

NODZU LABORATORY (April 1937~February 1955)

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and

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The main research problem of Nodzu Laboratory was the study on the reactivities of acetylene and its derivatives. This research theme has been continued by Kunichika Laboratory to synthesize various monomers by new methods, as possible as, not only from acetylene, but another raw materials, such as ethylene and propylene or their derivatives. At the same time, the efforts have been devoted to clarify the reaction mechanisms.

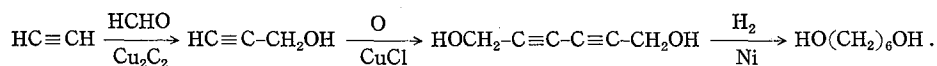
I. Studies on Reactions of Ketene

The reactions of ketene with compounds containing active methylenic hydrogen or hydroxy group were carried out under various conditions. C-acetyl or O-acetyl derivative was obtained according to the reaction conditions. For example, in the case of reaction of ketene with acetoacetate, C-compound $\text{CH}_3\text{-C}(\text{O})\text{-CH}(\text{COCH}_3)\text{-CO}_2\text{-C}_2\text{H}_5$ was obtained in good yield at 80° without catalyst, but in the presence of conc. sulfuric acid at the same temperature, O-acetyl compound $\text{CH}_3\text{-C}(\text{OOCCH}_3)=\text{CH-CO}_2\text{-C}_2\text{H}_5$ was obtained in good yield.

On the results of many experiments with various compounds, a possible reaction mechanism was postulated.

II. Studies on Reactivities of Acetylene and its Derivatives

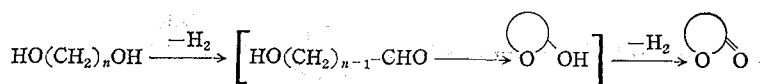
a) Acetylene, paraformaldehyde suspended in organic solvent, preferably methanol, and copper acetylide were charged in an autoclave and they were heated at 115° under about 45 kg/cm². Propargyl alcohol was easily obtained in 56% yield. Then, propargyl alcohol was converted to hexanediol-1,6 as following routes.



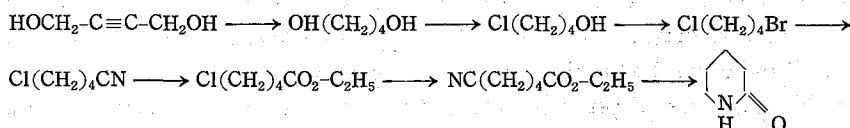
Hexanediol was passed with hydrogen over catalyst at 210° under reduced pressure and converted to ϵ -caprolactone in 78% conversion and 68% yield.

Similarly, butanediol-1,4 and pentanediol-1,5 was treated to give γ -butyrolactone and δ -valerolactone, respectively.

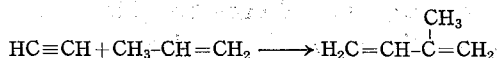
The reaction mechanism of lactone formation from diol in vapor phase was postulated as follows:



b) From butynediol ($\text{HOCH}_2\text{-C}\equiv\text{C-CH}_2\text{-OH}$) *via* the following processes, ϵ -caprolactam was prepared in considerably good yields in each process.



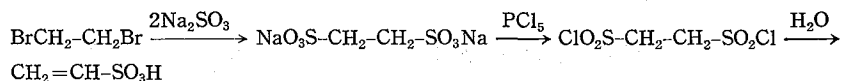
c) The reaction between acetylene and propylene by catalytic pyrolysis under ordinary pressure was tried to obtain isoprene.



Despite of various reaction conditions, isoprene was obtained only in a few volume % of product gas. From the results of the product analysis, a radical mechanisms for the formation of various products were proposed.

III. Studies on Reactivities of Ethylene and Propylene or their Derivatives

a) The various synthetic methods of vinyl sulfonic acid ($\text{CH}_2=\text{CHSO}_3\text{H}$) from ethylene or its derivatives were studied and it was found that the following process was the best for the laboratory scale:



Vinyl sulfonic acid was copolymerized with acrylonitril, and the monomer reactivity ratio was found, and Q and e values of the acid were estimated. The dyeability of acrylonitril-vinyl sulfonic acid copolymers to the cationic dye was tested and a good result was found.

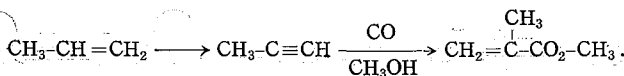
b) The Friedel-Crafts reaction of 1,2-dichloroethane with toluene has been carried out to obtain dimethyldibenzyls which would be raw materials for the manufacture of aromatic dibasic acids.



Until now, six isomers of dimethyldibenzyl were authentically prepared and analytical method of their mixtures by gas chromatography was successfully performed.

c) A new synthetic method for methyl methacrylate has been tried. Namely, propylene was pyrolyzed to give methylacetylene, and then methylacetylene was

carboxylated with carbon monoxide and methanol in the presence of catalyst under pressure to obtain methacrylate.



The first step, pyrolysis, was carried out at 1000~1200°, under reduced pressure (50, 100, 200 mm Hg), and short contact time ($4.4 \times 10^{-3} \sim 2.3$ sec.). Under proper conditions, the sum of yields of methylacetylene and allene ($\text{CH}_2=\text{C}=\text{CH}_2$ is isomer of methylacetylene and converts easily to methylacetylene at high temperature) was 38 mole per 100 mole of propylene pyrolyzed.

For this pyrolysis, a possible free radical chain reaction mechanism was proposed. On the basis of this mechanism, the pyrolysis was studied in the presence of catalysts (radical sources which have a lower dissociation energy than that of $\alpha(\text{C-H})$ of propylene and abstract hydrogen atom from propylene). Among catalysts tested, chlorine, bromine, and hydrogen bromide were most effective.

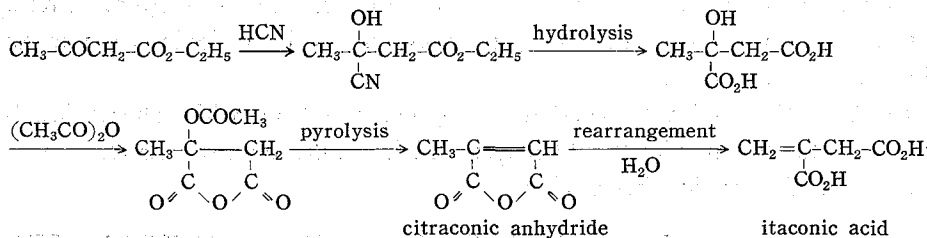
The carboxylation reaction of methylacetylene was proceeded in the presence of nickel carbonyl and methacrylic acid as co-catalyst at about 130°, under about 13.5 atm. press., and the yield of methyl methacrylate was 86% and very high catalytic level of 93.8% was recognized.

Allene was also carboxylated by the similar procedure in 62% yield of methacrylate.

d) Selective reduction of acrolein to allyl alcohol was achieved by a vapor phase hydrogen transfer reaction using isopropyl alcohol as a hydrogen donor. It was found that the preferred catalyst was 50 wt.% of zinc oxide-magnesium oxide catalyst. The optimum conditions were found as follows: temp., 200°, total feed rate, 45 moles/l. of catalyst/hr., feed ratio of isopropyl alcohol per acrolein, 10 moles. The yield of allyl alcohol was 80~65% at 80~90% conversion of acrolein.

IV. Synthesis of Itaconic Acid

Itaconic acid is a co-monomer for various synthetic resins. The synthesis of the acid was tried by the following routes.



Consequently, satisfactory results were obtained in each process of the reaction.

Publications

(* indicates an article published in Japanese)

1. S. Kunichika, H. Ohta and M. Morimura: Studies on Polyvinylidenechloride. (II). Pyrolysis of Polymer and Copolymers, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **55**, 748 (1952)*.
2. S. Kunichika, S. Oka, M. Yokoi and T. Nakajima: Studies on Polyvinylidenechloride. (III). Synthese of Solvents, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **56**, 931 (1953)*.
3. R. Nodzu, S. Kunichika and T. Isoshima: Reaction of Ketene with Silk, *Bull. Inst. Chem. Res., Kyoto Univ.*, **31**, 380 (1953).
4. T. Isoshima: Reaction of Ketene with Ethylacetoacetate, *Bull. Inst. Chem. Res., Kyoto Univ.*, **31**, 382 (1953).
5. R. Nodzu and T. Isoshima: Reaction of Ketene with Ethylacetoacetate in the Presence of Some Organic Bases, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 37 (1954).
6. R. Nodzu and T. Isoshima: Reaction of Ketene with Compounds Containing Active Methylenic Hydrogen, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 37 (1954).
7. R. Nodzu, T. Isoshima, K. Hara and S. Fukai: Reaction of Ketene with Acetone, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 39 (1954).
8. R. Nodzu and T. Isoshima: Reaction of Ketene with Phenol, Resorcine, Phloroglucine, and Dimedone, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 139 (1954).
9. T. Isoshima: Reaction of Ketene with Ethyl Acetoacetate in the Presence of Pyridine, *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 140 (1954).
10. T. Isoshima: Reaction of Ketene with Compounds Containing Active Methylenic Hydrogen. (I~III), *J. Chem. Soc., Japan, Pure Chem. Sec.*, **77**, 55 (1956)*.
11. T. Isoshima: Reaction of Ketene with Compounds Containing Active Methylenic Hydrogen. (IV~VI), *J. Chem. Soc., Japan, Pure Chem. Sec.*, **77**, 425 (1956)*.
12. T. Isoshima: Quantitative Analysis of Each Component of the Mixture of Acetic Acid, Acetaldehyde, and Acetone, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **57**, 743 (1954)*.
13. T. Isoshima: Quantitative Analysis of Each Component of the Mixture of Acetic Acid, Acetaldehyde, Acetone, Ethylacetate, and Ethylalcohol, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **57**, 745 (1954)*.
14. S. Kunichika, S. Oka and T. Yoshikawa: Reaction of Aldehydes and Acetylene under Pressure. (II), *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 99 (1954).
15. S. Kunichika, S. Oka and T. Yoshikawa: Preparation of Caprolactam from Propargyl Alcohol (I), *Bull. Inst. Chem. Res., Kyoto Univ.*, **32**, 101 (1954).
16. S. Kunichika and S. Oka: Oxidative Coupling of Acetylenic Compounds, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **61**, 13 (1958)*.
17. S. Oka: Synthesis of δ -Valerolactone, *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 322 (1961).
18. S. Oka: Studies on Lactone Formation in Vapor Phase. (I). Synthesis of γ -Butyrolactone, *Bull. Chem. Soc., Japan*, **34**, 12 (1961).
19. S. Oka: Studies on Lactone Formation in Vapor Phase. (II). Synthesis of ϵ -Caprolactone, *Bull. Chem. Soc., Japan*, **35**, 562 (1962).
20. S. Oka: Studies on Lactone Formation from Diols, *Bull. Chem. Soc., Japan*, **35**, 986 (1962).
21. S. Kunichika and Y. Sakakibara: Synthesis and Polymerization of Butanediolmonovinylether, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **60**, 761 (1957)*.
22. S. Kunichika and Y. Sakakibara: Synthesis of ϵ -Caprolactam from Acetylene. (I~III), *J. Chem. Soc., Japan, Pure Chem. Sec.*, **81**, 140, 154 (1960)*.
23. S. Kunichika and Y. Sakakibara: Synthesis of ϵ -Caprolactam from Acetylene, *Bull. Inst. Chem. Res., Kyoto Univ.*, **38**, 392 (1960).
24. T. Katagiri: Reaction between Acetylene and Propylene. (I). Reaction Products by Catalytic Pyrolysis under Atmospheric Pressure, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 159 (1963).
25. T. Katagiri: Reaction between Acetylene and Propylene. (II). The Reaction Mechanism, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 170 (1963).
26. S. Kunichika and T. Katagiri: Synthesis and Reactivity Ratio of Vinylsulfonic Acid and of its Copolymers, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **64**, 929 (1961)*.

27. S. Kunichika and T. Katagiri: Studies on Vinylsulfonic Acid, *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 215 (1961).
28. S. Kunichika, S. Oka and T. Sugiyama: Synthesis of Dimethyldibenzyls, *Bull. Inst. Chem. Res., Kyoto Univ.*, **43**, 250 (1965).
29. Y. Sakakibara: The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (I). The Effect of Pyrolysis Conditions on Product Yields, *Bull. Chem. Soc., Japan*, **37**, 1262 (1964).
30. Y. Sakakibara: The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (II). The Mechanism of the Pyrolysis, *Bull. Chem. Soc., Japan*, **37**, 1268 (1964).
31. S. Kunichika, Y. Sakakibara and M. Taniuchi: Synthesis of Methylacetylene by Pyrolysis of Propylene. (III). Effect of Catalysts on Product Yields, *Bull. Inst. Chem. Res., Kyoto Univ.*, **43**, 469 (1965).
32. S. Kunichika and Y. Sakakibara: Synthesis of Methyl Methacrylate from Propylene, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 270 (1964).
33. Y. Sakakibara: Synthesis of Methacrylic Esters by Carboxylation Reaction of Methylacetylene. (I). Methyl Methacrylate. Reaction Conditions and Products, *Bull. Chem. Soc., Japan*, **37**, 1601 (1964).
34. S. Kunichika, S. Oka and M. Sakai: Selective Reduction of Acrolein to Allyl Alcohol by a Vapor Phase Hydrogen Transfer Reaction, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 215 (1966).
35. S. Kunichika, S. Oka and K. Tanaka: Synthesis of Itaconic Acid from Ethyl Acetoacetate, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 221 (1966).

Reviews

1. S. Kunichika: The Recent View of Reppe's Synthese, *Kagaku no Ryoiki*, **6**, 281 (1952)*.
2. S. Kunichika: Cyclopolylefins Derived from Acetylene, *Bull. Inst. Chem. Res., Kyoto Univ.*, **31**, 323 (1953).
3. S. Kunichika: Acetylene as Industrial Raw Material, *Kobunshi (High Polymers, Japan)*, **4**, 31 (1955)*.
4. S. Kunichika: Chemistry of Acetylene, *Kagaku no Ryoiki*, **10**, 327 (1956)*.
5. S. Kunichika: A Narrow View of Petroleum Chemistry, *Valker Reviews*, **7**, 4 (1963)*.
6. S. Kunichika and H. Suzuki: Oxidative Coupling, *J. Soc. Org. Syn. Chem., Japan*, **22**, 91 (1964)*.

Patent

- S. Kunichika and Y. Sakakibara: Manufacture of ϵ -Caprolactam from ϵ -Aminocaproic Acid Ester. Publication Date, Feb. 4, 1963.

Books

1. S. Kunichika: "Vinylidene Chloride Resins", Publication Society of Polymer Chemistry, (1952)*.
2. S. Kunichika: "Acetylene and its Derivatives", Kyoritsu Pub. Co. (1954)*.
3. S. Kunichika and S. Oka: "Polymerization", Experimental Chemistry, Vol. 18, Maruzen (1957)*.
4. S. Kunichika and Y. Sakakibara: "Synthetic Methods of Monomers", Experimental Chemistry of High Polymers, Vol. 9, Chap. 1, Kyoritsu Pub. Co. (1957)*.