14α-methyl-5α-cholest-8-ene (IV) as a solid which crystallized from methanol as large flat needles (460 mg): mp 114–117°; λ_{max} 254 mμ, (ε 9417); ν_{max} 1745, 1660, 1583 cm^{-1}; nmr, δ 0.66 (18-Me), 0.80, 0.90, 1.18 (19-Me), 4.70; $[\alpha]_D$ +19.5° (*c* 1.30); ORD (*c* 0.06 in ligroin), $[\alpha]_{450}$ +32°, $[\alpha]_{400}$ +94°, $[\alpha]_{367}$ +160° (peak), $[\alpha]_{344}$ 0°, $[\alpha]_{300}$ −480°, $[\alpha]_{280}$ −897°, $[\alpha]_{260}$ −2180°.

Anal. Calcd for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found: C, 78.89; H, 10.62.

Registry No.—I, 5259-20-1; II, 5535–18-2; III, 14156-34-6; IV, 15963-76-5; VIb, 15963-75-4.

The Reaction of α,β-Unsaturated Nitriles with Concentrated Sulfuric Acid

Albert Zilkha, Israel Barzilay, Jacob Naiman, and Ben-Ami Feit[1]

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

Received September 20, 1967

Ritter and coworkers[2] have shown that the reaction between nitriles and branched olefins or tertiary alcohols in the presence of concentrated sulfuric acid led to the formation of N-alkylamides. This reaction was further studied,[3-9] and the general view[3,9] is that the reaction proceeds through a carbonium ion, formed from the olefin or alcohol which attacks the nitrogen of the nitrile group. Hydrolysis and tautomerism of the intermediate product leads to formation of the N-substituted amide.

Since an unsaturated nitrile contains both a nitrile group and a double bond, there is the possibility of interaction between these groups. Ritter[2f] carried out such a reaction between acrylonitrile (AN) and sulfuric acid in the presence of acetic acid and represented the polymer obtained as polyalanine (I) in the absence of any evidence.

$$CH_2{=}CHCN \xrightarrow{H_2SO_4} CH_2{=}CHCO[NHCH(CH_3)CO]_nNHCH(CH_3)CN$$

I

Formation of I is possible if propagation of the polymerization is through the α-carbon atom of the nitrile. Magat[10] reported the formation of a soluble polymer, of unidentified structure, on reaction of methacrylonitrile with a large excess of sulfuric acid.

The reaction of α,β-unsaturated nitriles with concentrated sulfuric acid seemed therefore to be an interesting method for the preparation of amino acids.

We reinvestigated the reaction between AN and sulfuric acid in the presence of acetic acid.[2f] An insoluble polymer was formed which on acid hydrolysis gave traces of an amino acid which was not alanine.

Owing to the insolubility of the polymer formed under these conditions[2f] we decided to investigate the reaction using excess sulfuric acid to obtain soluble polymers.[10] In fact under these conditions, a water-soluble product was formed. The chromatogram of its hydrolyzate showed several spots, among them a strong one belonging to β-alanine.

The effect of various factors on the yield of β-alanine was studied. The low yields obtained prompted us to try to find out what happened to the major portion of the AN. Distillation of the dilute reaction mixture, before hydrolysis, in the presence of 40% sodium hydroxide solution, was found to evolve ammonia, which was determined quantitatively by titration. The origin of the ammonia is from ammonium salts or possibly acrylamide, formed by total or partial hydrolysis of the nitrile groups, respectively, in the presence of sulfuric acid. Under these distillation conditions β-alanine did not evolve ammonia as opposed to the behavior acrylamide. The amount of the ammonia evolved was calculated as the per cent of "labile nitrogen" obtained at the end of the reaction, out of the initial amount of acrylonitrile introduced.

Increasing the acid concentration from 92 to 98% or the molar ratio of concentrated sulfuric acid (98%) to AN, increased the yield of β-alanine (Table I). The lowering in yield of β-alanine and the increase in the per cent of "labile nitrogen" at the low sulfuric acid concentration seems to be due to the increase in the amount of water present, which leads to extensive hydrolysis.

Table I

Effect of Various Factors on the Yield of β-Alanine

$[H_2SO_4]/[AN]^a$	Acid concn, %	β-Alanine yield, %	"Labile nitrogen," %
1	98	2.5	75.0
2.5	98	13.5	78.5
6	98	14.3	77.5
11.25	98	17.5	82.0
2.5	92	5.5	
7.5	92	2.9	96.5
10	92	3.0	97.0
b		5.5	60.0
b		5.2	65.0
c		0.6	

[a] 150 mmol of AN was used. [b] AN–chlorosulfonic acid–sulfuric acid (1:3:1) was used. [c] AN–sulfuric acid–acetic acid (1:2.5:1) was used.

We investigated the reaction of AN with a mixture of sulfuric acid and chlorosulfonic acid hoping to increase the yield of β-alanine by eliminating the water present in the reaction mixture. However, the yield decreased (Table I), but there was also a decrease in the per cent of "labile nitrogen." We tried also the reaction conditions of Ritter,[2f] using a mixture of sulfuric acid and acetic acid, but in the presence of the latter a large decrease in yield of β-alanine was observed (Table I).

The results of these experiments pointed out that the maximum yield of β-alanine will be obtained using concentrated sulfuric acid or by using fuming sulfuric

---

(1) Address correspondence to this author at the Department of Chemistry, The University, Tel Aviv, Israel.

(2) (a) J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045 (1948); (b) J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948); (c) F. R. Benson and J. J. Ritter, *ibid.*, **71**, 4128 (1949); (d) L. W. Hartzel and J. J. Ritter, *ibid.*, **71**, 4130 (1949); (e) R. M. Lusskin and J. J. Ritter, *ibid.*, **72**, 5577 (1950); (f) H. Plout and J. J. Ritter, *ibid.*, **73**, 4076 (1951).

(3) E. M. Smoline, *J. Org. Chem.*, **20**, 295 (1955).

(4) E. T. Roe and D. Swern, *J. Amer. Chem. Soc.*, **77**, 5408 (1955).

(5) R Jacquier and H. Cristol, *Bull. Soc. Chim. Fr.*, 596 (1957).

(6) C. L. Parris and R. M. Christenson, *J. Org. Chem.*, **25**, 331 (1960).

(7) T. Clark, J. Devine, and D. W. Dicker, *Abura Kagaku*, **41**, 78 (1964).

(8) F. L. Ramp, *J. Polym. Sci., Part A*, **3**, 1877 (1965).

(9) I. Weil, R. G. Goebel, E. R. Tulp, and A. Cahn, *Amer. Chem. Soc. Div. Petrol. Chem., Preprints*, **8**, 95 (1963); *Chem. Abstr.*, **62**, 1562 (1965).

(10) E. E. Magat, U. S. Patent 2,628,216 (Feb 10, 1953); *Chem. Abstr.*, **47**, 5129 (1953).

TABLE II

REACTION OF ACRYLONITRILE WITH OLEUM (30% SO_3)

Oleum, mmol[a]	[Oleum]/ [AN]	β-Alanine yield, %	α-Sulfo-β-amino-propionic acid, %	"Labile nitrogen," %
450	3	2.7	1.8	
1125	7.5	5.6	6.3	53
1350	9	4.8	2.9	53
1920	12.8	1.9	1.1	59

[a] Equivalent to sulfuric acid.

acid. This led us to carry out experiments using oleum (30% SO_3) (Table II).

It is seen that the yield of β-alanine decreased considerably on using oleum instead of sulfuric acid. On the other hand, the chromatograms showed the formation in relatively high quantity, of a new amino acid, having a smaller R_f than β-alanine, besides that of very small amounts of other amino acids, one of which was identified as taurine by an amino acid analyzer. This amino acid was identified as α-sulfo-β-aminopropionic acid. It was also obtained using 98% sulfuric acid but in very small amounts.

The formation of α-sulfo-β-amino acids by the reaction of α,β-unsaturated nitriles with oleum seemed to be a general reaction. Thus, with methacrylonitrile (MAN) the results in Table III were obtained.

TABLE III

REACTION OF METHACRYLONITRILE WITH SULFURIC ACID OR OLEUM

Acid (mmol)	[Acid]/ [MAN]	β-Amino-isobutyric acid yield, %	α-Sulfo-β-amino-isobutyric acid yield, %	"Labile nitrogen," %
H_2SO_4 (480)	4	3.9	4.3	85
Oleum (1125)	9.4	12.8	8.8	61

The amino acids isolated were identified as β-aminoisobutyric acid and α-sulfo-β-aminoisobutyric acid. The chromatograms showed the presence of traces of other amino acids.

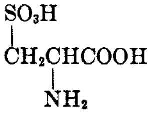
In a similar reaction of crotononitrile with concentrated sulfuric acid, β-aminobutyric acid was obtained in 9.7% yield, whereas with oleum (30% SO_3), it was obtained in 1.2% yield; besides a sulfoamino acid was obtained in 3.9% yield which was not isolated. This amino acid, by analogy to the other sulfoamino acids obtained, seems to be α-sulfo-β-aminobutyric acid.

The infrared spectra of the products obtained before hydrolysis from AN or MAN on reaction with concentrated sulfuric acid or oleum did not show the characteristic absorption peak for the nitrile group, but showed the characteristic absorptions for amide groups and for the $-SO_3H$ group at 1310, 1210–1240, and 1045 cm^{-1}. These products on being dried became insoluble in water and other solvents. Their elementary analysis showed that their composition was not constant and differed from batch to batch.

Establishing the Structure of the Amino Acids.—β-Alanine and α-sulfo-β-aminopropionic acid were isolated by ion exchange technique. The structure of β-alanine was proved from melting point and mixture melting point determinations, elementary analysis, chromatography from various solvent mixtures using authentic β-alanine as a marker, its infrared spectrum, and formation of its N-carbobenzoxy derivative.

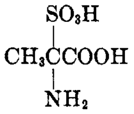
The structure of α-sulfo-β-aminopropionic acid (V) was proved as follows. Its elementary analysis showed it to have the empirical formula $C_3H_7NO_5S$, the same as that of cysteic acid. It was soluble in water and had a strongly acid reaction. Potentiometric titration in 0.1 *N* sodium chloride solution with 0.2 *N* sodium hydroxide or 0.2 *N* hydrochloric acid gave a molecular weight of 167 (calcd 169). The pK_a of the various groups in comparison with cysteic acid[11] were as follows: cysteic acid, $pK_a^1 = 1.12$, $pK_a^2 = 1.88$, $pK_a^3 = 8.7$; α-sulfo-β-aminopropionic acid, $pK_a^1 < 2$, $pK_a^2 = 2.8$, $pK_a^3 = 8.7$. Chromatographically the amino acid was different from cysteic acid. In high voltage electrophoresis (1000 V) using a buffer solution (pH 2.6), it migrated in the opposite direction to β-alanine and in the same direction as cysteic acid. The migration was smaller than that of cysteic acid (2.8 and 5.4 cm, respectively). This proves further that the amino acid is acidic, but less than cysteic acid.

Now the four sulfoaminopropionic acids (II–V), which have the empirical formula $C_3H_7NO_5S$, are possible. Structure II is that of cysteic acid. Structures III and IV are those of α-aminosulfonic acids, and it is known[12] that such amino acids are completely unstable in acid solution, and if present could not have remained after a long acid hydrolysis. Therefore, the structure of the sulfoamino acid is V, namely α-sulfo-β-aminopropionic acid. This amino acid will exist mostly in the form of a zwitterion between the sulfonic acid group and the amino group, since the less acidic carboxyl group is the same distance apart from the amino group as is the sulfonic group. That is why this amino acid is expected to be less acidic than cysteic acid, as found.



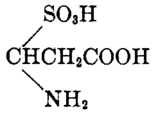
$\overset{SO_3H}{CH_2}\underset{NH_2}{CH}COOH$

II



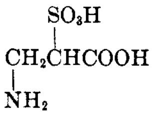
$CH_3\overset{SO_3H}{\underset{NH_2}{C}}COOH$

III



$\overset{SO_3H}{\underset{NH_2}{CH}}CH_2COOH$

IV



$\underset{NH_2}{CH_2}\overset{SO_3H}{CH}COOH$

V

The traces of taurine found in some of the acid hydrolyzates may be the result of decarboxylation of traces of α-sulfo-β-aminopropionic acid.

α-Sulfo-β-aminopropionic acid was prepared previously in low over-all yield using a multistep synthesis starting from β-alanine.[13] Our present one-step synthesis from AN is simpler. The structures of β-aminoisobutyric acid and α-sulfo-β-aminoisobutyric acid formed from MAN were established using similar evidence and reasoning as in the case of the amino acids obtained from AN.

Discussion

The reaction of α,β-unsaturated nitriles with concentrated sulfuric acid (or oleum) was shown to lead to the formation of a product which on subsequent acid

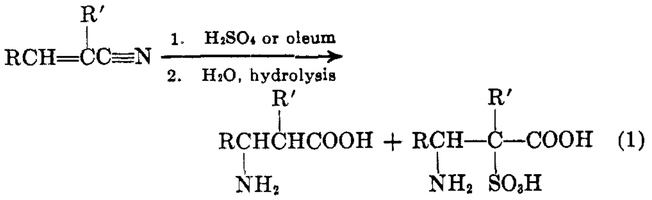
---

[11] C. L. Andrews and A. Schmidt, *J. Biol. Chem.*, **73**, 655 (1927).

[12] P. Moses, Ph.D. Thesis, The Hebrew University of Jerusalem, 1959.

[13] A. Schöberl and H. Braun, *Ann.*, **542**, 274 (1939); S. Gabriel, *Ber.*, **38**, 642 (1905).

hydrolysis gave a mixture of β-amino acids and α-sulfo-β-amino acids. The reaction may be schematically shown as in eq 1. This course of the reaction is



$$\mathrm{RCH{=}\overset{R'}{\overset{|}{C}}C{\equiv}N} \xrightarrow[\text{2. H}_2\text{O, hydrolysis}]{\text{1. H}_2\text{SO}_4\text{ or oleum}} \mathrm{\underset{NH_2}{\underset{|}{RCH}}\overset{R'}{\overset{|}{C}}HCOOH + \underset{NH_2}{\underset{|}{RCH}}{-}\underset{SO_3H}{\underset{|}{\overset{R'}{\overset{|}{C}}}}{-}COOH} \quad (1)$$

different from that given by Ritter.[2f] The reaction between α,β-unsaturated nitriles and concentrated sulfuric acid or oleum is quite complex. The fact that a high percentage of the nitrogen of the nitrile group is converted into "labile nitrogen" shows that hydrolytic (60–95%) reactions of the nitrile groups to ammonia or primary amide groups are very prominent, especially in the more dilute sulfuric acid solutions. For this reason the total yield of amino acids obtained in the reaction (after hydrolysis) did not exceed 20%. Because of this the structure of the product of the reaction, before hydrolysis, is expected to be very complex, and not to have exactly the same structure from batch to batch.

The reactions in eq 2–4 may describe the formation of β-alanine from AN in the presence of sulfuric acid. It seems that formation of a carbonium ion on the β carbon atom of AN is a prerequisite for the formation of β-alanine, and it is plausible that this could occur under the reaction conditions. This carbonium ion may be formed either by electrophilic addition of a proton to the double bond or by protonation of the nitrile group (eq 2). The β-carbonium ion can then add to a free nitrile group of AN. This reaction may continue. Addition of sulfuric acid to the C=N double bond will yield VI, which on subsequent acid hydrolysis will give β-alanine.

$$\mathrm{\overset{\delta+}{C}H_2{=}\overset{\delta-}{C}HC{\equiv}N \xrightarrow{H^+}}$$

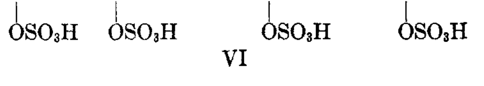
$$\mathrm{\overset{+}{C}H_2CH_2C{\equiv}N} \text{ or } \mathrm{CH_2{=}CH\overset{+}{C}{=}NH \longleftrightarrow \overset{+}{C}H_2CH{=}C{=}NH} \quad (2)$$

$$\mathrm{CH_2{=}CHC{\equiv}N + \overset{+}{C}H_2CH_2CN \longrightarrow}$$

$$\mathrm{CH_2{=}CH\overset{+}{C}{=}NCH_2CH_2CN \longleftrightarrow \overset{+}{C}H_2CH{=}C{=}NCH_2CH_2CN} \quad (3)$$

$$\mathrm{CH_2{=}CHC{\equiv}N \longrightarrow}$$

$$\mathrm{CH_2{=}CH\overset{+}{C}{=}NCH_2CH{=}C{=}NCH_2CH_2CN} \quad (4)$$

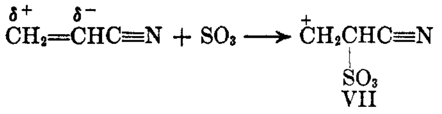


$$\mathrm{\underset{OSO_3H}{\underset{|}{CH_2CH}}{=}\underset{OSO_3H}{\underset{|}{C}}NHCH_2CH{=}\underset{OSO_3H}{\underset{|}{C}}NHCH_2CH_2\underset{OSO_3H}{\underset{|}{C}}{=}NH}$$

VI

Addition of sulfuric acid to the nitrile group and subsequent hydrolysis can explain why the hydrolysis reaction was so dominant.

The formation of α-sulfo-β-aminopropionic acid can be also explained in terms of electrophilic addition to the double bond. In concentrated sulfuric acid, and of course in oleum, there exists the electrophilic molecule SO_3[14] which adds to the nucleophilic double bond forming a C–S bond, which, contrary to C–O–S bonds, is stable to acid hydrolysis. The fact that with oleum the yield of the sulfonic acid increased gives support to the electrophilic addition of the SO_3 to the double bond.



$$\mathrm{\overset{\delta+}{C}H_2{=}\overset{\delta-}{C}HC{\equiv}N + SO_3 \longrightarrow \overset{+}{C}H_2\underset{SO_3}{\underset{|}{C}}HC{\equiv}N}$$

VII

The β-carbonium ion (VII) can add to the nitrile group of AN, as described before, leading in a series of addition reactions and subsequent hydrolysis to the formation of the α-sulfo-β-amino acid besides β-alanine.

These mechanisms apply equally well to the formation of the other β-amino acids and α-sulfo-β-amino acids from α,β-unsaturated nitriles. They are also consistent with the approved mechanism for the Ritter reaction,[3,9] according to which it is improbable that the propagation will proceed through the α-carbon atom of the nitrile to give poly-α-amino acids but only through the β-carbon atom to give poly-β-amino acids. However, the formation of products having partial structures of polymers or oligomers of β-amino acids, formed by "polymerization" of the α,β-unsaturated nitrile through the nitrile group as shown, is not the dominant reaction, since most of the monomer suffers hydrolysis of the nitrile groups in the course of the reaction, and only unhydrolyzed nitrile groups can participate in the poly-β-amino acid formation.

Experimental Section

Reaction of Acrylonitrile with Sulfuric Acid.—The reaction was carried out under anhydrous conditions and in an argon atmosphere. Redistilled purified dry AN[15] (8 g, 0.15 mol) was added dropwise with stirring to cooled concentrated sulfuric acid (98%, 25 ml), such that the temperature of the reaction mixture did not exceed 10°. The mixture was stirred at room temperature for 24 hr, ice water was added to stop the reaction, and the mixture was diluted to 225 ml so that the acid concentration was 4 *N*, and the solution was refluxed for 24 hr to affect hydrolysis. The hydrolyzate was neutralized with solid barium hydroxide and centrifuged from barium sulfate. The amount of the amino acids present in the filtrate was determined by paper chromatography. The reactions with methacrylonitrile and crotononitrile were carried out similarly.

α-Sulfo-β-aminopropionic Acid.—Acrylonitrile was added dropwise with stirring at the rate of about 0.4 ml every half minute to 25 ml of oleum (30% SO_3) cooled in an ice bath. The temperature rose to about 70° and was kept there until the end of the addition. The reaction mixture was stirred at room temperature for 24 hr, diluted with ice water until the concentration of the acid was 5 *N*, and refluxed for 24 hr to affect hydrolysis. The solution was neutralized with the calculated amount of solid barium hydroxide, and centrifuged from barium sulfate. The supernatent solution was stirred for 3 hr with Dowex 50W (H^+, 25 g) and filtered. The filtrate was evaporated to dryness *in vacuo*, and α-sulfo-β-aminopropionic acid crystallized out on standing under absolute ethanol. It was recrystallized from water–absolute ethanol to yield 1.6 g (6.3%): mp 250–260° dec; R_f (descending from butanol–acetic acid–water) 0.13 (cysteic acid, R_f 0.11). The nmr spectrum in D_2O showed a doublet centered at 3.53 ($-CH_2-$) and a triplet centered at 4.15 ppm (-CH-). *Anal.* Calcd for $C_3H_7NO_5S$: C, 21.30; H, 4.17; N, 8.28; S, 18.96. Found: C, 21.30; H, 4.10; N, 8.67; S, 18.40.

β-Alanine.—The Dowex resin left from the isolation of α-sulfo-β-aminopropionic acid was suspended in 1% ammonia solution (120 ml) and stirred for 1 hr to extract the β-alanine. The extract was evaporated to dryness *in vacuo*, and the β-alanine crystallized out on standing under absolute ethanol. It was recrystallized from water–dry acetone, yield 0.5 g (3.7%).

---

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 299.

(15) C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc.* (London), **A216**, 515 (1953).

Isolation of the Product of Reaction between Acrylonitrile and Sulfuric Acid.—The diluted reaction mixture before hydrolysis was neutralized with solid barium hydroxide and centrifuged from the precipitated barium sulfate. The precipitate was extracted with hot water. The filtrate and extract were combined, Dowex 50W (H^+, 25 g) was added to remove excess barium ions, if present, and other basic materials and the mixture was stirred for 3 hr. The filtrate from the ion-exchange resin was evaporated to dryness *in vacuo*, and the residue solidified on standing under absolute ethanol. In the reaction between AN (0.15 mol) and 98% sulfuric acid (0.48 mol), 9.8 g of a product were obtained. *Anal.* Found: C, 45.09; H, 7.64; N, 12.70; S, 1.66%.

In the reaction between acrylonitrile (0.15 mol) and oleum (30% SO_3) (1.125 mol), 10.2 g of a product were obtained. *Anal.* Found: C, 33.35; H, 5.43; N, 9.70; S, 12.90%.

α-Sulfo-β-aminoisobutyric Acid.—The reaction mixture obtained from methacrylonitrile (8 g, 0.12 mol) and oleum (30% SO_3, 25 ml), was diluted with ice water to 225 ml and refluxed for 24 hr. It was neutralized with barium hydroxide, centrifuged, and stirred with Dowex 50W (25 g) for 3 hr. The filtrate was evaporated to dryness *in vacuo*, and the residue was dissolved in hot ethanol (10 ml) and precipitated by diluting with dry acetone, scratching, and cooling in liquid air; a crude yield of 2.8 g (12.7%) was obtained. α-Sulfo-β-aminoisobutyric acid was recrystallized from ethanol–acetone: mp 240° dec; R_f 0.16 (descending from butanol–acetic acid–water). The nmr spectrum in D_2O showed only absorptions at 1.52 ($-CH_3$) and 3.45 ppm ($-CH_2-$). *Anal.* Calcd for $C_4H_9NO_5S$: C, 26.23; H, 4.92; N, 7.65; S, 17.49. Found: C, 26.37; H, 4.80; N, 8.00; S, 17.95.

β-Aminoisobutyric Acid.—The Dowex resin left from the isolation of α-sulfo-β-aminoisobutyric acid was suspended in 1% ammonia solution (150 ml) stirred for 1 hr and filtered. The filtrate was evaporated to dryness *in vacuo*, and the residue was extracted by hot absolute ethanol. The insoluble β-aminoisobutyric acid was filtered and washed with acetone. Another crop of the product was obtained on addition of acetone to the filtrate to give a total yield of 0.24 g (2%). It was recrystallized from ethanol–acetone.

Quantitative Determination of the Amino Acids by Paper Chromatography.—The descending method of paper chromatography was used and the developing solvent was composed of *n*-butyl alcohol–acetic acid–water (25:6:25). The chromatograms were sprayed with 0.5% ninhydrin solution in 85% aqueous acetone. Spots from the unknown as well as from markers were eluted with 75% aqueous ethanol and their absorbancy at 565 mμ was measured.

Registry No.—Sulfuric acid, 76649-93-9; acrylonitrile, 107-13-1; methacrylonitrile, 126-98-7; β-alanine, 107-95-9; IV, 15924-28-4; β-aminoisobutyric acid, 144-90-1; α-sulfo-β-aminoisobutyric acid, 15924-29-5.

Hydrogenation of Conjugated Diolefins with Transition Metal π Complexes

YOSHIO TAJIMA AND ETSUO KUNIOKA

Central Research Laboratories, Toyo Rayon Company, Ltd., Otsu, Shiga, Japan

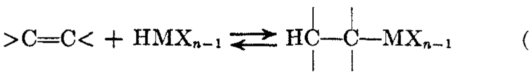
Received August 31, 1967

It has already been found by Sloan, Matlack, and Breslow[1] that a number of transition metal compounds combined with organometallic derivatives are soluble catalysts for the hydrogenation of olefins such as cyclohexene, 1-octene, 2-pentene, etc. Transition metals in groups IV–VIII, mostly as acetylacetonates or as alkoxides, have been found to be active when combined with, preferably, a trialkylaluminum compound. Mono-, di-, tri-, and tetrasubstituted olefins have been hydrogenated. They postulated the mechanism for the hydrogenation with the soluble catalysts as follows.

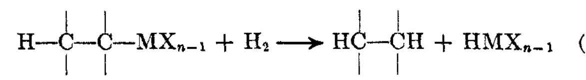
The reaction of transition metal derivatives with aluminum alkyls has as its first step alkylation of the transition metal derivative (eq 1). This step is followed by hydrogenolysis of the metal–alkyl bond formed to yield a metal hydride (eq 2), which then adds to an olefin forming a new metal alkyl (eq 3). Hydrogenolysis of the latter yields saturated hydrocarbon with regeneration of the metal hydride (eq 4).

$$R_3Al + MX_n \longrightarrow R_2AlX + RMX_{n-1} \qquad (1)$$

$$RMX_{n-1} + H_2 \longrightarrow RH + HMX_{n-1} \qquad (2)$$



$$>C{=}C< + HMX_{n-1} \rightleftarrows HC{-}C{-}MX_{n-1} \qquad (3)$$



$$H{-}C{-}C{-}MX_{n-1} + H_2 \longrightarrow HC{-}CH + HMX_{n-1} \qquad (4)$$

The hydrogenation of olefins by Ziegler catalysts was also investigated by Heck,[2] who postulated insertion reaction mechanisms of metal complexes. On the other hand, selective hydrogenation of conjugated diolefins, such as butadiene to monoolefins (butene-1, butene-2) by pentacyanocobaltate (II) complexes was studied by Kwiatek.[3]

In this paper, hydrogenation of butadiene or isoprene by binary catalysts systems of transition metal π complexes and organometallic compounds was studied. Transition metal π complexes tried were biscyclopentadienyl transition metal dichloride (Cp_2TiCl_2, Cp_2VCl_2, and Cp_2ZrCl_2), π-allyl-π-cyclopentadienylnickel ($C_5H_5NiC_3H_4$), cyclopentadienyldicarbonylcobalt ($CpCo(CO)_2$), and cyclopentadienyldicarbonylchloroiron $CpFe(CO)_2Cl$. Organometallic compounds used were organolithium compounds (for example, n-C_4H_9Li), Grignard reagents (for example, PhMgBr), and organoaluminum compounds ($AlEt_3$, $AlBu_3$).

The results are shown in Tables I–III. In Table I, the results of hydrogenation of butadiene by biscyclopentadienyl transition metal dichlorides are shown. In Cp_2TiCl_2–BuLi (or PhMgBr) catalyst systems, quantitative hydrogenation of butadiene to saturated hydrocarbon (butane) was observed, and little unsaturation

TABLE I

HYDROGENATION OF BUTADIENE BY BISCYCLOPENTADIENYL TRANSITION METAL COMPOUNDS[a]

Catalyst system	Conversion, %	Content, %			
		Butene-1	*cis*-Butene-2	*trans*-Butene-2	Butane
Cp_2TiCl_2–BuLi	100.0	0	0	0	100.0
Cp_2TiCl_2–PhMgBr	99.0	0	0.2	2.3	97.5
Cp_2VCl_2–BuLi	62.2	2.3	13.9	84.8	0
Cp_2VCl_2–PhMgBr	43.1	1.7	26.1	72.2	0
Cp_2ZrCl_2–BuLi	0				
Cp_2ZrCl_2–PhMgBr	0				

[a] The hydrogenation reactions were carried out at 40–45° for 15 hr using the catalyst system 2 mmol of Cp_2MCl_2 (M: Ti, V, Zr) and 4.8 mmol of BuLi (or 7 mmol of PhMgBr) and 50 ml of benzene as the solvent. The initial hydrogen pressure was 60 kg/cm²; 7 ml of butadiene was used in each experiment.

---

[1] M. F. Sloan, A. S. Matlack, and David S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963).

[2] R. F. Heck, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 181.

[3] J. Kwiatek and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 201.