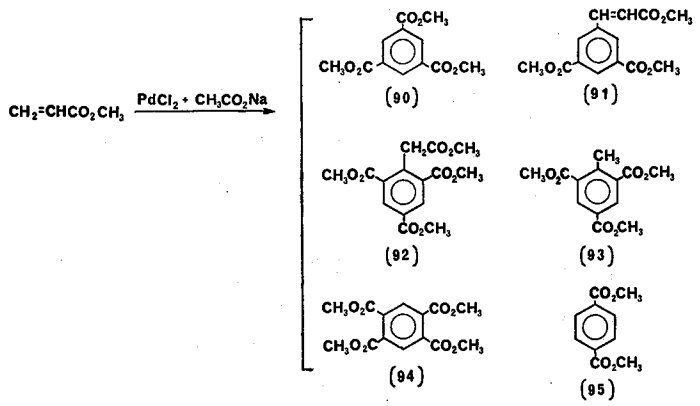
A patent literature[220] claims that the reaction of ethylene and acrylonitrile at 300–350°C and at 1000–3000 atm in the presence of 1-dodecanethiol give cyanocyclobutane (**88**). Also, the reaction of acetylene with acrylonitrile and with methyl acrylate is found to give high yields of 2,4,6-heptatrienenitrile (**89**, Y=CN) and methyl 2,4,6-heptatrienoate (**89**, $Y=CO_2CH_3$), respectively.[221] The most effective type of catalyst found for synthesis of these triene derivatives is a compound of nickel modified by the addition of a phosphine or a phosphite. Thus, the catalyst is ordinarily prepared by adding nickel carbonyl and triphenylphosphine to the acrylic compound. Such a mixture probably gives rise to the complex, $Ni(CO)_2[P(C_6H_5)_3]_2$

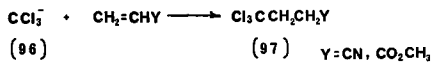


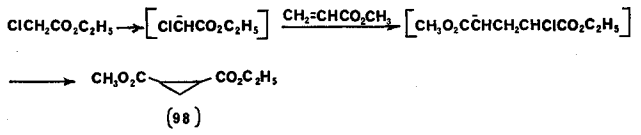


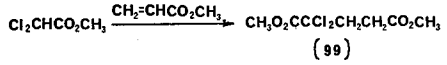
and $Ni(CO)_3[P(C_6H_5)_3]$.[221]

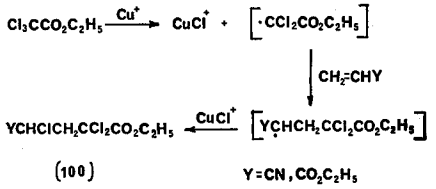
The reaction of methyl acrylate with $PdCl_2$ and sodium acetate at 100°C give trimethyl trimesate (**90**), albeit in the low yield, along with smaller amounts of other aromatic compounds such as **91**, **92**, **93**, **94**, and **95**.[222] Trichlorocarbanion (**96**)

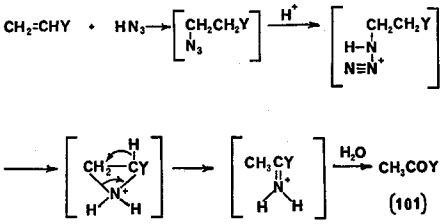












generated from chloroform with 50% aqueous NaOH in the presence of benzyltriethylammonium chloride reacts with acrylonitrile and with methyl acrylate to give **97** (Y=CN) and **97** ($Y=CO_2CH_3$), respectively.[223] The condensation of ethyl chloroacetate with methyl acrylate in the presence of sodium methoxide leads to the formation of 1-carbethoxy-2-carbomethoxycyclopropane (**98**).[224] The employment of methyl dichloroacetate instead of ethyl chloroacetate under the analogous basic conditions leads to the formation of dimethyl 2,2-dichloroglutarate (**99**).[225] Also, when ethyl trichloroacetate and ethyl acrylate are heated under reflux in ethanol in the presence of CuCl, diethyl 2,2,4-trichloroglutarate (**100**, $Y=CO_2C_2H_5$) is obtained.[226] In the similar manner, ethyl 4-cyano-2,2,4-trichlorobutyrate (**100**, Y=CN) is obtained from acrylonitrile and ethyl trichloroacetate.[226] Interaction of the acrylic compounds and hydrazoic acid in the presence of hydrochloric acid gives considerable quantities of pyruvic acid derivatives **101**.[227] The reaction seems to be an anomalous Schmidt reaction.

X. SUMMARY

Although the present article deals only with reactions that are known from the literature, there remain some areas of the synthetic chemistry of the acrylic compounds. For example, some reactions such as the reaction with Grignard compounds and that with diazonium salts are not described in this article. However, this article together with the preceding article[1] will cover the major part, or probably more part of the previously reported reaction of the acrylic compounds. In this area, many efforts have been devoted toward the discovery of reaction of acrylonitrile and methyl and ethyl acrylate, and relatively little works have been done on the reaction of the remaining acrylamide. Thus, more informations concerning the synthetic behavior of acrylamide may be desirable.

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