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# Reaction Mechanism of Cathodic Crossed Coupling of Acetone with Unsaturated Compounds in Acidic Solution

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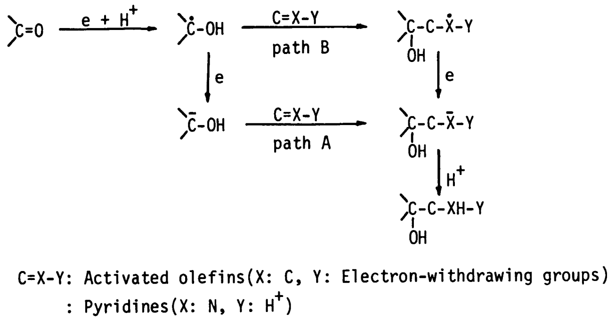
It was confirmed that the cathodic crossed coupling of acetone with unsaturated compounds in aqueous sulfuric acid could proceed smoothly, when the compounds which had radical-acceptable double bonds and were adsorbed on a mercury cathode were used. From this fact, it was concluded that the coupling occurs via the addition of a radical intermediate formed by the one-electron reduction of acetone to the double bonds on the cathode surface. Possibility of the addition of an anionic intermediate derived from acetone was excluded by no occurrence of the coupling of acetone with a polar acetylenic triple bond compound adsorbed on the cathode.

A number of electrochemical bimolecular reactions, e. g. dimerization, have been known and some of them have been used for purposes of syntheses in laboratories and industries. In previous works,[1—3] one (T. N.) of the authors reported a new type of crossed hydrocoupling reaction: When mixtures of acetone and activated olefins such as acrylic acid derivatives and maleic acid were reduced at a mercury cathode in aqueous sulfuric acid, their crossed hydrodimers were formed in good yields and current efficiencies. This reaction was successfully extended by using other aliphatic carbonyl compounds and C–N unsaturated compounds such as pyridines and amino nitriles instead of acetone and activated olefins, respectively.[4—13]

It should be generally important to clarify reaction mechanisms in order to design and optimize the reactions to be useful in a viewpoint of synthesis. A tentative mechanism (Scheme 1, path A, C=X-Y: $CH_2$=CH-CN) for the crossed hydrocoupling of acetone with acrylonitrile was first proposed by one(T. N.) of the authors. Afterward, Brown and Lister[14] also proposed another mechanism(Scheme 1, path B) on the basis of cyclic voltammetry of a mixture of acetone and acrylonitrile in aqueous sulfuric acid. However their mechanism was confuted by other investigators.[15]



C=X-Y: Activated olefins(X: C, Y: Electron-withdrawing groups)
: Pyridines(X: N, Y: $H^+$)

Scheme 1.

More recently, Shono et al.[16,17] have reported that the intramolecular electroreductive cyclization of carbonyl compounds having inactive olefinic parts can occur in good yields in neutral solutions. Although they have briefly mentioned a mechanism equivalent to path B as the most plausible one, they have not given any obvious evidence and not verified the path B in comparison with path A.

In this study, we wish to clarify the reaction mechanism of which the key step has been still ambiguous and to indicate more clearly the scope, e. g. the possible extension and limitation, of this remarkable reaction.

## Results and Discussion

Mixtures of acetone and various types of compounds having unsaturated carbon–carbon or carbon–nitrogen bonds were reduced at a mercury cathode in

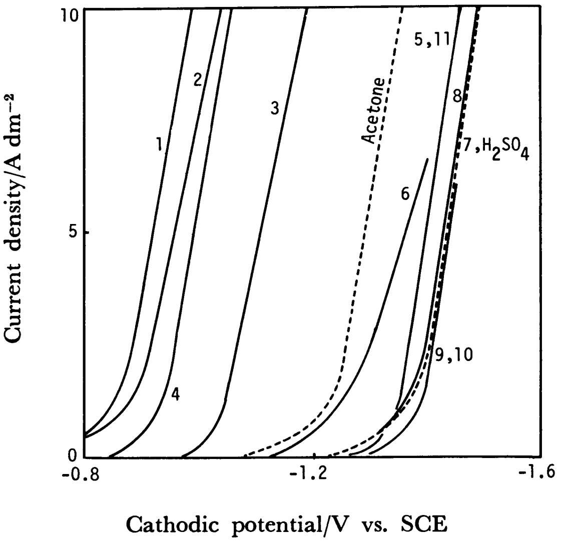


Fig. 1. Polarization curves of unsaturated compounds (**1**—**11**) and acetone at a mercury cathode in 20 wt% $H_2SO_4$. Concentration: **1**, **3**, and **8**, 0.1 mol $dm^{-3}$; **2**, **4**—**7**, and **9**—**10**, 0.4 mol $dm^{-3}$; **11**, saturated; acetone, 50 wt%.

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aqueous sulfuric acid.

Polarization curves of acetone and the unsaturated compounds measured in aqueous sulfuric acid by a steady state method are shown in Fig. 1. By comparing the reduction potentials of the unsaturated compounds with that of acetone, the compounds were classified into two groups: One consists of the compounds which seem to be more easily reduced than acetone, while those in the other group are more difficultly or can not be reduced.

The compounds such as phenyl vinyl sulfoxide (**1**), methyl vinyl sulfone (**2**), *N*-vinylpyridinium bromide (**3**), and quinoline (**4**), which belong to the former group, were reduced at less negative potentials than acetone to give the corresponding non-crossed coupling products by their own reduction. When a mixture of **1** and acetone was electrolyzed by passing 2.0 F (1 F= 96480 C) $\text{mol}^{-1}$ of charge, 1,2'-bis(phenylthio)ethane was formed in 66% yield and 33% of the starting **1** were recovered. The reaction scheme of this reduction may be written down as in Scheme 2 on the basis of material and charge balances observed. According to this scheme, current efficiency for the reaction was estimated to be about 100%, though ethylene was not quantitatively analyzed. The reduction of **2** consumed coulometrically 2 F $\text{mol}^{-1}$, but any reduction products[18] were not separated. The reduction of **3** and **4** gave the corresponding dimeric hydropyridine and hydroquinoline, respectively, but their exact molecular structures could not be determined.

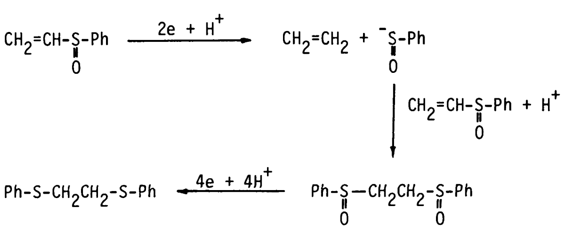
The unsaturated compounds having more negative reduction potentials than that of acetone could give the corresponding crossed coupling products with acetone as shown in Table 1. From a fact that considerable amounts of 2-propanol and 2,3-dimethyl-2,3-butanediol were formed as by-products in all the electrolyses, the occurrence of acetone reduction was confirmed.

It had been found that the addition of acetone to the 2-position of an *N*-unsubstituted pyridinium ring occurred exclusively.[4] However, though *N*-ethylpyridinium bromide (**5**) gave three crossed coupling products, their complete molecular structures (positions of 1-hydroxy-1-methylethyl groups and unsaturated bonds on the hydropyridine rings) could not be determined, as shown in Table 1. Isoquinoline (**6**) gave a sole crossed coupling product, though another isomeric one could be also expected to be formed as shown in Scheme 3. This result is rationalized as due to a more favorable limiting structure **6** than **6'** (in Scheme 3). Diethyl vinylphosphonate (**7**) behaved as a typical activated olefin to give the crossed coupling product with acetone as well as acrylonitrile.[2] The unsaturated bonds of **5**—**7** are highly polarized and they are so-called Michael acceptors[19] which should be able to accept a carbanion intermediate formed by the two-electron reduction of acetone. Therefore, the probability of path A in Scheme 1 can not be excluded.

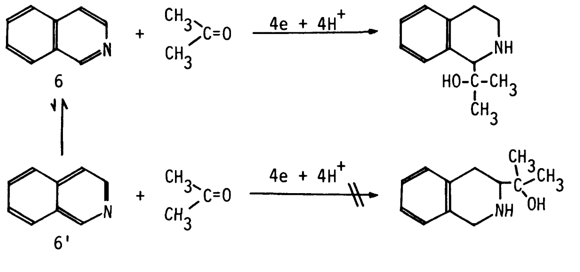
Results described above are interesting but not very important to discuss the reaction mechanism in detail. The most important result for clarification of the mechanism was obtained in the reaction of trimethylvinylammonium bromide (**8**) with acetone.

Since a nitrogen atom has not d-orbital which can accept an electron, nitrogen ylids are generally very unstable and difficultly formed.[20] This is a reason for that vinylammoniums can not undergo Michael addition[21] which should proceed via nitrogen ylid intermediates, though their double bonds should be highly polarized. On the other hand, vinylsulfoniums and vinylphosphoniums can undergo the addition,[19,21] since both sulfur and phosphorus atoms have d-orbitals. As shown in Table 1, trimethylvinylammonium bromide (**8**) gave the corresponding crossed coupling product with acetone, though **8** is not a Michael acceptor but a polarized olefin. This fact should exclude path A and consequently supports path B.

A further evidence for path B was obtained by using inactive olefins such as allylamine (**9**) and allyl alcohol (**10**). The former and the latter gave the corresponding crossed coupling products in reasonable and much lower yields, respectively, in aqueous sulfuric acid. It was independently confirmed that the olefins themselves could not be reduced under electrolytic conditions. Since lifetimes of aliphatic radicals, except for allylic and benzylic ones, are generally very short, the addition of a radical intermediate derived from acetone to the olefins in

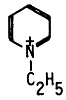
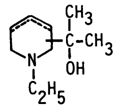
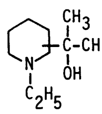
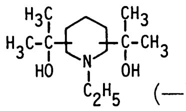
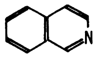
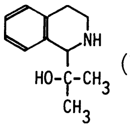
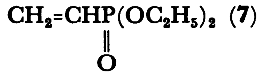
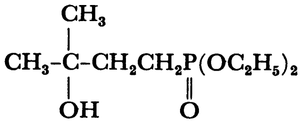
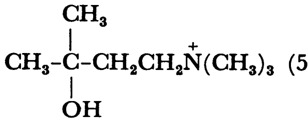
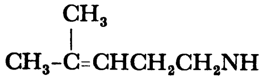
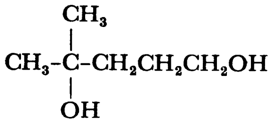
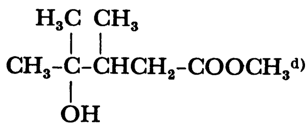


Scheme 2.



Scheme 3.

Table 1. Electrolytic Results of Mixtures of Unsaturated Compounds (**5**—**12**) and Acetone

| Unsaturated compounds | Cathodic potential /V vs. SCE | Charge passed /F mol$^{-1}$ | Crossed hydrocoupling products (Yield[a]/%) |
|---|---|---|---|
|  (**5**) | −1.30 | 4.0 |  (22)<br> (11)<br> (—[b]) |
|  (**6**) | −1.30 | 4.0 |  (78) |
|  $CH_2{=}CH\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$ (**7**) | −1.24 | 2.0 |  $CH_3\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}CH_2CH_2\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$ (39) |
| $CH_2{=}CH\overset{+}{N}(CH_3)_3$ (**8**) | −1.25 | 40.0 |  $CH_3\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}CH_2CH_2\overset{+}{N}(CH_3)_3$ (54) |
| $CH_2{=}CHCH_2NH_2$ (**9**) | −1.24 | 2.0 |  $CH_3\text{-}\overset{CH_3}{C}{=}CHCH_2CH_2NH_2$ (26) |
| $CH_2{=}CHCH_2OH$ (**10**) | −1.24 | 2.0 |  $CH_3\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}CH_2CH_2CH_2OH$ (1) |
| $CH_3\text{-}C{\equiv}C\text{-}COOCH_3$ (**11**) | −1.30 | 2.0 | Recovered **11** (94) |
| $CH_3\text{-}CH{=}CH\text{-}COOCH_3$ (**12**) | —[c] | 4.0 |  $CH_3\text{-}\underset{OH}{\overset{H_3C}{C}}\text{-}\overset{CH_3}{C}HCH_2\text{-}COOCH_3$[d] (38[e]) |

a) Based on the starting unsaturated compounds. b) Not estimated. c) Under galvanostatic conditions at 6 A dm$^{-2}$ of current density. d) Isolated as a mixture of the corresponding cis and trans-lactones. e) Estimated from a result reported in previous work.[27]

path B should take place on surface or vicinity of cathode in competition with its own coupling to form 2,3-dimethyl-2,3-butanediol and its further reduction to form 2-propanol. On the basis of this consideration, the higher yield with **9** is rationalized as due to its higher concentration on the cathode surface. Such a higher concentration is achieved by adsorption of protonated **9** ($CH_2{=}CH\text{-}CH_2\text{-}NH_3^+$) which is electrostatically attracted to the negatively polarized cathode: It had been confirmed by electrode-interfacial capacity measurement and AC-polarography that acrylonitrile and pyridinium adsorb in aqueous sulfuric acid.[22] On the other hand, the protonation of **10** does not seem to be so sufficient that it can adsorb strongly and undergo easily the addition of the radical intermediate on the cathode surface.

In contrast, in the case of the intramolecular reductive cyclization of unsaturated carbonyl compounds,[16,17] high yields of the cyclized product should be reasonably expected, since the unsaturated part should exist in the vicinity of radical part formed: In this case, the high yields can be expected regardless of the adsorption. Recently, Little et al.[23] have reported that the intramolecular reductive cyclization of ketones having activated olefinic double bonds can proceed efficiently in not only acidic but also neutral media. More recently, Shono et al.[24] have reported an improved intermolecular reductive coupling of ketones with inactive olefins: They electrolyzed mixtures of aliphatic ketones and olefins in the presence of trimethylchlorosilane at a zinc cathode in DMF containing tetraethylammonium tetrafluoroborate to obtain the corresponding crossed coupling products in good yields but in low current efficiencies. They have shown a path B-like mechanism for this reaction. This method was also applicable to activated olefins and aldehydes.[25]

Regioselective addition of radicals in the intramolecular cyclization may be explained on the basis of ease and difficulty of formation of substituted ring systems in each case. However, regioselectivity observed in the intermolecular addition of radicals to polarized double bonds has not been rationalized yet. In this work, it was attempted to calculate reaction indexes for radical addition and collate with experimental results. The reaction indexes of acrylonitrile and pyridinium as typical sample molecules are given in Table 2. Table 2 shows that all the indexes indicate 3- and 2-positions in acrylonitrile and pyridinium, respectively, as the most favorable ones for the radical addition and in fact the addition took place at these positions. This coincidence may be one of evidences for path B.

It is generally known that acetylenes are less reactive than olefins towards free radicals while more reactive towards nucleophiles.[26] In fact, acetylenecarboxylic acid derivatives undergo Michael addition.[19] The reduction potential of methyl 2-butynoate (**11**) seemed more negative than that of acetone but it gave no crossed hydrocoupling product with acetone: The starting **11** was almost completely recovered. On the other hand, in a previous work[27] methyl crotonate (**12**) as an olefinic analogue of **11** had been found to give the corresponding crossed coupling product with acetone in a reasonable yield. In this work, it was also confirmed by the electrode-interfacial capacity measurement that the adsorption of **11** on a mercury cathode occurred similarly to that of **12**. These facts also exclude path A.

Path A might be also excluded to rationalize stereochemistry of the crossed hydrocoupling products of cyclohexenecarboxylic acid derivatives with acetone.[28]

It is known that the reduction of acetone in acidic solutions gives 2-propanol as a main product at a mercury cathode and propane as a sole product at other cathodes such as cadmium, aluminum, and zinc.[29] The formation of 2-propanol is obviously via the carbanion intermediate, while propane seems to be formed via the radical intermediate. In a previous work,[13] the cathodes other than mercury were also found to result in the formation of the crossed coupling product of acrylonitrile with acetone in considerable yields. This fact also may support path B.

Table 2. Reaction Indexes for Radical Addition to Acrylonitrile and Pyridinium

| Reaction index | Positions | | | | |
|---|---|---|---|---|---|
| | Acrylonitrile | | Pyridinium | | |
| | 2 | 3[a] | 2[a] | 3 | 4 |
| Free atomic valence | 0.3678 | 0.8877 | 0.4094 | 0.3977 | 0.4051 |
| Localization energy | 2.5532 | 1.7136 | 2.5011 | 2.5413 | 2.5311 |
| Frontier electron density | 0.4061 | 0.7615 | 0.4094 | 0.2842 | 0.3052 |
| Super delocalizability | 0.8443 | 2.0210 | 0.8695 | 0.8336 | 0.8621 |

[a] Position at which the addition occurred actually in electrolyses.

## Conclusion

1) The crossed hydrocoupling of carbonyl compounds with unsaturated ones proceeds via the addition of radical intermediates genarated by the one-electrone reduction of the formers to the latters, as shown in path B, Scheme 1.

2) Radical-acceptable unsaturated bonds are available for the crossed coupling, regardless of their polarization.

3) Under conditions where concentration of the unsaturated compounds on the surface or vicinity of cathodes can be kept high by their adsorption, the crossed coupling can smoothly proceed: The composition of electrolytic solutions is not an essential factor, if they adsorb sufficiently.

4) In intramolecular coupling, so-called cyclization, the adsorption is not an important matter.

5) To obtain synthetically satisfactory results, it is required to use the unsaturated compounds reduced at more negative potentials than the carbonyl compounds.

## Experimental

**Materials. Methyl Vinyl Sulfone (2):** To prepare **2**, methyl 2-hydroxyethyl sulfide was first synthesized from 2-chloroethanol and methanethiol by the modified method of Kirner and Richtery.[30] Yield 65%; bp 53—54 °C/8 Torr (1 Torr=133.322 Pa) (lit,[30] 68—70 °C/20 Torr). The sulfide obtained thus was converted into methyl 2-chloroethyl sulfide by treatment with thionyl chloride. Yield 67%; bp, 57—59 °C/12 Torr (lit,[31] 55—56 °C/30 Torr). This sulfide was oxidized to the corresponding sulfone with 30% hydrogen peroxide solution in acetic acid and then the reaction mixture was evaporated to dryness. The residual oily material was treated with triethylamine to convert it into the titled sulfone (**2**).[32] Yield 68%; bp 105—107 °C/17 Torr (lit,[32] 115—117 °C/19 Torr); IR (liquid film), 3030, 2950, 1300, 1140, and 960 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$=2.90 (s, 3H, $C\underline{H}_3$) and 6.7—7.0 (m, 3H, $C\underline{H}{=}C\underline{H}_2$).

***N*-Vinylpyridinium Bromide (3):** A mixture of pyridine (5.1 $cm^3$, 0.063 mol) and 1,2-dibromoethane (6.5 $cm^3$, 0.076 mol) was allowed to stand for 14 d at room temperature and then *N*-(2-bromoethyl)pyridinium bromide crystallized out was collected.[33] Yield, 65%. A mixture of the bromide thus obtained and potassium hydroxide in ethanol was stirred for 1.5 h at room temperature. The potassium bromide precipitated was filtered off and the filtrate was treated with charcoal. The decolored ethanol solution was poured into ether, and then the titled compound (**3**) was collected and recrystallized from a mixture of ethanol and ether. Yield, 62%; mp 154—155 °C; $^1$H-NMR ($D_2O$) $\delta$=5.8—6.3 (m, 2H, $CH=C\underline{H}_2$), 7.3—7.8 (m, 1H, $C\underline{H}=CH_2$), and 8.0—9.1 (m, 5H, pyridine-$\underline{H}$).

***N*-Ethylpyridinium Bromide (5):** Pyridine (10.0 g, 0.13 mol) was reacted with ethyl bromide (14.5 g, 0.13 mol) for 2 d at room temperature and then precipitated **5** was collected and recrystallized from a mixture of ethanol and ether. Yield 81%; mp 120—121 °C; $^1$H-NMR ($D_2O$) $\delta$=1.78 (t, 3H, $C\underline{H}_3$), 4.80 (q, 2H, $C\underline{H}_2$), and 8.1—9.0 (m, 5H, pyridine-$\underline{H}$).

Other chemicals used were commercially supplied.

**Electrolysis.** An H-type divided cell with a sintered glass diaphragm was used. The cathode and anode were a mercury pool (7.1 cm$^2$) and a platinum plate, respectively.

Before electrolysis, polarization curves were measured by a steady state method. The electrolysis was carried out by a controlled potential method at 30 °C. The electrolytic solution was a mixture of acetone (30 g) and aqueous sulfuric acid (20 wt%, 30 g) containing substrates (**1**—**11**, 5—20 mmol).

**Product Analysis.** A general procedure was as follows. After the cathodic solution was neutralized (pH 1) with sodium hydroxide solution (20 wt%), it was extracted with organic solvents (mainly ether). When basic products were expected, the resulting aqueous layer was made strongly alkaline by addition of excess sodium hydroxide and then extracted again. All the extracts were dried over anhydrous sodium sulfate and analyzed by gas chromatography (PEG 20 M, 2 m, 190 °C for diethyl 3-hydroxy-3-methylbutylphosphonate; PEG 6000, 2 m, 70—170 °C for 2-propanol, 2,3-dimethyl-2,3-butanediol, 4-methyl-1,4-pentanediol, and methyl 3-methyl-2-butenyl sulfone; Tritone X305, 2 m, 170—180 °C or PEG-5% KOH, 1—2 m, 150—180 °C for 1-ethyl-2-(1-hydroxy-1-methylethyl)tetrahydropyridine, 1-ethyl-2-(1-hydroxy-1-methylethyl)piperidine, 1-ethyl-2,5-bis(1-hydroxy-1-methylethyl)piperidine, 4-methyl-3-pentenylamine, 2,2′-bi(1,2,3,4-tetrahydroquinoline), and 1-(1-hydroxy-1-methylethyl)-1,2,3,4-tetrahydroisoquinoline).

**Reduction Product of Phenyl Vinyl Sulfoxide (1):** 1,2-Bis(phenylthio)ethane crystallized out from the cathodic solution, when the solution was allowed to stand overnight. Mp 68—69 °C; IR (KBr), 1580, 1480, 1440, 740, and 690 cm$^{-1}$; MS (*m/z*), 246 (M$^+$). Found: C, 68.02; H, 5.71; S, 25.93%. Calcd for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73; S, 26.03%.

**Reduction Products of Methyl Vinyl Sulfone (2):** The ethereal extract was evaporated and then the residual oil was distilled. The main fraction was methyl ethyl sulfone and also few drops of a higher boiling point fraction were obtained at ca. 120 °C/Torr. The high resolution mass spectrum indicated that the latter fraction would be methyl 3-methyl-2-butenyl sulfone which might be formed by dehydration of the original crossed hydrocoupling product (methyl 3-methyl-3-hydroxybutyl sulfone) with acetone. Found: *m/z* 148.0502. Calcd for $C_6H_{12}O_2S$: M 148.0556.

**Reduction Product of *N*-Vinylpyridinium Bromide (3):** A strongly basic product was separated by preparative gas chromatography. From the mass spectrum, it seemed to be 1,1′-divinyl-2,2′-bipiperidine or 1,4-bis(1-tetrahydropyridyl)butane. MS (*m/z*), 220 (M$^+$).

**Reduction Product of Quinoline (4):** A solid crystallized out from the cathodic solution made alkaline seemed to be a 2,2′-bi(1,2,3,4-tetrahydroquinoline). Mp 112—114 °C; MS (*m/z*), 262 (M$^+$); IR (KBr), 3360, 2940, 1605, 1490, 1260, 1120, and 750 cm$^{-1}$.

**Crossed Hydrocoupling Products of *N*-Ethylpyridinium Bromide (5) with Acetone:** Three fractions, which seemed to be isomeric mixtures, were separated by preparative gas chromatography, but the complete structures of products could not be determined by NMR study. 1-Ethyl-?-(1-hydroxy-1-methylethyl)-?,?,?,?-tetrahydropyridine. MS (*m/z*), 169 (M$^+$). 1-Ethyl-?-(1-hydroxy-1-methylethyl)piperidine. MS (*m/z*), 171 (M$^+$). Picrate: Mp, 156—157 °C. Found: C, 47.62; H, 6.00; N, 13.83%. Calcd for $C_{16}H_{24}N_4O_8$: C, 47.99; H, 6.04; N, 13.99%. 1-Ethyl-?,?-di(1-hydroxy-1-methylethyl)-piperidine. MS (*m/z*), 227 (M$^+$).

**Crossed Hydrocoupling Product of Isoquinoline (6) with Acetone:** 1-(1-Hydroxy-1-methylethyl)-1,2,3,4-tetrahydroiso quinoline was separated by preparative gas chromatography. Mp 82—83 °C; MS (*m/z*), 191 (M$^+$); IR (KBr), 3310, 3200, 2990, 2940, 2910, 1490, 1370, 1260, 1210, 1160, 1110, 970, 860, and 750 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$=1.04 (s, 3H, $C\underline{H}_3$), 1.32 (s, 3H, $C\underline{H}_3$), 2.6—3.4 (m combined, 6H, $C\underline{H}_2C\underline{H}_2$-$N\underline{H}$-CH-C-$O\underline{H}$), 3.95 (s, 1H, $C\underline{H}$), and 7.1—7.3 ppm (m combined, 4H, benzo-$\underline{H}$). On adding $D_2O$, the total relative intensity of the complicatedly combined multiplets at $\delta$ 2.6—3.4 ppm decreased by one third and a singlet peak for HDO appeared. The IR and NMR spectra suggested an intermolecular hydrogen bonding between the hydroxyl and amino groups. Found: C, 75.23; H, 9.25; N, 7.32%. Calcd for $C_{12}H_{17}NO$: C, 75.12; H, 8.97; N, 7.32%.

**Crossed Hydrocoupling Product of Diethyl Vinylphosphonate (7) with Acetone:** Distillation of a chloroform extraction afforded diethyl 3-hydroxy-3-methylphosphonate. Bp 125 °C/6 Torr; IR (liquid film), 3370, 2990, 2950, 1220, 1030, and 960 cm$^{-1}$; MS (*m/z*), 224 (M$^+$); $^1$H-NMR ($CDCl_3$) $\delta$=1.2 (s, 6H, $C\underline{H}_3$-C-OH), 1.3 (t, 6H, $C\underline{H}_3$-$CH_2$-O), 1.7—2.2 (m, 4H, $C\underline{H}_2$-$C\underline{H}_2$), 3.0 (s, 1H, $O\underline{H}$), and 3.8—4.3 (overrapping m, 4H, $C\underline{H}_2$-O).

**Crossed Hydrocoupling Product of Trimethylvinylammonium Bromide (8) with Acetone:** The cathodic solution was neutralized (pH 6.0) and then extracted with ether. The aqueous layer was evaporated to dryness under reduced pressure and extracted with ethanol. The ethanolic extract was poured into ether, trimethyl(3-hydroxy-3-methylbutyl)ammonium bromide precipitated was collected, and recrystallized from a mixture of ethanol and ether. Mp 172—173 °C; MS (*m/z*), 94 and 96 ($CH_3Br$), 59 ($(CH_3)_2C=OH^+$), and 85 ($(CH_3)_2N=CH_2^+$); $^1$H-NMR ($CD_3OD$) $\delta$=1.30 (s, 6H, $C\underline{H}_3$), 1.8—2.1 (m, 2H, $C\underline{H}_2$-$CH_2$-N), 3.23 (s, 9H, $(C\underline{H}_3)_3$-$N^+$), and 3.4—3.7 (m, 2H, $C\underline{H}_2$-N). Found: C, 42.79; H, 9.35; N, 6.16%. Calcd for $C_8H_{20}NBrO$: C, 42.49; H, 8.91; N, 6.19%.

**Crossed Hydrocoupling Product of Allyl Amine (9) with Acetone:** 4-Methyl-3-pentenylamine, which corresponds to the dehydration product of 4-methyl-4-hydroxypentylamine, was separated by preparative gas chromatography. MS (*m/z*), 99 (M$^+$), 82 (M$^+$—$NH_3$), and 41 ($C_3H_5^+$).

**Crossed Hydrocoupling Product of Allyl Alcohol (10) with Acetone:** 4-Methyl-1,4-pentanediol was separated by distillation of the ethereal extract of the cathodic solution. Bp 100 °C/11 Torr. Identified with the authentic sample prepared from $\gamma$-butyrolactone and 2 equiv methylmagnesium iodide.

**Electrode-Interfacial Capacity Measurement.** The capacity was measured by an impedance-bridge method similar to that used in previous work.[22)]

**Calculation of Reaction Indexes.** The indexes were calculated by a HMO method using a computing program given by Kikuchi.[34)] Following HMO parameters concerning with nitrogen atom were used. Acrylonitrile: Coulomb integrations of N and C in the cyano group, 1.2 and 0.1, respectively; resonance integration of C≡N, 1.0. Pyridinium: Coulomb integrations of $N^+$ and C adjacent to the $N^+$, 0.6 and 0.3, respectively; resonance integration of $^+N=C$, 1.0.

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