BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 784—790 (1966)

The Synthesis of Glycidylferrocenes and Related Compounds

By Hamao WATANABE, Izumi MOTOYAMA and Kazuo HATA

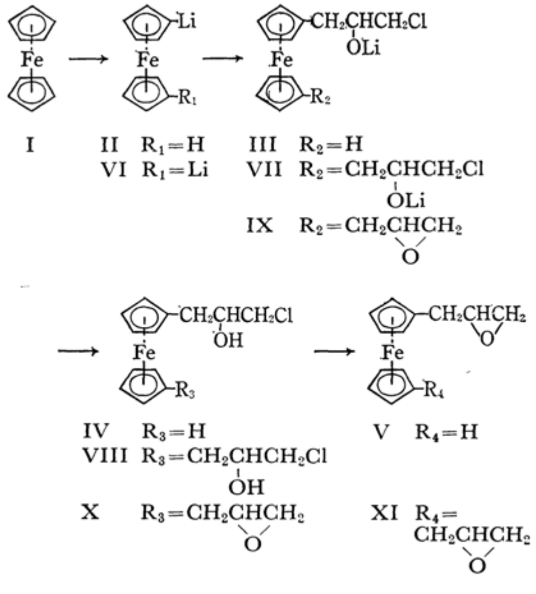
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received September 10, 1965)

Ferrocene derivatives with one or two glycidyl substituents, desired for the formation of polymeric ferrocene compounds, were synthesized by the epoxidation of chlorohydrin compounds obtained from the products of the addition of ferrocenyllithium to epichlorohydrin at −40—−78°C. In the course of this synthesis, mono- and di-chlorohydrin compound and a disubstituted ferrocene with a 3-chloro-2-hydroxypropyl and a glycidyl substituent were isolated. All of them are stable liquid compounds. The investigation of the relationship between the reaction conditions and the yield of glycidylferrocenes revealed that the larger molar ratio of each reactant to ferrocene at each reaction step causes a higher conversion into glycidylferrocenes. In the epoxidation reaction of chlorohydrins with caustic alkali, a small amount of ethers, formed by the reaction of epoxides and the solvent ethanol, was obtained under some reaction conditions. In all cases, a small amount of biferrocenyl was isolated; the formation of this compound was considered to be attributable to the Wurtz-type coupling reaction of ferrocenyl radicals. The structures of all these products were confirmed by their infrared absorption spectra and, in part, by the NMR spectra.

In a previous communication[1] it was briefly reported that ferrocene derivatives with one or two glycidyl substituents were obtained by the epoxidation of chlorohydrins which had been derived from the products of the addition of ferrocenyllithium to epichlorohydrin. It seemed that these epoxy derivatives are promising monomers for the formation of various types of polymers. The present paper will deal with the synthesis of glycidylferrocenes and the related compounds in full detail.

The reaction of phenyllithium with epichlorohydrin has been reported by Gilman and his coworkers.[2] However, no reaction of this type on the ferrocene derivatives has yet been reported. In the present study a similar reaction was applied to the addition of ferrocenyllithium to epichlorohydrin in order to obtain the compounds which can lead to epoxy compounds.



I

II $R_1=H$

VI $R_1=Li$

III $R_2=H$

VII $R_2=\mathrm{CH_2\underset{OLi}{C}HCH_2Cl}$

IX $R_2=\mathrm{CH_2\underbrace{CHCH_2}_{O}}$

IV $R_3=H$

VIII $R_3=\mathrm{CH_2\underset{OH}{C}HCH_2Cl}$

X $R_3=\mathrm{CH_2\underbrace{CHCH_2}_{O}}$

V $R_4=H$

XI $R_4=\mathrm{CH_2\underbrace{CHCH_2}_{O}}$

---

[1] K. Hata, I. Motoyama and H. Watanabe, This Bulletin, **36**, 1698 (1963).

[2] H. Gilman, B. Hofferth and J. B. Honeycutt, *J. Am. Chem. Soc.*, **74**, 1594 (1952).

TABLE I. THE REACTION CONDITIONS AND THE PRODUCTS

Exp. No.	Lithiation		Addition reaction		Product and yield, %[c]		
	Mol. ratio *n*-BuLi/FcH[a]	Time, hr. Temp., °C	Mol. ratio EpCl[b]/FcH	Time, hr. Temp., °C	V	XI	XII
207	2.14	$64^{2}/_{3}$ −20 to room temp.	5	4 −65 to −45	12.8	ca. 0.3	0.2
208	1	$2^{3}/_{4}$ −15 to room temp.	2	$3^{1}/_{4}$ −70 to −55	1.2	0	0.1
210	2	114 −30 to room temp.	5	$23^{2}/_{3}$ −65 to −40	14.6	16.3	0.3

a) Ferrocene
b) Epichlorohydrin
c) Total summation of the final products which were obtained by the procedures described in the experimental part.

TABLE II. A RESULT OBTAINED BY CHROMATOGRAPHIC SEPARATION OF THE REACTION PRODUCT (Exp. No. 210)

Order of the elution	Eluent	Product	Band color in the column	Composition of the product, %
1st	Benzene	I	Orange	—
2nd	Benzene	XII	Light orange	1.1
3rd	Benzene	V	Orange yellow	16.7
4th	Benzene	XI	Orange yellow	10.0
5th	Benzene	IV	Orange yellow	18.0
6th	Benzene-ether (1 : 1)*	X	Orange yellow	20.0
7th	Ether-methanol (9 : 1)*	VIII	Orange yellow	32.2
8th (last)	Methanol	Mixture	—	1.1

* Ratio by volume

Results and Discussion

The route and the products of the reactions are as follows:

Ferrocene (I) was converted into lithium derivatives (II and VI) by treatment with *n*-butyllithium in anhydrous ether under an atmosphere of nitrogen.[3] When a suspension of ferrocenyllithium was treated with epichlorohydrin at −40 to −78°C, a mixture of addition products (III, VII and IX) was obtained. The mixture was hydrolyzed to give chlorohydrin derivatives (IV, VIII and X). The chlorohydrin compounds were separated from the reaction mixture by adequate procedures, and each chlorohydrin compound was separated by means of vacuum distillation and/or chromatography on alumina. Each chlorohydrin was then epoxidized in an ethanol solution[4] by treatment with a 30% aqueous solution of potassium hydroxide. Monoglycidylferrocene (V) and diglycidylferrocene (XI) were thus obtained as dark red liquids. These epoxides were also obtained by a direct epoxidation of the chlorohydrin mixture (IV, VIII and X) without the previous separation of each chlorohydrin. Glycidylferrocenes (V and XI) were isolated from the reaction mixture by chromatography on alumina.

The Reaction of Ferrocenyllithium and Epichlorohydrin.—The preparation of ferrocenyllithium from ferrocene, followed by the addition reaction with epichlorohydrin, was attempted under various conditions, and the resultant lithium compounds were hydrolyzed. The reaction conditions and the results are listed in Table I, in which the yields of the final products are calculated on the basis of the ferrocene used. The addition reaction of ferrocenyllithium to epichlorohydrin could be accomplished at a low temperature, but not at an ordinary temperature, as has been shown by Gliman and his co-workers.[2] A similar reaction was also attempted with ferrocenylsodium[5] and epichlorohydrin. In this attempt also, no successful reaction

---

3) R. A. Benkeser, D. Goggin and G. Schroll, ibid., **76**, 4025 (1954); M. D. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

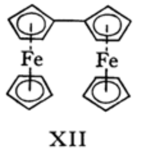
4) S. Winstein, T. L. Jacobs, G. B. Linden, D. Seymour, E. F. Levy, B. F. Day, J. H. Robson, R. B. Henderson and W. H. Florsheim, *J. Am. Chem. Soc.*, **68**, 1831 (1946).

5) A. N. Nesmeyanov, E. G. Perevalova and Z. A. Bienoravichute, *Doklady Akad. Nauk S. S. S. R.*, **112**, 439 (1957); *Chem. Abstr.*, **51**, 13855 (1957); S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg and M. D. Rausch, *J. Org. Chem.*, **24**, 824 (1959); M. Okawara, Y. Takemoto, H. Kitaoka, E. Haruki and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 685 (1962).

occurred without cooling, or when the mixture was heated in toluene, but the reaction may be expected to occur here also if it is undertaken at a low temperature. The conversion of ferrocene into ferrocenyllithium and its addition reaction with epichlorohydrin was facilitated by the increase in the molar ratios of *n*-butyllithium and of epichlorohydrin to ferrocene, and by the elongation of each reaction time. The reaction products were separated by vacuum distillation or chromatography on alumina. Besides two chlorohydrin compounds (IV and VIII), two epoxy compounds (V and XI) and a mixed epoxy-chlorohydrin compound (X) were isolated in significant amounts. These results indicate that the epoxy-ring formation from the compounds III, VII and IX occurred at least in part in the course of the addition reaction. When each step of the reaction was cut to a shorter reaction time (Exp. Nos. 207 and 208), however, the product was found to consist mainly of chlorohydrin derivatives.

Monochlorohydrin IV could be separated by vacuum distillation from the reaction product. It was found, however, that the reaction product was apt to decompose during the distillation, so the temperature must be carefully controlled under a high vacuum. Therefore, the method for separation and purification by means of alumina chromatography was recommended. A typical example is shown in Table II. Each product was successively eluted with benzene and other solvents.

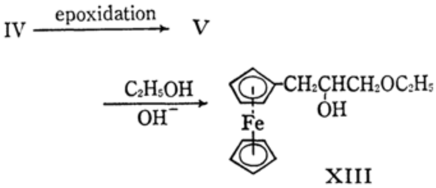
In the separation procedure of the chromatography, a small amount of orange crystals was isolated from the early-eluted fraction next to the ferrocene recovered. This compound was identified as biferrocenyl (XII), as has been reported in another communication by the present authors.[6] The mechanism of the formation of biferrocenyl in the course of the reaction was inferred to be as follows: ferrocenyllithium was subjected to homolytic fission between the ferrocenyl group and lithium to afford ferrocenyl radical, which then coupled to give biferrocenyl. Further investigations of this problem will be reported in a following paper.[7]



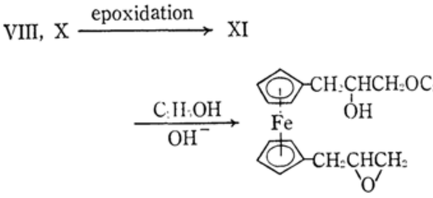
XII

By a comparison of the rate of elution in the chromatography, the adsorbability to alumina was estimated to be in the following order: I< XII<V<XI<IV<X<VIII.

Epoxidation Reaction.—*The Separate Epoxidation of Each Chlorohydrin.*—Each chlorohydrin separated by the chromatography was dissolved in ethanol and treated with a 30% aqueous solution of potassium hydroxide under cooling with ice water and high-speed stirring. After the epoxidation reaction was over, a large quantity of water and ether was added, and the crude epoxide (V or XI) was obtained from the ethereal layer and purified by alumina chromatography. The epoxidation of the chlorohydrin derivatives gave, in general, good yields of the corresponding glycidylferrocenes. In some exceptional instances, it was found that the reaction mixture was contaminated by a small amount of a liquid compound other than epoxy compound. These compounds were isolated after the separation of each product from the epoxidized mixture and purification by alumina chromatography. From the various analytical results, the compounds were found to be addition products of the glycidylferrocenes and ethanol used as the solvent.



XIII



XIV

Compounds XIII and XIV were supposed to be formed by the addition of ethanol to glycidylferrocenes during the epoxidation reaction in the presence of potassium hydroxide. This presumption was proved by an experiment, in which epoxide(XI) dissolved in ethanol was treated with a potassium hydroxide solution by a work-up similar to that described above; a part of the epoxide (XI) was converted into XIV, while most of it was recovered unchanged.

The yield of compound XIII or XIV was increased by the prolonged reaction time of epoxidation, as is shown in Table III. Compounds XIII and XIV are dark red liquids (n_D^{20} 1.5796 and 1.5711 respectively), the former being more viscous than the latter. It was shown that these compounds have slightly higher adsorbabilities than the corresponding epoxides.

The Direct Epoxidation of the Chlorohydrin Mixture.—The reaction product obtained by the reaction of ferrocenyllithium and epichlorohydrin was dissolved in ethanol without any further separation process, and directly epoxidized by treatment with

---

[6] K. Hata, I. Motoyama and H. Watanabe, This Bulletion, **37**, 1719 (1964).

[7] K. Hata, I. Motoyama and H. Watanabe, ibid., **39**, 790 (1966).

TABLE III. EPOXIDATION REACTIONS AND THE PRODUCTS

Compound	Mol. ratio C_2H_5OH : KOH : EpCl[a]	Reaction temp., °C	Reaction time min.	Product and yield, %			
				V	XIII	XI	XIV
IV	70 : 10 : 1	0—10	10	91.0	+[c]	—	—
			25 (+35)[b]	87.6	++[c]	—	—
VIII	50 : 10 : 1	0—10	12	—	—	92.0	0
			30 (+45)[b]	—	—	66.9	++[c]
X	70 : 10 : 1	0—10	25 (+35)[b]	—	—	77.3	+[c]

a) Epichlorohydrin substituent $-CH_2CH(OH)CH_2Cl$
b) Time in parentheses is additional stirring period without cooling.
c) + trace, ++ small amount

TABLE IV. A RESULT OBTAINED BY CHROMATOGRAPHIC SEPARATION OF THE EPOXIDATION PRODUCT
(Sample obtained from Exp. No. 210)

Order of the elution	Eluent	Product	Band color in the column	Composition of the product, %*
1st	Benzene	XII	Light orange	0.6
2nd	Benzene	V	Deep yellow	35.8
3rd	Benzene	Unknown	Light pink	2.3
4th	Benzene	XI	Light yellow	53.2
5th (last)	Methanol	Mixture	Orange red	8.0

* Calculated after the exclusion of recovered ferrocene.

TABLE V. PHYSICAL PROPERTIES OF THE LIQUID PRODUCTS

Product	Color	B. p., °C/mmHg	n_D^{20}	Relative viscosity
IV*	Dark red	156—158/0.80—0.90 or 144/0.52—0.53	1.6102	High
V	Dark red	111—115/0.17—0.18	1.6093	Low (very fluid)
VIII	Dark red	—	1.6069	High
X	Dark red	—	1.6014	Medium
XI	Dark red	160—161/0.09—0.12	1.5968	Low (very fluid)

* Epoxy equivalent, 0.99 (HCl - dioxane method)

potassium hydroxide under the reaction conditions similar to those described in the above section. When the reaction mixture was submitted to a vacuum distillation, compounds V and XI were obtained, boiling at 111—115°C under 0.17—0.18 mmHg and at 160—161°C under 0.09—0.12 mmHg respectively. A small amount of biferrocenyl was also isolated from the residue of the vacuum distillation.

The chromatography to separate the products into each compound gave the results shown in Table IV. By the chromatographic separation, biferrocenyl was again isolated besides another unknown substance.

The Assignment of the Structures of the Products.—Compounds IV, V, VIII, X, XII, XIII and XIV were stable in air. These compounds were identified by means of their elemental analyses, infrared spectra and NMR spectra, and by a study of their chemical natures.

The physical properties of the various products are summarized in Table V. All of these products are dark red liquids. Mono- and di-chlorohydrin derivatives (IV and VIII) have higher viscosities than those of the corresponding glycidylferrocenes, which are fairly fluid. The viscosity of the compound X falls between those of VIII and XI. As a whole, the order of the viscosity of these compounds as determined by visual observation is: VIII$\geqq$IV$>$X$>$XI$>$V. The epoxy equivalent of monoglycidylferrocene (V) was determined by the hydrochloric acid - dioxane method,[8] using cresol red as an indicator, to be 0.99; this value agrees well with the theoretical value (1.00).

It has been shown in the previous paper[1] that when a mixture of glycidylferrocenes was treated with a hydrochloric acid - dioxane mixture in order to obtain the corresponding chlorohydrin mixture, only bischlorohydrin (VIII) was isolated by chromatography on alumina, and it was reconverted into diglycidylferrocene with potassium hydroxide. A similar ring-opening reaction was observed in the measurement of the epoxy equivalent of the

---

[8] G. King, *Nature*, **164**, 706 (1949); "Organic Analysis," Vol. 1, 135; "Kobunshi Jikkengaku Koza," Vol. 9, Kyoritsu Shuppan, Tokyo (1958), p. 259.

compound V: a dark red, viscous liquid material obtained after the measurement was found to be identical with an authentic chlorohydrin compound IV. From these results it is obvious that a reversible epoxy-ring closure and opening reaction was effected between these compounds by alkali and hydrochloric acid.

It was substantiated that the disubstituted ferrocenes described above are heteroannularly-substituted compounds, from the fact that their infrared absorption spectra lack the absorption bands at 1100 and 1000 cm^{-1}. This assignment has been designated as the 9—10 rule.[9]

The infrared spectra of two chlorohydrins (IV and VIII) and two glycidylferrocenes (V and XI) exhibit essentially identical absorption bands in each pair, except for the region between 1100 and 1000 cm^{-1}. The characteristic peaks for the chlorohydrin group in IV and VIII appear at 3400 (ν_{C-H}), 1090—1050 (ν_{C-O}) and 760—690 cm^{-1} (ν_{C-Cl}), while the characteristic peaks for the epoxy group in V and XI appear at 3050 and 2970 cm^{-1} (ν_{C-H}) and at 1256, 960—900, and 845 cm^{-1} (epoxy ring). Compound X shows the absorption bands due to both the chlorohydrin group and the epoxy group.

Further confirmation was obtained by the examination of the NMR spectra of two glycidylferrocenes (V and XI). In the spectrum of the monoglycidylferrocene a singlet signal was observed at τ 6.[10] This is attributable to the overlapping of the signal of unsubstituted ring protons (5H) and that of monosubstituted ring protons (4H) because of the close resemblance of their chemical shifts. The signal was yet a sharp peak in spite of the overlapping. On the other hand, the NMR spectrum of diglycidylferrocene showed a singlet signal at τ 5.96 assignable to the heteroannularly-disubstituted ring protons (8H), and no other signals assignable to any homoannularly-disubstituted ring protons were observed. Two other complex signals, centered at τ7.0 and τ7.4, were assigned to the protons of glycidyl groups, the former due to the methine proton in the oxide group, and the latter to the two protons of methylene and two protons of oxide methylene.

Experimental

The temperatures in the reactions and measurements were uncorrected. The infrared spectra were determined on a Model EPI-S2 recording spectrometer (Hitachi Co.), and the NMR spectra were determined at 60 Mc. on a Model JNM-C-60 spectrometer (Japan Electron Optics Laboratory Co.), employing a room-temperature method in deuteriochloroform containing tetramethylsilane as an internal standard and ca. 30% (by volume) of the sample.

All column chromatographies were performed on Sumitomo Chemicals' activated alumina (150—250 meshes) which had previously been exposed to air for eigtht hours in order to diminish its adsorption ability. A benzene solution of the sample was placed on the alumina and developed with the same solvent.

1. The Reaction of Ferrocenyllithium and Epichlorohydrin.—The lithiations of ferrocene with *n*-butyllithium and the subsequent reactions of ferrocenyllithium with epichlorohydrin were carried out with stirring in anhydrous ether under an atmosphere of nitrogen. Three runs of the reaction were accomplished by essentially identical procedures except for the molar ratios of the reactants and the reaction times (Table I). A typical procedure for the preparation of ferrocenyllithiums and their reaction with epichlorohydrin is as follows (Exp. No. 210).

A solution of 0.6 mol. of *n*-butyllithium was prepared, according to the method described in the literature,[11] from 82.8 g. (0.6 mol.) of *n*-butyl bromide in 120 ml. of ether and 10.35 g. (1.5 g.-atom) of suspended lithium, cut into pieces as small as possible, in 240 ml. of ether, the temperature being kept at −30°C by cooling in a dry ice - acetone bath. In another vessel 55.8 g. (0.3 mol.) of ferrocene was dissolved in 650 ml. of ether and cooled to −20—−30°C in a dry ice - acetone bath. The solution of *n*-butyllithium previously prepared was added to the ferrocene solution through a siphon, the inlet tube of which was covered with glass wool in order to filter off solid impurities. After the addition was complete, the mixture was allowed to warm up to room temperature with stirring over a 20-hr. period. Further stirring was continued for 94 hr. Since the spontaneous evaporation of the solvent under a stream of nitrogen was observed during this period, 400 ml. of ether was added in two portions (150 and 250 ml.).

The orange suspension of ferrocenyllithium thus obtained was cooled to ca. −65°C in a dry ice - acetone bath, and 138.8 g. (1.5 mol.) of epichlorohydrin (b. p. 115.0—115.4°C) in 100 ml. of ether was then added to the suspension during a 2-hr. period so as to maintain the temperature at −60°C or below. After the addition was complete, the mixture was kept at this temperature for 7 hr., and then allowed to warm up to −40°C over a 16.5-hr. period. Then, the cooling bath was removed and the mixture was allowed to come to room temperature, after which the contents were poured into a large amount of ice water in order to hydrolyze the lithium compounds.

The ethereal layer was separated, and the aqueous layer was extracted with ether. The combined ethereal solution was dried over magnesium sulfate and evaporated in order to remove the ether and the remaining epichlorohydrin. On concentration, a large quantity of unreacted ferrocene separated out as orange crystals; it was removed by filtration. The filtrate was placed in a Claisen-type flask fitted with a Vigraux-column and evaporated under 1.5 mmHg at 130°C on an oil bath, thus removing materials of a lower boiling point and/or a higher vapor pressure (the remaining ferrocene

---

[9] K. L. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957); M. Rosenblum and R. B. Woodward, ibid., **80**, 5443 (1958); A. N. Nesmeyanov, L. A. Kazitzyna, B. V. Lokshin and V. D. Vil'chevskaya, *Doklady Akad. Nauk S. S. S. R.*, **125**, 1037 (1959); *Chem. Abstr.*, **53**, 21857 (1959).

[10] Y. Nagai, J. Hooz and R. A. Benkeser, This Bulletin, **37**, 53 (1964).

[11] "Organic Reactions," Vol. 6, 352 (1951).

sublimed inside the Vigraux-column). After the vacuum evaporation, 36.8 g. of the reaction product was obtained as a dark red, very viscous liquid.

2. The Separation of Each Compound from the Reaction Mixture.—*a) Vacuum Distillation.*—As has been reported in a previous communication,1) a vacuum distillation of the reaction product (Exp. No. 207) gave a very viscous dark red liquid which was identified as the monochlorohydrin compound IV; b. p. 156—158°C/0.8—0.9 mmHg, or 144°C/0.52—0.53 mmHg; n_D^{20} 1.6102.

Found: C, 56.09; H, 5.33. Calcd. for $C_{13}H_{15}FeClO$: C, 56.05; H, 5.43%.

b) Separation by Means of Chromatography.—In order to make a more delicate separation, 9.2 g. of the reaction product described above (Exp. No. 210) was dissolved in a small amount of benzene and chromatographed on alumina using benzene as a developer. Elution was performed by successively changing the eluent. The results of the chromatography are shown in Table II.

The first elution with benzene gave ferrocene (0.03 g.).

The second elution with benzene yielded orange crystals (0.10 g.), which were then recrystallized from a mixture of benzene and petroleum ether; m. p. 233.8—234.5°C (in a sealed capillary). The compound was identified as biferrocenyl (XII); NMR spectrum, τ 5.68 (triplet), 5.85 (triplet), and 6.03 (singlet). These signals will be discussed in a following paper.7)

Found: C, 64.78; H, 5.05. Calcd. for $C_{20}H_{18}Fe_2$: C, 64.91; H, 4.90%. Mol. wt. Found: 370(Rast) and 330 (vapor pressure osmometer method). Calcd. 370.

The third elution with benzene gave rise to monoglycidylferrocene (V, 1.48 g.; n_D^{20} 1.6093), whose identification was established as will be described below (3-a).

The fourth elution with benzene yielded diglycidylferrocene (XI, 0.90 g.) as a slightly viscous, dark red liquid; n_D^{20} 1.5968. The identification was established as will be described below (3-b).

A very viscous, dark red liquid obtained from the fifth band was the monochlorohydrin compound (IV, 1.80 g.). It was identified as the same compound as had been described above (2-a).

The sixth elution, with benzene-ether (1 : 1), gave a relatively viscous, dark red liquid (1.79 g.) which gave a pure material upon rechromatography. The compound was identified as a heteroannularly-substituted ferrocene (X); n_D^{20} 1.6014.

Found: C, 57.31; H, 5.12. Calcd. for $C_{16}H_{19}\cdot FeClO_2$: C, 57.43; H, 5.72%.

The seventh elution, with ether-methanol (9 : 1), gave rise to the dichlorohydrin compound (VIII, 1.89 g.); n_D^{20} 1.6069.

Found: C, 51.83; H, 5.26. Calcd. for $C_{16}H_{20}\cdot FeCl_2O_2$: C, 51.79; H, 5.43%.

The product from the last elution with methanol was presumed to be a mixture of many compounds (0.10 g.), but their separation and the identification were not attempted.

3. Epoxidation.—The separate epoxidation of each chlorohydrin (IV, VIII, X) was effected under common reaction conditions; 50 or 70 mol. of ethanol (used as solvent) and 10 mol. of potassium hydroxide were used per mole of the chlorohydrin function. The reaction conditions of epoxidation are shown in Table III.

a) The Epoxidation of IV to V.—A solution of 0.82 g. (2.94 mmol.) of IV in 80 g. (0.208 mol.) of ethanol was cooled to 0—10°C in an ice-water bath. Into the cold solution 5.6 g. of a 30% aqueous solution of potassium hydroxide (containing 29.4 mmol. of potassium hydroxide) was added with vigorous stirring. After the addition, the stirring was continued for 8 min., after which large amounts of water and ether were added. The ethereal layer was separated, and the aqueous layer was repeatedly extracted with ether. The combined ethereal solution was filtered and evaporated to give a crude epoxy compound (0.77 g.). The crude product was dissolved in benzene and chromatographed on alumina, using the same solvent as a developer. Elution with benzene yielded pure epoxide V (0.65 g., 91% yield); n_D^{20} 1.6093.

Found: C, 64.41; H, 5.57. Calcd. for $C_{13}H_{14}FeO$: C, 64.50; H, 5.83%. Epoxy equivalent, 0.99 (HCl-dioxane method).8)

Vacuum distillation revealed the purity of the epoxide; b. p. 107—113°C/0.13—0.16 mmHg: n_D^{20} 1.6093.

When a similar epoxidation reaction of the same chlorohydrin (IV) was carreid out for a elongated stirring period, as is shown in Table III, a subsequent fraction was obtained by elution with benzene-ether (1 : 1). This fraction gave rise to a small amount of a dark red, relatively viscous liquid, which was found to be an addition product (XIII) between V and ethanol; n_D^{20} 1.5796.

Found: C, 62.85; H, 6.97. Calcd. for $C_{15}H_{20}FeO_2$: C, 62.52; H, 7.00%.

b) The Epoxidation of VIII to XI.—The epoxidation reaction was accomplished according to the procedure described above. A solution of 1.34 g. (7.22 mmol.) of VIII in 16 g. (0.348 mol.) of ethanol was treated with 15 g. of a 30% aqueous solution of potassium hydroxide (containing 72.2 mmol. of potassium hydroxide). After the addition of the alkaline solution under cooling in an ice-water bath had been complete, a vigorous stirring was continued without cooling so as to allow the temperature of the mixture to rise from 10 to 25°C in 45 min. The reaction mixture was then extracted with ether. After the evaporation of the ether, a slightly viscous, dark red liquid (1.11 g.) remained. It was separated by alumina chromatography much as in procedure 3-a.

Elution with benzene yielded diglycidylferrocene (XI, 0.72 g., 66.9%); n_D^{20} 1.5968.

Found: C, 64.40; H, 6.18. Calcd. for $C_{16}H_{18}FeO_2$: C, 64.45; H, 6.09%.

The attempted purification of XI by vacuum distillation resulted in its boiling at 160—161°C/0.09—0.12 mmHg; n_D^{20} 1.5968.

Elution with benzene-ether (1 : 1) gave rise to a dark red, slightly viscous liquid (0.16 g.) which was identified as compound XIV; n_D^{20} 1.5711.

Found: C, 62.68; H, 6.91. Calcd. for $C_{18}H_{24}FeO_3$: C, 62.81; H, 7.03%.

When the epoxidation of VIII was accomplished in a short reaction time (Table III, 12 min. at 0—10°C), the yield of XI increased to 92%, while the compound XIV was not detected.

c) The Epoxidation of X to XI.—A solution of 0.84 g. (2.51 mmol.) of X in 8 g. (0.17 mol.) of ethanol was treated with 4.3 g. of a 30% aqueous solution of potassium hydroxide (containing 22.6 mmol. of potassium hydroxide). The products were separated by the procedure described in 3-b.

Elution with benzene gave diglycidylferrocene (XI, 0.58 g., 77.3% yield) and compound XIV (0.10 g.).

d) The Reaction of Diepoxide XI with Alkali in Ethanol.—A solution of 1.27 g. (8.54 mmol.) of XI in 18 g. (0.348 mol.) of ethanol was vigorously stirred with 15 g. of a 30% aqueous solution of potassium hydroxide (containing 72.2 mmol. of potassium hydroxide) at 0—10°C for 25 min. The stirring was continued for further 40 min. without cooling. The following procedure was similar to that adopted for the epoxidation of chlorohydrin compounds. The product was chromatographed on alumina and eluted with benzene and benzene-ether.

Elution with benzene gave 1.03 g. of the recovered XI (81.1% recovery).

Elution with benzene-ether (1 : 1) gave a dark red, relatively viscous liquid (0.18 g.). The liquid was rechromatographed and identified as compound XIV by a comparison of its infrared spectrum and refractive index with those of an authentic material.

e) The Direct Epoxidation of the Chlorohydrin Mixture.—In the direct epoxidation of a mixture of chlorohydrins, it must be noted that a molar ratio calculation of the reactants was established on the basis of a composition analysis of the various components, which were determined from the results of alumina chromatography. The following example shows the epoxidation of the sample obtained by Exp. No. 210 (Table I); the composition of the sample is listed in Table II.

To a solution of 16.21 g. of the sample (containing 48.5 mmol. of chlorohydrin function) in 141 g. (3.06 mol.) of ethanol, 77.5 g. of a 30% aqueous solution of potassium hydroxide (containing 0.485 mol. of potassium hydroxide) was added under cooling in an ice-water bath, and the mixture was stirred for 10 min. After a treatment similar to that described above (3-a), 14.13 g. of a dark red liquid was obtained. The product was chromatographed on alumina. Five fractions were successively eluted with benzene and methanol, as is shown in Table IV.

The first elution with benzene gave rise to a mixture of ferrocene and biferrocenyl. Ferrocene (ca. 0.10 g.) was removed by vacuum sublimation, and the remaining red-brown solid material was purified by recrystallization from a mixture of benzene and petroleum ether to give 80 mg. of biferrocenyl (XII); m. p. 231.0—232.0°C (in a sealed capillary).

The second elution with benzene yielded 4.96 g. of monoglycidylferrocene (V).

The third elution with benzene gave a slightly viscous, dark red liquid (1.24 g.) on which no further analysis was attempted.

The fourth elution with benzene yielded 6.44 g. of diglycidylferrocene (XI).

The last elution, with methanol, gave a mixture (1.12 g.). Although it was supposed that the mixture might contain several compounds, such as XIII and XIV, no further attempt was made to separate and identify them.

Finally, as has been shown in a previous paper,[1] the epoxidized crude product was also purified by vacuum distillation to give V; b. p. 111—115°C/0.17—0.18 mmHg; n_D^{20} 1.6093. A small amount of biferrocenyl was separated as orange crystals by filtration from the residue of the vacuum distillation.

Thanks are due to the Ministry of Education for the financial support granted for this research.