Studies on Fluorene Derivatives. XV. The Clemmensen Reduction of Fluorenone*

By Kazuo SUZUKI

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There have been several investigations of the Clemmensen reduction of fluorenone (I). Harris et al.⁽¹⁾ obtained fluorenol (II), fluorene (III), 10, 10-diphenylene-9-phenanthrone (V), dibiphenylene-ethylene (IX) and -ethane (X) by reduction of I under various conditions in the presence of dilute ethanol.

Bradlow et al.⁽²⁾ produced III and V in toluene or ethanol, while Ritchie⁽³⁾ obtained III and X in an ethanolic solution. III was obtained in a fairly good yield in each of these experiments and also in another preparation⁽⁴⁾.

However, I has been best reduced to III by the Wolff-Kischner method with or without an alkaline catalyst, as has been observed by Weisburger and Grantham⁽⁵⁾.

This is interesting because a great part of I does not normally proceed by way of II in the Clemmensen reduction and also because many related products were obtained by an abnormal reaction. Moreover, some of them do not appear to have been previously reported as direct products from I in this reduction.

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* XIV of this series: S. Kajigaeshi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1712 (1961).

1) A. S. Harris, E. N. White and D. McNeil, *J. Chem. Soc.*, **1955**, 4216.

2) H. L. Bradlow and C. A. VanderWerf, *J. Am. Chem. Soc.*, **69**, 1254 (1947).

3) E. Ritchie, *J. Proc. Roy. Soc. N. S. W.*, **80**, 33 (1946).

4) H. R. Gutmann and J. H. Peters, *Cancer Res.*, **13**, 415 (1953); F. E. Ray and R. C. Geiser, ibid., **10**, 616 (1950).

5) J. H. Weisburger and P. H. Grantham, *J. Org. Chem.*, **21**, 1169 (1956).

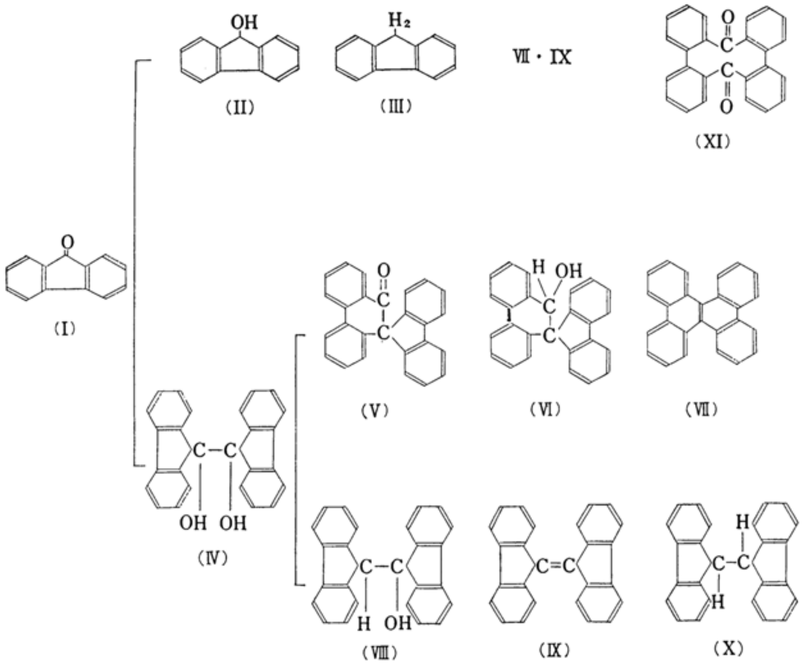

Chart 1

The present author carried out the reduction by the procedure of "Organic Reactions"[6]: I was dissolved in solvents such as toluene, benzene and xylene, which were mixed with the aqueous hydrochloric acid. The mixture was heated under reflux for a period of twenty-four hours, concentrated hydrochloric acid being added at intervals of about six hours. These results are summarized in Table I.

In this work, II, III and dimeric reaction products, namely, 9, 9′-dihydroxy-9, 9′-bifluorenyl (fluorenopinacol) (IV), V, 10, 10-diphenylene-9, 10-dihydro-9-phenanthrol (VI), 9, 10-diphenylene-phenanthrene or tetrabenzonaphthalene (VIII), 9-hydroxy-9, 9′-bifluorenyl (VIII), X and mixed crystals (VII · IX), were isolated by means of a combination of recrystallization and column chromatography. These reaction routes can be outliued as in Chart 1.

Fluorenol (II) and Fluorene (III). — III was obtained in a poor yield by means of steam distillation from the reaction mixture. II was isolated as an intermediate to III in the case of a short reduction period.

In general, it has often been stated heretofore that the carbonyl compound is not reduced to hydrocarbon by way of the corresponding alcohol. However, III was obtained as a normal product from II in a process independent of fluorenopinacol (IV) formation by the Clemmensen reduction.

In another analogous case in this series, 1- and 2-bromo-fluorenone[7] were attacked slowly under the same conditions, whereby substituted fluorenols were also produced, even after twenty-four hours.

III was obtained in an excellent yield and high purity by the reduction of II in a toluene system. In addition, a small amount of 2-(9′-fluorenyl)-fluorene was isolated as an abnormal product. This compound has already been reported by Suzuki et al.[8]

9, 9′-Dihydroxy-9, 9′-bifluorenyl (IV).—IV has been obtained previously by several procedures[9], but not from I by the Clemmensen reduction.

IV exhibits an interesting behavior in the course of the reaction since it reacts further (see Charts 2 and 3). Thus, IV is the main product in the case of a short reduction time such as two hours. Furthermore, the direct reduction of IV was attempted by using the same conditions and leading to other compounds, as are illustrated in Table I.

10, 10-Diphenylene-9-phenanthrone (V).—There have been several reports about V[10,11]. A

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[6] E. L. Martin, "Organic Reactions", Vol. 1, Chapman and Hall, London (1942), p. 155

[7] K. Suzuki, unpublished.

[8] A part of this research was presented at the 9th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1956.

[9] M. Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927); R. Criegee, *Ann.*, **583**, 11 (1953); M. D. Rausch, *J. Am. Chem. Soc.*, **76**, 3622 (1954).

[10] H. Meerwein, *Ann.*, **396**, 212 (1913); C. Graebe and H. Stindt, ibid., **291**, 1 (1896); A. Kliegl, *Ber.*, **43**, 2488 (1910); J. Schmidt et al., ibid., **43**, 1800 (1910); E. Bergmann and J. Hervey, ibid., **62**, 893 (1929).

[11] J. Suszko and R. Schillak, *Roczniki Chem.*, **14**, 1216 (1934); *Chem. Abstr.*, **29**, 6231 (1935).

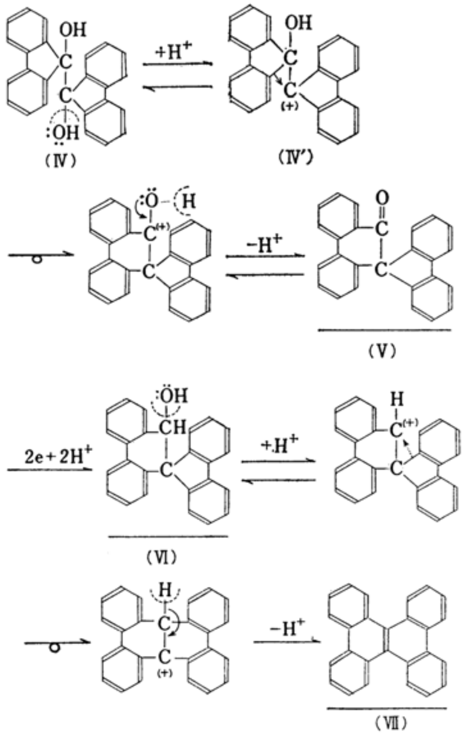
minor part of IV was converted into the β-isomeride of V through the carbonium ion IV′ by a pinacol rearrangement which on further reduction gave VII (10%) as the end-product, as is illustrated in Chart 2 and Table I. V was identical with an authentic specimen prepared by Meerwein's method[10].

9, 10 - Diphenylene - phenanthrene (VII). — VII[11-13] has been reported previously, but it has not been obtained heretofore by the Clemmensen reduction of I. VII would be formed through the intermediate VI. VI[11] was prepared from V by the use of zinc and ammonium hydroxide in an alcoholic solution, and was then converted to VII[cf. 14] by treating it under the same conditions as in the Clemmensen reduction but without zinc amalgam.

Furthermore, VII (80%) and intermediate VI (10%) could be isolated by the Clemmensen reduction of V for fifteen hours in the xylene system.

In order to polarize the central double bond, VII was oxidized to tetrabenzocyclodecane-1, 6-dione (XI)[11], which was then converted to VII and V by reduction.

The mechanism of the formation of VII via VI from V by the retropinacolone rearrangement involves the intramolecular transfer of the electron pair by formation of a carbonium ion. Thus, the reaction sequences can be written as in Chart 2.



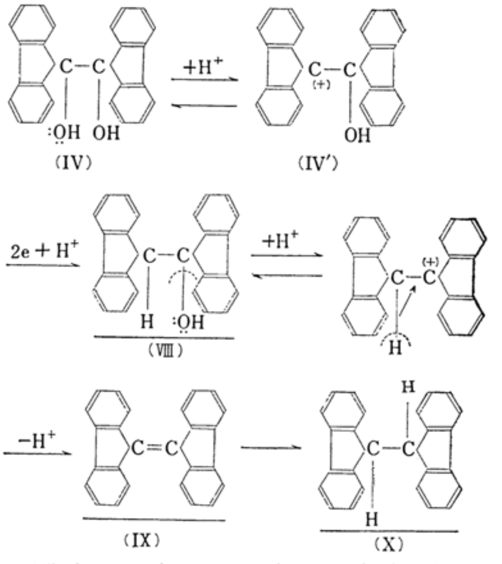
(Underscored compounds were isolated)
Chart 2

Dibiphenylene-ethylene (IX) and -ethane (X). —IX and X were reported by Harpe and Dorp[15] previously. In this reaction, a major part of IV through the IV′ carbonium ion was converted into VIII and then to IX, which on further reduction afforded the end-product X (56%) (see Chart 3 and Table I). VIII was isolated as an intermediate product by short reduction of I (2 hr.) or IV (3 hr). in the toluene solution, as is shown in Table I.

VIII was readily converted to IX[16] by hydrochloric acid in acetic acid. Therefore, IX could be obtained in a better yield by treating VIII under the same conditions as in the Clemmensen reduction but without the amalgamated zinc.

In general, an ethylenic link is reduced easily when it is conjugated with a carbonyl group. In contratst, the reduction of the ethylenic link in IX was extremely slow upon treatment with hydrochloric acid and amalgamated zinc in the toluene solution, and a red color remained even after twenty-four hours.

IX was isolated from the reaction mixture as mixed crystals (red prisms) with VII. However, VII was not obtained by Harris et al.[1] from an alcoholic solution; hence, their product was simply IX.



(Underscored compounds were isolated)
Chart 3

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12) E. Bergmann and S. Fujise, *Ann.*, **483**, 80 (1930); A. Werner and A. Grob, *Ber.*, **37**, 2887 (1904); F. Bergmann and H. E. Esckinazi, *J. Am. Chem. Soc.*, **66**, 183 (1944).

13) H. Klinger and C. Lonnes, *Ber.*, **29**, 2152 (1896).

14) W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 3857 (1933).

15) C. Harpe and W. Dorp, *Ber.*, **8**, 1049 (1875).

16) V. Grignard and C. Courot, *Compt. rend.*, **152**, 272 (1911).

TABLE I. REDUCTION OF I AND IV UNDER VARIOUS CONDITIONS

Red. of	g.	Solvent	ml.	React. time, hr.	II g.	III g.	IV g.	V g.	VII g.	VII · IX g.	VIII g.	X g.	Recovd. g.
I	10.0	Xylene	20	24		1.3	1.0	0.75	1.3	0.5		2.4	
I	10.0	Toluene	20	24		0.9	0.05	0.11	0.1	1.2		2.9	
I	10.0	Toluene	20	2	0.1	1.1	5.1	0.03		0.05	0.65	0.5	I 0.3
I	10.0	Toluene	20	72		0.8			0.9			5.1	
I	10.0	Benzene	20	24		0.9	1.3	0.1	Trace	0.2		0.3	
IV	2.0	Xylene	6.0	24					0.31			0.3	
IV	2.0	Toluene	6.0	24					0.1	0.25		0.3	IV 0.1
IV	2.0	Toluene	6.0	3				0.01		0.15	0.02	0.1	IV 0.9
IV	2.0	Benzene	6.0	24				0.1		0.06		0.1	IV 1.0

The reaction sequences of IX and X can be visualized as in Chart 3.

Mixed Crystals (VII·IX). — The mixed crystals gave 9, 9′-dibromo-9, 9′-bifluorenyl[17] and VII (no reaction) by bromination; with the Clemmensen reduction of zinc and ammonium hydroxide, they gave X and VII, and with oxidation, I and XI. Therefore, the mixed crystals can be supposed to consist of VII and IX. Moreover, the ultraviolet spectrum showed maxima in the regions of 220∼350 and 450 mμ, as is illustrated in Fig. 1. These maxima were almost identical with those of VII and IX respectively[18,19].

The infrared spectrum also indicated a mixture, and the analytical results were identical with $C_{26}H_{16}$.

The same mixed crystals were produced in nearly a quantitative yield from the solution of VII : IX (0.2 : 1) in acetic ester.

VII is slightly yellow, even when recrystallized several times from different solvents. It is best to purify it by reduction and then by recrystallization.

Effects of the Solvents.—The yields in Table I were slightly different depending on the solvents. In the case of benzene, the reaction went slowly and a large amount of I was recovered, perhaps because of the lower boiling point of benzene as compared with these of toluene and xylene.

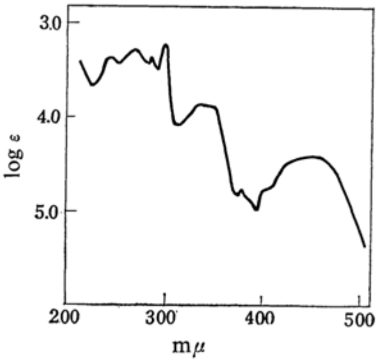

Fig. 1. Ultraviolet spectra of the mixed crystals.

In this study fluorenone was converted to fluorene and the other intermediates, II, IV, V VI, VIII and IX, after a short reduction time (2 hr.) in toluene, as has been described above.

Furthermore, V, VIII and X were increased, but IV was decreased and IV remained almost constant when the reaction was continued for twenty-four hours (red colored toluene). Three kinds of end-products, VII (10%), X (55.6%) and (III, 8.7%) were obtained, as is shown in Chart I and Table I, by extending the refluxing periods for seventy-two hours (almost colorless). VII and X were then obtained in approximately a ratio of 1 : 5.6.

It may, therefore, be assumed that V and VIII were also formed from IV through the positively charged ion IV′ by the action of the acidic medium in the Clemmensen reduction.

In view of these observations, the behavior of each intermediate in the course of the Clemmensen-Martin reduction of fluorenone can be explained. There have also been some other discussions reported recently of the mechanism of the Clemmensen reduction[20].

Experimental*

General Procedure for the Clemmensen Reduction of Fluorenone Materials.—Amalgamated zinc filings were prepared according to Martin's method[6].

A mixture of amalgamated zinc (20 g.), water (15 ml.), xylene (20 ml.), concentrated hydrochloric acid (35 ml.) and fluorenone (10 g.) was refluxed briskly for twenty-four hours in a 500 ml. round-bottomed flask. A 10 ml. portion of concentrated hydrochloric acid was added every six hours during the heating period. The xylene layer turned a bright red color after ten minutes.

The red reaction mixture was cooled to room temperature after 24 hr., and the deposited crystals

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[17] C. Graebe and B. Mantz, *Ann.*, **290**, 241 ((1896).

[18] E. Bergmann and Y. Hirshberg, *Bull. soc. chim. France*, **17**, 1091 (1905).

[19] E. Bergmann, E. Fischer and J. Jaffe, *J. Am. Chem. Soc.*, **75**, 3230 (1953).

[20] D. Staschewski, *Angew. Chem.*, **71**, 726 (1956); T. Nakabayashi, *J. Am. Chem. Soc.*, **82**, 3900 (1960).

* All the melting points are uncorrected.

in the xylene layer were collected and washed free of acid with a small amount of water and then recrystallized from benzene. Colorless crystalline needless of X (1.6 g.) were obtained. (Part of X coats the surface of the zinc; m. p. and mixed m. p. 224°C). The mother liquor was evaporated to half volume. The deposited crystals were filtered and recrystallized from acetic ester to yield V (0.75 g.) as colorless prisms, m. p. 258°C (Found: C, 90.91; H, 4.86%). This was identical with those of a specimen which was prepared from IV with sulfuric acid in acetic acid following the procedure of Gomberg and Bachmann[9]. Further evaporation of the mother liquor to half volume yielded VII (slightly yellow), which recrystallized several times from benzene as nearly colorless material, (1.3 g.), m. p. 214∼215°C.

Found: C, 95.28; H, 5.20. Calcd. for $C_{26}H_{16}$; C, 95.09%; H, 49.1%; Picrate, Found: C, 69.21; H, 3.64 N, 7.60. Calcd. for $C_{32}H_{19}O_7N_3$: C, 68.94; H, 3.44; N, 7.54%.

VII, $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 265 (4.73), 286 (4.69), 299 (4.84), 335 (4.22), 350 (4.20).

The xylene was separated from the water layer and submitted to steam distillation for one hour to remove both the solvent and the fluorene which was recrystallized from alcohol (1.3 g.), m. p. 113∼114°C. This was confirmed by mixed melting point.

The red residue was filtered, dried, and recrystallized from benzene to yield additional X (0.8 g.) (total 2.4 g.), m. p. 243∼244°C.

The last benzene mother liquor was evaporated to a small volume, and the deposited red crystals were recrystallized from acetic ester in a red prism to give mixed crystals (0.5 g.), m. p. 185°C.

Found: C, 95.10; H, 5.19. Calcd. for $C_{26}H_{16}$: C, 95.09; 4.91%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 244 (4.62), 268 (4.71), 286 (4.63), 299 (4.76), 335 (4.15), 348 (4.13) 382 (3.23), 450 (3.60).

Then, IV was isolated from the mother liquor as colorless needles (1.0 g.), m. p. 192°C (Found: C, 86.24; H, 5.14%). The identity of this compound was confirmed by mixed melting point with an authentic sample.

The separation of the reaction products was much simpler when the reduction time was longer (72 hr.). In this reduction, the amalgamated zinc and hydrochloric acid were changed every 24 hr.

In the case of a short reduction period (2 hr.) the first deposited crystals were almost pure IV (m. p. 192°C). II (0.1 g., m. p. 158°C) was extracted by 20% boiling alcohol from the red residue of the steam distillation; furthermore, other compounds were separated by the method described above. The last residual benzene solution was chromatographed on alumina, and two products, VIII (0.65 g., m. p. 192∼193°C) and I (0.3 g., m. p. 80°C), were isolated; their identity was confirmed by mixed melting point with authentic samples.

In the case of a short reduction period (3 hr.). of IV, each product was separated by a procedure almost identical to that employed for the reduction products of I.

Oxidation of 9, 10-Diphenylene-phenanthrene (VII).—VII (1 g.) was dissolved in a mixture of acetic acid (25 ml.) and sodium bichromate (5 g.) and refluxed for 2 hr., and the reaction mixture was then poured into cold water. The white amorphous products were filtered, dried, and recrystallized from benzene to yield XI (0.42 g.) as colorless prisms, m. p. 269∼271°C[12,13].

Found: C, 86.73; H, 4.38. Calcd. for $C_{26}H_{16}O_2$: C, 86.65; H, 4.48%.

I (0.15 g.), m. p. 80°C, was isolated from the mother solution, as shown by mixed melting point with an authentic sample.

Reduction of Tetrabenzocyclodecane-1,6-dione (XI).—A mixture of XI (0.2 g.), red phosphorus (0.1 g.), hydrogen iodide (3 ml.) and acetic acid (5 ml.) was refluxed for 9 hr. After it had been cooled, the reaction mixture was filtered, and the filtrate was poured into water.

The white deposited product was filtered and recrystallized from benzene, m. p. 256∼257°C (0.1 g.). This compound was identical with V, as shown by mixed melting point.

To the benzene mother liquor was added 0.1 g. of picric acid. Dark-red crystalline needles (m. p. 198∼200°C) were deposited; this picrate was filtered and decomposed by ammonium hydroxide. The product recrystallized from acetone yielded VII (0.045 g.) as colorless needles, m. p. 214∼215°C.

Reactions of the Mixed Crystals.—*Reduction.*—A mixture of amalgamated zinc (4 g.), water (3 ml.), concentrated hydrochloric acid (7 ml.), toluene (8 ml.) and mixed crystals (2 g.) was refluxed for 10 hr. The crude product (1.6 g., m. p. 224∼237°C) was isolated from the toluene; from this X (1.1 g., m. p. 242∼243°C) and VII (0.2 g., m. p. 212∼214°C) were separated by recrystallization. Both X (0.45 g.) and VII (0.08 g.) were also obtained from mixed crystals (0.6 g.) by the use of zinc and ammonium hydroxide in an alcoholic solution; X and VII were confirmed by identity with authentic samples.

Bromination.—To the mixed crystals (0.82 g.) dissolved in carbon tetrachloride (30 ml.) there was added 0.4 g. of bromine in 5 ml. of carbon tetrachloride at room temperature. After the mixture had been let standing for 3 hr., the deposited crystals were filtered and recrystallized from benzene (0.6 g.). This was identical with 9,9′-dibromodibiphenyleneethane (m. p. 235°C) prepared by Graebe and Mantz's method[17]. VII (0.1 g., m. p. 213∼214°C) was isolated from the mother solution and did not react with bromine.

Oxidation (*1*).—Mixed crystals (1.0 g.), acetic acid (25 ml.) and potassium bichromate (5 g.) were refluxed for 2 hr. After being poured into cold water, the light yellow precipitate obtained was recrystallized from benzene to yield XI (0.2 g. m. p. 269.5∼271°C); this was confirmed by comparison with an authentic sample. I (0.5 g., m. p. 81°C) was isolated from the mother liquor.

Oxidation (*2*).—To the mixed crystals (0.5 g.) dissolved in 50 ml. of acetone there were added 2 g. of potassium permanganate during 2 hr. at room temperature. Then, most of the acetone was evaporated by reduced pressure and poured into water.

The deposited material was filtered off and refluxed with 3 ml. of alcohol. I (0.4 g., m. p. 81°C) was obtained from the soluble part, while VII (0.1 g., m. p. 213∼214°C) was obtained from the alcohol-insoluble part and was recrystallized from benzene.

Formation of Mixed Crystals.—IX (1.0 g.) and VII (0.2 g.) were dissolved in acetic ester by heating. Upon the cooling of the mixture, bright mixed crystals (red prisms) were deposited and were recrystallized from acetic ester, m. p. 185°C (1.0 g.).

Found: C, 95.10; H, 5.19. Calcd. for $C_{26}H_{16}$: C, 95.11; H, 4.89%.

Reduction of 10, 10-Diphenylene-9-phenanthrone (V) to 9, 10-Diphenylene-phenanthrene (VII).—V (2.0 g.), amalgamated zinc (8 g.), concentrated hydrochloric acid (14 ml.) xylene (40 ml.) and water (6 ml.) were refluxed for 15 hr., a 4 ml. portion of hydrochloric acid being added every 6 hr. After the reaction period, the xylene layer was separated and washed with water, and the xylene was steam-distilled. The white residue was filtered, dried, and then chromatographed in benzene on alumina.

Fractional crystallization yielded VII (1.52 g. m. p. 214∼215°C) and VI (0.2 g. m. p. 178∼179°C), which were confirmed by mixed melting polnt.

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Department of Chemistry
Faculty of Technology
Yamaguchi University
Tokiwadai, Ube