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Catalytic Dimerization of Acrylonitrile

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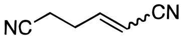
Summary: A new catalytic system using the combination $RuCl_2(DMSO)_4/CH_3CH_2COONa/DMSO$/carboxylic acid which enables selective dimerization of acrylonitrile to linear dimers without formation of propionitrile as a byproduct has been developed on the basis of a new working hypothesis of the desirable reaction mechanism involving protonolysis of a C−Ru bond in the intermediate.

Hexamethylenediamine, an important intermediate for nylon 66, is currently produced by reduction of C_6 dinitriles **1**−**3**.[1] These dinitriles have been produced in very large scale either by nickel-catalyzed addition of hydrogen cyanide to butadiene or by electrochemical hydrodimerization of acrylonitrile.[1] On the other hand, the catalytic dimerization of acrylonitrile has been attracting significant attention.[2] Ru-based catalysts[3,4] are important candidates for this reaction due to the high reactivity (the TNO, catalyst turnover number, has been about 1000) and high selectivity (almost complete) for the linear dimers (**1**−**3**). However, the inevitable use of hydrogen as an extra agent to keep the reaction catalytic resulted in formation of a large amount of propionitrile as an undesirable byproduct.[3,4]



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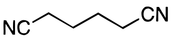

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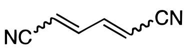

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In this communication, we wish to report an efficient catalytic system for dimerization of acrylonitrile in which the use of hydrogen is not necessary. In the new Ru-based catalyst system, a carboxylic acid is used instead of hydrogen according to our hypothesis on the propionitrile byproduct formation (vide infra). We have analyzed the problems of the conventional Ru-catalyzed dimerization of acrylonitrile.[3,4] (1) The dimerization takes place in a catalytic manner only in the presence of molecular hydrogen, without which the reaction is known to give a small amount of 1,4-dicyanobutadiene (**3**).[5] (2) It seems that in all the previously reported data[3,6] the molar ratio of acrylonitrile dimers to the byproduct propionitrile does not exceed 1:1 (within the range of experimental error). We suggest that there is a theoretical limit in the selectivity of acrylonitrile dimers, i.e., a maximum of 66.6% based on acrylonitrile consumed. (3) We have found that the *cis* to *trans* ratio of the 1,4-dicyanobutenes **1** decreases according to reaction time with *cis* rich at the initial period (Figure 1).[7] A proposed mechanism is shown in the left half of Scheme 1 in a simplified manner.[8] The carbon−hydrogen bond *cis* to the cyano group would be cleaved by Ru(0) to give **4**,[9] which undergoes carbometalation of the second acrylonitrile, leading to the intermediate

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) For a general review, see: (a) Wittcoff, H. *J. Chem. Educ.* **1979**, *56*, 654. Addition of HCN to butadiene: (b) Drinkard, W. C., Jr.; Taylor, B. W. Ger. Patent 1,807,089 (E. I. du Pont de Nemours and Co.), 1969; *Chem. Abstr.* **1969**, *71*, 101350. Electrochemical hydrodimerization of acrylonitrile: (c) Baizer, M. M. *CHEMTECH* **1980**, 161. (d) Danly, D. E. *CHEMTECH* **1980**, 302. (e) Baizer, M. M. Fr. Patent 1,328,327 (Monsanto Chem. Co.), 1963; *Chem. Abstr.* **1963**, *59*, 12649. Adipic acid method: (f) Lazier, W., A. U.S. Patent 2,144,340 (E. I. du Pont de Nemours and Co.), 1939; *Chem. Abstr.* **1939**, *33*, 3398 (and 2539).

(2) Phosphinite catalyst: (a) Jennings, J. R.; Cozens, R. J.; Lalkham, M. J. U.S. Patent 4,263,224, 1981; *Chem. Abstr.* **1981**, *95*, 61550. Bi catalyst: (b) Shoda, K.; Yasui, A.; Japan 5,485 (Kuraray Co., Ltd.), 1971; *Chem. Abstr.* **1971**, *75*, 48475. Co catalyst: (c) Umemura, S.; Hashimoto, T. Jpn. Kokai Tokkyo Koho 142,514 (Ube Industries, Ltd.), 1975; *Chem. Abstr.* **1976**, *84*, 135141. Ni catalyst: (d) Nomura, K.; Ishino, M. *J. Mol. Catal.* **1992**, *73*, L15.

(3) Ru-based catalyst: (a) Rhone-Poulenc, Neth. Patent 6,603,115, 1966; *Chem. Abstr.* **1967**, *66*, 85483. (b) Misono, A.; Uchida, Y.; Hidai, M.; Kanai, H. *Chem. Commun.* **1967**, 357. (c) McClure, J. D.; Owyang, R.; Slaugh, L. H. *J. Organomet. Chem.* **1968**, *12*, 8. (d) Billing, E.; Strow, C. B.; Pruett, R. L. *Chem. Commun.* **1968**, 1307. (e) Misono, A.; Uchida, Y.; Hidai, M.; Inomata, I. *Chem. Commun.* **1968**, 704. (f) Misono, A.; Uchida, Y.; Hidai, M.; Shinohara, H.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 396. (g) Misono, A.; Uchida, Y.; Hidai, M.; Inomata, I.; Watanabe, Y.; Takeda, M. *Kogyo Kagaku Zasshi* **1969**, *72*, 1801; *Chem. Abstr.* **1970**, *72*, 42713. (h) Watanabe, Y.; Takeda, M. *Nippon Kagaku Kaishi* **1972**, 2023; *Chem. Abstr.* **1973**, *78*, 57347. (i) Strohmeier, W.; Kaiser, A. *J. Organomet. Chem.* **1976**, *114*, 273. (j) Tsou, D. T.; Burrington, J. D.; Maher, E. A.; Grasselli, R. K. *J. Mol. Catal.* **1985**, *30*, 219. (k) Tsou, D. T.; Burrington, J. D.; Maher, E. A.; Grasselli, R. K. *J. Mol. Catal.* **1983**, *22*, 29. (l) Nagano, T.; Hirano, M.; Fukuoka, A.; Komiya, S. *Abstracts of the 69th Annual Meeting of the Chemical Society of Japan*, Kyoto, Japan; Chemical Society of Japan: Tokyo, 1995; 3H438. (m) Fukuoka, A.; Furuta, S.; Nagano, T.; Hirano, M.; Komiya, S. *Abstracts of the 70th Annual Meeting of the Chemical Society of Japan*, Tokyo, Japan; Chemical Society of Japan: Tokyo, 1996; 4J206.

(4) Recently we have reported an improved method using $RuCl_2$/Bu_3SnH as the catalyst precursor and also hydrogen as the coreactant. Murai, S.; Oodan, K.; Sugise, R.; Shirai, M.; Shimakawa, T. Jpn. Kokai Tokkyo Koho 09, 531 (Ube Industiries, Ltd.), 1994; *Chem. Abstr.* **1994**, *120*, 191146. See also ref 6.

(5) Milner, D. J.; Whelan, R. *J. Organomet. Chem.* **1978**, *152*, 193.

(6) For a representative example of the results obtained by our improved method,[4] a solution of acrylonitrile (377 mmol), $RuCl_3 \cdot nH_2O$ (38 wt % Ru, 0.39 mmol), Bu_3SnH (1.92 mmol), and ethylbenzene (38 mmol, internal standard for GC) was heated at 115 °C for 2 h under pressure of H_2 (20 kg/cm^2) to give 85% conversion with 64% selectivity to dimers (*cis*-**1**, 47.5%; *trans*-**1**, 44.5%; **2**, 8.0%) and 33% selectivity to propionitrile. The lower pressure of H_2 (10 kg/cm^2) gave lower conversion (33%) with similar dimer distribution (64% dimer contents of *cis*-**1**, *trans*-**1**, and **2** were 55, 37, and 8%, respectively, and 33% propionitrile). The higher H_2 pressure (30 kg/cm^2) resulted in higher conversion (95%) with lower selectivities to dimers (58%) and propionitrile (39%) with similar dimer distribution (47, 47, and 7%, respectively).

(7) Masada reported that *cis*-**1** was the major product in a gas-phase dimerization of acrylonitrile: Masada, T.; Yasui, T. *Kogyo Kagaku Zasshi* **1971**, *74*, 2405; *Chem. Abstr.* **1972**, *76*, 33919.

(8) A similar catalytic cycle involving C−H bond cleavage and a catalytic cycle not involving C−H bond cleavage but involving initial hydrometalation were postulated.[3]

(9) Similar *cis* cleavage has been postulated in the work of ref 7. See also a similar stoichiometric reaction of an α,β-unsaturated ester: Komiya, S.; Yamamoto, A. *Chem. Lett.* **1975**, 475. In contrast, *trans* cleavage has also been suggested; see: Billiing, E.; Strow, C. B.; Pruett, R. L. *Chem. Commun.* **1968**, 1307.

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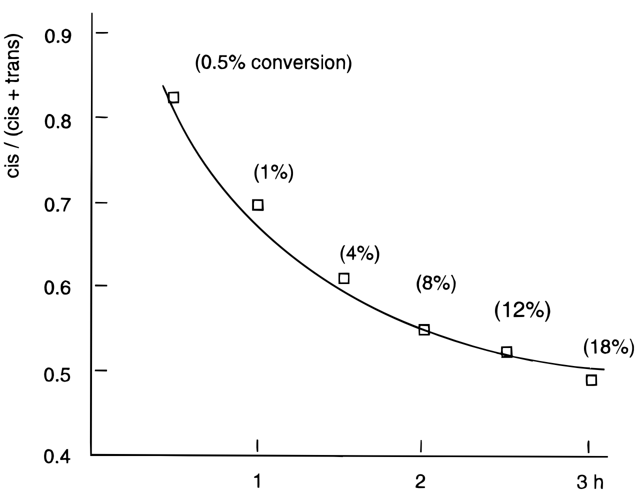
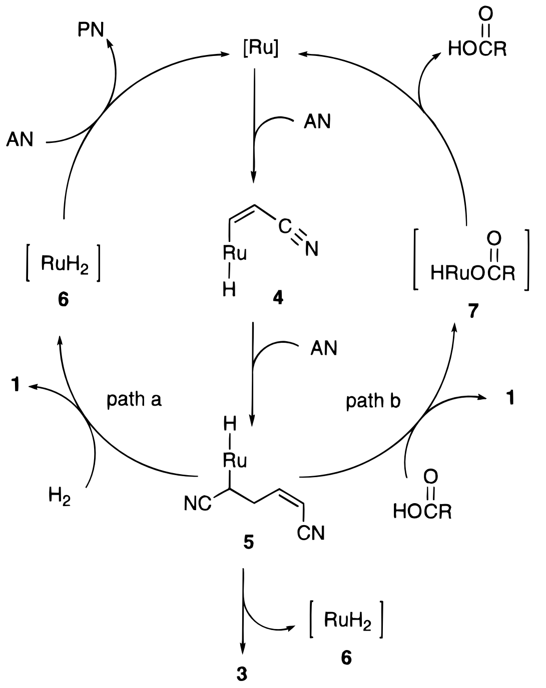


Figure 1. The ratio *cis*-**1**/(*cis*- and *trans*-**1**) vs time in the reaction of $RuCl_3 \cdot nH_2O$ (38 wt % Ru, 0.75 mmol), acrylonitrile (456 mmol), and EtOH (60 mL) under H_2 (20 kg/cm^2) at 120 °C. The combined yields of dicyanobutenes **1**−**3** are shown in parentheses.

Scheme 1. Working Hypothesis of the Hydrogenolysis Process (Left Half) and Protonolysis Process (Right Half) for Dimerization of AN[a]



[a] Alternative possibilities are not shown for simplicity. AN and PN stand for acrylonitrile and propionitrile, respectively.

Ru complex **5**. The carbon−ruthenium bond in **5** would be cleaved by molecular hydrogen to give the dimer **1** before (this possibility is shown as path a in Scheme 1) or after (this possibility is not shown in Scheme 1) taking up another molecule of acrylonitrile, leading to the byproduct propionitrile (path a). In any event, one molecule of acrylonitrile is consumed to give propionitrile in the process of regenerating the catalyst [Ru(0)], thus rendering the limitation to this system. Obviously a new catalytic system, in which molecular hydrogen is not required, should be devised.[10]

Following this line of assumption, we have concentrated our efforts to devise a new catalytic cycle which involves a different way of the conversion of the key intermediate **5** to the product **1**. The working hypothesis of utilizing protonolysis[11] (path b in Scheme 1) has finally led us to discover an entirely new method for catalytic dimerization of acrylonitrile. We have carried out a considerable number of experiments using various types of acids for protonolysis, additives, and catalyst precursors under various reaction conditions. A representative example of the successful results is as follows.

A mixture of $RuCl_2(DMSO)_4$[12] (18.5 mg, 0.038 mmol), CH_3CH_2COONa (11.0 mg, 0.12 mmol), DMSO (0.50 g, 6.4 mmol), thiophene-2-carboxylic acid as an organic carboxylic acid (5.73 mmol, acid/Ru (molar ratio) = 150), and anisole (an internal standard for GC analysis, 2.0 g) was stirred at room temperature under argon for 30 min. Then acrylonitrile (15.0 g, 283 mmol, acrylonitrile/Ru (molar ratio) = 7400) was added by syringe. An appropriate portion (e.g. 1 mL) of the mixture was heated in a stainless steel pressure vessel at 150 °C for 6 h. GC analysis of the reaction mixture on a 10% PEG20M/Chromosorb W (AW-DMCS) column indicated the presence of unreacted acrylonitrile (88.2%, conversion 11.8%), a mixture of linear dimers (**1**−**3**; 10.1% total yield) (turnover number 747),[13] and an acid−acrylonitrile adduct (β-cyanoethyl ester of the organic acid; 0.5% yield).[14] Only a small amount (0.6%) of propionitrile, an undesired byproduct, was formed.

Important features of the new catalytic reaction (protonolysis method) are as follows. (1) Catalytic conversion of acrylonitrile to linear dimers occurred with the highest selectivity (87.3% in the above example), which represents a breakthrough of the intrinsic limit of 66.6% in the conventional hydrogenolysis method. (2) No branched dimer was formed. (3) Comparable or better catalyst turnover numbers (vide infra) were obtained. (4) Acrylonitrile can be a reactant and a solvent at the same time, which will be an advantage in a large-scale operation.

The reaction conditions and the catalyst with additives have been semioptimized. DMSO is a weak ligand and cannot be replaced with phosphines, isocyanides, amines, or nitriles without decrease in the yields of the products. The removal of the chloride ligand on the Ru seemed necessary and may be attained either by RCOONa or by R_3SnH.[4] Some selected results obtained by changing the structure of the organic acid for protonolysis are given in Table 1. Aromatic acids having a substituent at the ortho position seem to give

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(10) Some examples not using H_2 but with lower turnover numbers have been reported. For a catalyst of $RuCl_3$ with an amine or an acid (an example using salicyclic acid and 180 °C, 1 h, in benzonitrile) giving 4.7% yield of a mixture of dimers with turnover number of 43 (the highest example) (selectivities are not reported), see: Kollar, J. Canadian Patent 819,146, 1969. For Cp*Ru(olefin)Cl, see: Bonnet, M. C.; Chaudret, C. B.; Guibert, I.; He, X. D.; Tkatchenko, I. 30th International Conference on Coordination Chemistry, July 24, 1994, Kyoto, Japan; Abstract p 56. See also: Yorise, T.; Kaneshima, T. Jpn. Kokai 08-245539, 1996 (in which 28% yields of dimers with turnover number 100 are reported).

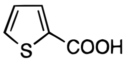
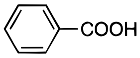
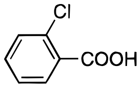
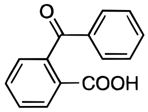
(11) Protonolysis of a Ru−C bond has been known as the key step in catalytic hydrogenation: Ohta, T.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1990**, *131*, 7189. Ashby M. T.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 589.

(12) DMSO stands for dimethyl sulfoxide. For the preparation of $RuCl_2(DMSO)_4$, see: Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(13) The dimers were *cis*-**1**, *trans*-**1**, **2**, *cis,cis*-**3**, *cis,trans*-**3**, and *trans,trans*-**3** in yields of 4.07, 5.60, 0.18, 0.20, 0.48, and 0.17%, respectively.

(14) Details of experiments and analysis of the products are given in the Supporting Information.

Table 1. Ru-Catalyzed Dimerization of Acrylonitrile (AN) in the Presence of Carboxylic Acid[a]

carboxylic acid	conversion of AN (%)	combined yield of dimers **1-3** (%), and (TON)		yield of cyanoethyl ester (%)
CH_3COOH	5.9	2.6	(193)	1.7
	11.8	10.1	(747)	0.5
	8.3	6.5	(480)	nd [b]
	14.0	11.6	(858)	nd [b]
	15.5 19.3 [c]	13.0 16.3	(960) (1206)	1.0 1.2

[a] Reaction conditions: acid/Ru = 150, AN/Ru = 7400 (see text). Although they are not shown in the table, about 0.5% yields of propionic acid were generally formed. [b] Not determined. [c] The amount of the acid was 9.55 mmol (acid/Ru = 250).

better yields of dimers. The use of a larger amount of the acid improved the yields with a high turnover number (>1200). With other acids such as trifluoroacetic acid, oxalic acid, *p*-toluenesulfonic acid, and phenol, the reaction did not proceed. The study using a series of substituted benzoic acids in separate runs indicated that the stronger acid gave a better yield. However, the relation between the reactivity of carboxylic acids and their structures in not clear at the present time.

In conclusion, a new catalytic route to acrylonitrile linear dimers using the protonolysis method has been developed, and this method has various advantages over existing methods. Mechanistically, the present reaction seems to involve insertion of Ru into a C−H bond similar to that observed in Ru-catalyzed C−H/olefin coupling[15] and appears to be different from that of Rh-catalyzed dimerization of acrylic esters, which proceeds via initial hydrometalation of the olefin.[16] Efforts to improve the effectiveness of the new acrylonitrile dimerization process by studying the mechanism, reaction conditions, and catalyst deactivation processes are being made.

Supporting Information Available: Text giving experimental details and methods for the analysis of the products (2 pages). Ordering information is given on any current masthead page.

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(15) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature (London)* **1993**, *366*, 529. Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679. Sonoda, M.; Kakiuchi, F.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1995**, *504*, 151. Sonoda, M.; Kakiuchi, F.; Kamatani, A.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 109. Kakiuchi, F.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 111.

(16) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. Brookhart, M.; Hauptman, E. *J. Am. Chem. Soc.* **1992**, *114*, 4437. Hauptman, E.; Sabo-Etienne, S.; White, P. S.; Brookhart, M.; Garner, J. M.; Fagan, P. J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 8038.