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# A Route from 1,1,1,3-Tetrachloro-3-phenylpropane to Ethynyl Phenyl Ketone Involving Elimination of Hydrogen Chloride and 1,3-Proton Transfer

Takeo AKIYAMA,* Yasuki YOSHIDA, Tokiko HANAWA, and Akira SUGIMORI

*Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102*

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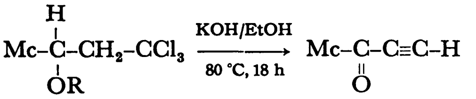
The treatment of 1,1,1,3-tetrachloro-3-phenylpropane with alkali in ethanol affords ethynyl phenyl ketone and its acetal in good yields. This reaction proceeds through the elimination of hydrogen chloride and an efficient 1,3-proton transfer catalyzed by base. Ethyl cinnamate is obtained in only 2% yield.

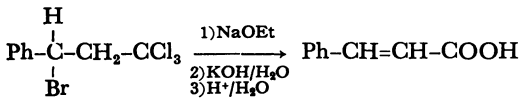
We have already reported the formation of ethynyl metallocenyl ketones in the reaction of 1,1,1-trichloro-3-alkoxy-3-metallocenylpropanes with alkali in ethanol.[1] The expected product, ethyl 3-metallocenylacrylate (Mc–CH=CH–COOEt) has not been obtained.



$$\mathrm{Mc{-}\underset{\displaystyle OR}{\overset{\displaystyle H}{C}}{-}CH_2{-}CCl_3 \xrightarrow[80\,^{\circ}C,\,18\,h]{KOH/EtOH} Mc{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}C{\equiv}C{-}H} \qquad (1)$$

Mc: $(\eta^5-C_5H_5)_2M$, M = Fe, Ru; R = $-CH_3$, $-C_2H_5$

On the other hand, Kharasch *et al.* reported[2] that the treatment of 1,1,1-trichloro-3-bromo-3-phenylpropane, a bromotrichloromethane adduct to styrene, with sodium ethoxide in ethanol followed by hydrolysis gave cinnamic acid.



$$\mathrm{Ph{-}\underset{\displaystyle Br}{\overset{\displaystyle H}{C}}{-}CH_2{-}CCl_3 \xrightarrow[\substack{2)KOH/H_2O\\ 3)H^+/H_2O}]{1)NaOEt} Ph{-}CH{=}CH{-}COOH} \qquad (2)$$

In order to clarify whether the unusual reaction shown in Eq. 1 is favored specifically by metallocenyl group attached at 3-position or whether it occurs in the normal carbon tetrachloride adduct of alkenes, we reinvestigated the solvolysis of 1,1,1,3-tetrachloro-3-phenylpropane (**1**) in the alkali–ethanol systems.

## Experimental

*Materials.* Styrene (Wako Pure Chemical Co., G. R.) was distilled under reduced pressure just before use. Chlorotris(triphenylphosphine)ruthenium(II) was prepared according to the method given in the literature.[3] Sodium ethoxide was prepared from sodium metal and absolute ethanol. Ethanol-*d* ($CH_3CH_2OD$) (Commissariat a l'Energie Atomique, France, deuterium content: 99%) was used as received.

1,1,1,3-Tetrachloro-3-phenylpropane(**1**) was prepared from styrene according to Matsumoto *et al.*[4] Styrene (15.6 g, 0.15 mol) and chlorotris(triphenylphosphine)ruthenium(II) (0.78 g, 0.8 mmol) were dissolved in carbon tetrachloride (76 g, 50 cm$^3$) and the solution was refluxed for 5 h under nitrogen atmosphere. After the reaction, carbon tetrachloride was removed under reduced pressure and the residue was submitted to column chromatography on silica gel (Wakogel C-200, 200 mesh, eluent: $C_6H_6$). **1** was obtained in 95% yield. The spectral data (IR and $^1$H NMR spectra) of **1** were identical with those obtained by Matsumoto[5a] and Asahara.[5b] 1,1,1,3-Tetrachloro-4-phenylbutane (**13**) was prepared by the similar method from allylbenzene and carbon tetrachloride in 82% yield. The IR and $^1$H NMR spectra of **13** were identical with those obtained by Matsumoto.[6]

*Measurements.* $^1$H NMR spectra were recorded on a Hitachi R-22 (90 MHz) spectrometer. IR spectra were measured on a Hitachi 260-50 spectrophotometer. Mass spectra and GC-mass spectra were obtained on a JEOL JMA D-300 GC-mass spectrometer (column: OV-1, 5%, 1 m glass column).

Quantitative gas chromatography was performed on a Shimadzu GC-6AFP gas chromatograph (column: OV-1, 5%, 2 m glass column, temperature: 90—120 °C) equipped with an integrator (Shimadzu Chromatopak, E-1a).

*Reactions. Reaction of 1,1,1,3-tetrachloro-3-phenylpropane (1) with Potassium Hydroxide in Ethanol Solution:* **1** (3.0 g, 11.6 mmol) and potassium hydroxide (10 g, 0.178 mol) were added to ethanol (100 cm$^3$) and the solution was refluxed for 18 h at 80 °C. After the reaction, the reaction mixture was neutralized with aqueous sulfuric acid (0.1 mol dm$^{-3}$) and the organic substances were extracted with dichloromethane. After the solvent was removed under reduced pressure, the residue was submitted to column chromatography on silica gel (Wakogel C-200, eluent: $C_6H_6$). Compounds **2**, **3**, **6**, **8**, and **9** were obtained in almost pure form.

*Reaction of 1,1,1,3-tetrachloro-4-phenylbutane (13) with Potassium Hydroxide in Ethanol Solution:* The procedure is the same as described for the reaction of **1**. **13** (2.0 g, 7.3 mmol) was added to the ethanol solution containing potassium hydroxide (10 g/100 cm$^3$) and the solution was refluxed for 18 h.

*Reaction of 1,1,1,3-tetrachloro-3-phenylpropane (1) with Sodium Ethoxide in Ethanol Solution.* To the absolute ethanol solution of sodium ethoxide (12.0 g, 0.176 mol in 100 cm$^3$) was added 3 g of **1** (11.6 mmol) and the solution was refluxed for 18 h at 80 °C. The separation method of the reaction products was the same as described above.

*Reaction of 1,1-dichloro-3-ethoxy-3-phenylpropane (10) with Sodium Ethoxide in Ethanol Solution:* **10** (200 mg, 0.86 mmol) was refluxed in a sodium ethoxide–ethanol solution (3 g in 25 cm$^3$) for 18 h at 80 °C. After the reaction, the solution was neutralized and the organic substances were extracted with dichloromethane. Dichloromethane was removed under reduced pressure and the residue was dissolved in carbon tetrachloride for $^1$H NMR spectra measurement. The $^1$H NMR spectra of the product mixture show the presence of only three compounds, **2**, **3**, and **5** (100% conversion). A trace of **4** was detected by GC-mass spectra of the mixture. The yields of the products were calculated from the integrals of the peak areas.

*Reaction of 1,1-dichloro-3-ethoxy-3-phenylpropane (10) with Sodium Ethoxide in Ethanol-*d *($C_2H_5OD$) Solution:* **10** (300 mg, 1.3 mmol) was refluxed in sodium ethoxide–ethanol-*d* solution (1.0 g in 30 cm$^3$) for 8 h at 80 °C. After the reaction, the products were extracted with dichloromethane and the solvent was removed under reduced pressure. The residue was dissolved in carbon tetrachloride for the measurement of $^1$H NMR spectra. The $^1$H NMR spectra showed the presence of **5**, **5-*d***, **2**, **2-*d***, **10**, **10-*d***, and **3**. The ratio of **5** *versus* **5-*d*** was calculated based on the area of the peak of proton; the ratio of the area $\delta$=5.76 (s, -CH=CDCl) *versus* $\delta$=5.76 (d, $J$=13 Hz, -C$\underline{H}$=CHCl) was 2 : 1. Similar calculations were done for **2**, **2-*d***, **10**, **10-*d***. The ratios obtained were: 2/2-*d*=2/1, and 10/10-*d*=1/1. No deuterium incorporation was observed for **3**. The similar reaction was carried out at 60 °C for 2 h in order to detect the compound **11**. The $^1$H NMR spectra showed the peaks of compound **10**, **3**, and **5**. No deuterium incorporation was observed for these compounds. The peak attributable to the presence of **11** could not be observed. The GC-mass spectra of the same sample showed no increase of the intensities of the fragment peaks plus one (P+1) compared with those of the compounds **10**, **3**, and **5** which were obtained in the reaction of **10** in sodium ethoxide–ethanol system.

*Identification of the Products.* *1-Phenyl-2-propyn-1-one-(Ethynyl Phenyl Ketone) (**2**)*: A colorless liquid substance. IR (neat) 3240 (≡C–H), 3055, 3030 (arom. C–H), 2095 (C≡C), and 1650 cm$^{-1}$ (C=O). $^1$H NMR (CCl$_4$) $\delta$=3.34 (1H, s, C≡C–H), 7.30—7.65 (3H, m, meta and para protons of C$_6$H$_5$–), and 8.00—8.20 (2H, m, ortho protons of C$_6$H$_5$–). GC–MS (OV-1, 110 °C, 23 eV) *m/e* (rel intensity) 130 (M$^+$, 100), 105 (Ph-CO, 5.27), 102 (M$^+$–CO, 77.09), 78 (C$_6$H$_6$, 5.88), and 77 (C$_6$H$_5$, 2.54). Found: *m/e* 130.0440. Calcd for C$_9$H$_6$O: M, 130.0418.

*3,3-Diethoxy-3-phenyl-1-propyne (**3**)*: A pale yellow liquid substance. IR (neat) 3270 (≡C–H), 3060, 3030 (arom. C–H), 2980, 2930, 2880 (aliph. C–H), 2110 (C≡C), 1110 and 1045 cm$^{-1}$ (C–O–C). $^1$H NMR (CCl$_4$) $\delta$=1.19 (6H, t, -OCH$_2$-C$\underline{H}_3$), 2.59 (1H, s, C≡C–H), 3.53 (4H, m, -OC$\underline{H}_2$-CH$_3$), and 7.20—7.55 (5H, m, C$_6$H$_5$–). GC–MS (OV-1, 126 °C, 70 eV) *m/e* (rel intensity) 204 (M$^+$, 1.54), (M$^+$–C$_2$H$_5$, 29.7), 159 (M$^+$–OC$_2$H$_5$, 100), 131 (M$^+$–O(C$_2$H$_5$)$_2$+H, 65.4), and 77 (C$_6$H$_5$, 1.9). Found: *m/e* 204.1131. Calcd for C$_{13}$H$_{16}$O$_2$: M, 204.1150.

*(Z)3-Chloro-1-phenyl-2-propen-1-one (**4**)*: A colorless liquid substance. IR (neat) 3060, 3030 (arom. C–H), 1670 (C=O), 1650 (C=C), and 670 cm$^{-1}$ (*cis* CH=CHCl). $^1$H NMR (CCl$_4$) $\delta$=6.63 (1H, d, $J$=8 Hz, -CH=CHCl), 6.87 (1H, d, $J$=8 Hz, -CH=CHCl), and 7.15—7.6 (5H, m, C$_6$H$_5$–). GC–MS (OV-1, 110 °C, 23 eV) *m/e* (rel intensity) 166 (M$^+$, 41.1, M$^+$+2/M$^+$=0.322 (Cl×1)), 138 (M$^+$–CO, 13.3), 131 (M$^+$–Cl, 55.5), 105 (Ph-CO, 100), and 77 (C$_6$H$_5$, 36.7). Found: *m/e* 166.0168. Calcd for C$_9$H$_7$OCl: M, 166.01861.

*(E)1-Chloro-3,3-diethoxy-3-phenylpropene (**5**)*: A colorless liquid substance. IR (neat) 3070, 3030 (arom. C–H), 2980, 2940, 2880 (aliph. C–H), 1660 (C=C), 1070—1060 (C–O–C), and 942 cm$^{-1}$ (*trans* CH=CHCl). $^1$H NMR (CCl$_4$) $\delta$=1.17 (6H, t, -OCH$_2$-C$\underline{H}_3$), 3.36 (4H, m, -OC$\underline{H}_2$-CH$_3$), 5.76 (1H, d, $J$=13 Hz, -C$\underline{H}$=CHCl), 6.50 (1H, d, $J$=13 Hz, -CH=C$\underline{H}$Cl), and 7.10—7.55 (5H, m, C$_6$H$_5$–). GC–MS (OV-1, 96 °C, 70 eV) *m/e* (rel intensity) 240 (M$^+$, 0.12, M$^+$+2/M$^+$=0.323 (Cl×1)), 205 (M$^+$–Cl, 100), 195 (M$^+$–OC$_2$H$_5$, 79.23), 167 (M$^+$–O(C$_2$H$_5$)$_2$+H, 60.35), 131 (M$^+$–O(C$_2$H$_5$)$_2$–Cl, 70.84), 105 (Ph-CO, 86.63), and 77 (C$_6$H$_5$, 62.92). Found: *m/e* 240.0925. Calcd for C$_{13}$H$_{17}$O$_2$Cl: M, 240.09181.

*3,3-Diethoxy-1-phenyl-1-propanone (**6**)*: The dimethyl acetal of **6** which was prepared from **4** with sodium methoxide was reported by T. Matsumoto, *et al.*[7] A colorless liquid substance. IR (neat) 3070, 3030 (arom. C–H), 2980, 2940, 2890 (aliph. C–H), 1690 (C=O), and 1125 cm$^{-1}$ (C–CO–C). $^1$H NMR (CCl$_4$) $\delta$=1.13 (6H, t, -OCH$_2$-C$\underline{H}_3$), 3.17 (2H, d, $J$=5 Hz, -C$\underline{H}_2$-CH(OC$_2$H$_5$)$_2$), 3.61 (4H, m, -C$\underline{H}_2$-CH$_3$), 5.03 (1H, t, $J$=5 Hz, -CH$_2$-C$\underline{H}$(OC$_2$H$_5$)$_2$), 7.11—7.66 (3H, m, meta and para protons of C$_6$H$_5$–), and 7.77—8.11 (2H, m, ortho protons of C$_6$H$_5$–). GC–MS (OV-1, 110 °C, 23 eV) *m/e* (rel intensity) 222 (M$^+$, 1.33), 193 (M$^+$–C$_2$H$_5$, 29.86), 177 (M$^+$–OC$_2$H$_5$, 5.87), 176 (M$^+$–HOC$_2$H$_5$, 5.53), 147 (M$^+$–O(C$_2$H$_5$)$_2$+H, 12.27), 133 (M$^+$–(OC$_2$H$_5$)$_2$+H, 13.99), 105 (Ph-CO, 100), and 78 (C$_6$H$_6$, 8.59). Found: *m/e* 222.1264. Calcd for C$_{13}$H$_{18}$O$_3$: M, 222.12564.

*3,3-Diethoxy-1-phenylpropyne (**7**)*: A colorless liquid substance. IR and $^1$H NMR spectra of this compound were identical with those reported by Kiely *et al.*[8] Found: *m/e* 204.1164. Calcd for C$_{13}$H$_{16}$O$_2$: M, 204.1150.

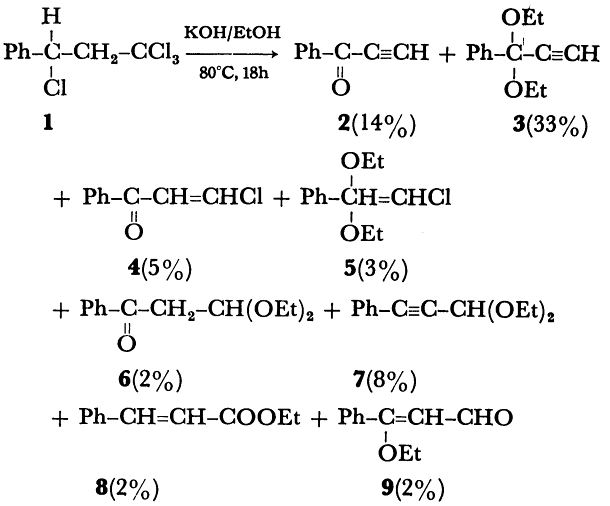
*Ethyl Cinnamate (**8**)*: The IR and $^1$H NMR spectra of **8** were identical with those of authentic sample.

*3-Ethoxy-3-phenyl-2-propenal (**9**)*: A colorless liquid substance. IR (neat) 3070, 3030 (arom. C–H), 2980, 2940, 2880 (aliph. C–H), 1660 (-C=C-CHO), and 1378 cm$^{-1}$ (C–H of CHO). $^1$H NMR (CCl$_4$) $\delta$=1.13 (3H, t, -OCH$_2$-C$\underline{H}_3$), 3.36 (2H, q, -OC$\underline{H}_2$-CH$_3$), 5.47 (1H, d, $J$=8 Hz, =C$\underline{H}$-CHO), 7.0—7.51 (5H, m, C$_6$H$_5$–), and 9.30 (1H, d, $J$=8 Hz, C$\underline{H}$O). GC–MS (OV-1, 110 °C, 23 eV) *m/e* (rel intensity) 176 (M$^+$, 20.92), 175 (M$^+$–H, 31.98), 147 (M$^+$–CHO, 25.49), 131 (M$^+$–OC$_2$H$_5$, 100), and 78 (C$_6$H$_6$, 13.10). Found: *m/e* 176.0841. Calcd for C$_{11}$H$_{12}$O$_2$: M, 176.08376.

*1,1-Dichloro-3-ethoxy-3-phenylpropene (**10**)*: A pale yellow liquid substance. IR (neat) 3060, 3030 (arom. C–H), 2960, 2920, 2890 (aliph. C–H), and 1610 cm$^{-1}$ (C=C). $^1$H NMR (CCl$_4$) $\delta$=1.13 (3H, t, -OCH$_2$-C$\underline{H}_3$), 3.38 (2H, m, -OC$\underline{H}_2$-CH$_3$), 5.03 (1H, d, $J$=8 Hz, -CH(OEt)-C$\underline{H}$=CCl$_2$), 5.93 (1H, d, $J$=8 Hz, -C$\underline{H}$(OEt)-CH=CCl$_2$), and 7.0—7.4 (5H, m, C$_6$H$_5$–). GC–MS (OV-1, 110 °C, 23 eV) *m/e* (rel intensity) 230 (M$^+$, 0.26, M$^+$+2/M$^+$=0.66 (Cl×2)), 195 (M$^+$–Cl, 100), 185 (M$^+$–OC$_2$H$_5$, 5.94), 167 (M$^+$–Cl–C$_2$H$_5$+H, 36.64), 131 (M$^+$–2Cl–C$_2$H$_5$, 15.90), and 105 (Ph-CO, 6.3). Found: *m/e* 230.0198. Calcd for C$_{11}$H$_{12}$OCl$_2$: M, 230.0264.

## Results and Discussion

When **1** (3.0 g, 11.6 mmol) was refluxed in an ethanolic solution of potassium hydroxide (10 g/100 cm$^3$) for 18 h followed by neutralization with acid, eight compounds were obtained. The main products were ethynyl phenyl ketone (**2**) (14%) and its acetal (**3**) (33%); these are the phenyl analogs of the compounds obtained in the case of 1,1,1-trichloro-3-ethoxy-3-metallocenylpropane.[1]



$$\mathrm{Ph{-}\underset{Cl}{\overset{H}{C}}{-}CH_2{-}CCl_3 \xrightarrow[80^\circ C,\ 18h]{KOH/EtOH} Ph{-}\underset{O}{\underset{\|}{C}}{-}C{\equiv}CH + Ph{-}\underset{OEt}{\overset{OEt}{C}}{-}C{\equiv}CH}$$

**1** **2**(14%) **3**(33%)

$$\mathrm{+\ Ph{-}\underset{O}{\underset{\|}{C}}{-}CH{=}CHCl + Ph{-}\underset{OEt}{\overset{OEt}{C}}H{=}CHCl}$$

**4**(5%) **5**(3%)

$$\mathrm{+\ Ph{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}CH(OEt)_2 + Ph{-}C{\equiv}C{-}CH(OEt)_2}$$

**6**(2%) **7**(8%)

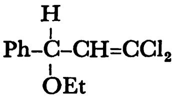
$$\mathrm{+\ Ph{-}CH{=}CH{-}COOEt + Ph{-}\underset{OEt}{C}{=}CH{-}CHO}$$

**8**(2%) **9**(2%)

These facts indicate that this type of unusual reaction is favored not only by a metallocenyl group attached to the 3-position but also by a phenyl group at the 3-position.

The products from **1** except for **8** which is the product expected from the report by Kharasch *et al.*[2] have one similar feature, *i.e.* these compounds have a hydrogen atom at the terminal carbon which originally had three chlorine atoms.

When the reaction of **1** was carried out with ethanolic sodium ethoxide (12 g/100 cm$^3$), compounds **2**, **3**, **4**, **5**, and **10** were obtained in 59, 2, 2, 2, and 22% yields, respectively.



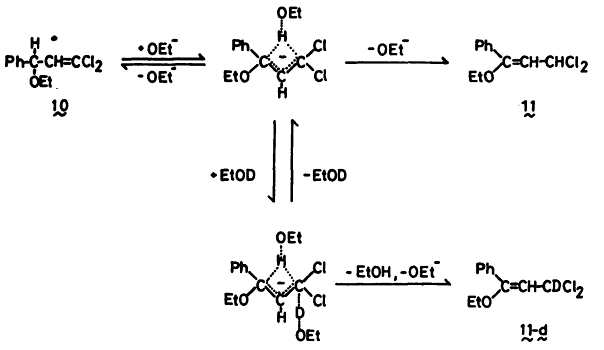
$$\text{Ph-}\overset{\text{H}}{\underset{\text{OEt}}{\text{C}}}\text{-CH=CCl}_2$$

**10** (22%)

Compound **10** has a different type of structure from **2**, **3**, **4**, and **5** and is considered to be a precursor to **2** and **3**, since i) **10** is the compound which is formed by the normal substitution of chloride ion by ethoxide ion at benzylic position of **1**; ii) the hydrogen atom at the benzylic position in **1** is still at the original position in **10**; and iii) the terminal carbon has no hydrogen atom yet.

The treatment of **10** (200 mg) with sodium ethoxide in ethanol (3 g/25 cm$^3$) afforded a mixture of products, the composition of which is similar to that of the product from **1** on treatment with sodium ethoxide except for **10**. **2**, **3**, **4**, and **5** were obtained in 18, 72, <1, and 9% yields, respectively.

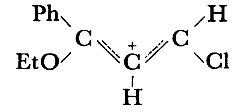
The formation of **5** from **10** strongly suggests that the base-catalyzed 1,3-proton transfer[9] takes place effectively and this results in the formation of the rearranged product **11** as shown in Scheme 1.



Scheme 1.

If this 1,3-proton transfer occurs intramolecularly, the incorporation of deuterium from the solvent (EtOD) would not be observed in the products. The results that the alkali-solvolysis of **10** (300 mg) with sodium ethoxide in monodeuterated ethanol (EtOD) (1.0 g/30 cm$^3$) at 80 °C for 8 h shows the 33% incorporation of deuterium in **5** but no incorporation of deuterium in **3** indicate that the 1,3-proton transfer occurs mainly intramolecular fashion. Cram and Uyeda[9] reported the base-catalyzed rearrangement of 3-phenyl-1-butene to *cis*-2-phenyl-2-butene and they showed that both intra- and intermolecular 1,3-hydrogen transfer were involved in the rearrangement. However, the fact that no deuterium incorporation was observed for **3** indicates that the primary reaction of **10** with ethoxide ion to produce **11** is almost intramolecular fashion and the secondary solvolysis of **11** is faster than H–D exchange reaction. When the reaction of **10** with sodium ethoxide in EtOD was carried out at 60 °C for 2 h, formation of **3** and **5** without deuterium were observed, although the formation of **11** was not observed. These results strongly suggest that the intramolecular 1,3-proton transfer occurs effectively in this reaction, when the H–D exchange process is slow enough compared with the solvolysis.

The tentative reaction pathway from **11** to **5** is as follows; i) the rearranged product **11** loses one of the two chlorine atoms as a chloride ion and forms carbenium ion, such as **12**, and ii) **12** is attacked by ethoxide ion at the *α*-position to phenyl group to produce **5**.



**12**

No similar reaction involving 1,3-proton transfer was observed in the treatment of 1,1,1,3-tetrachloro-4-phenylbutane (**13**), a carbon tetrachloride adduct to allylbenzene, with potassium hydroxide in ethanol solution.[10]

For this base-catalyzed 1,3-proton transfer reaction, the stabilization of the transition state by conjugation with an aromatic group seems to play an important role: When an ethoxide ion attacks the hydrogen atom at the 3-position of **10** and abstracts it as a proton, the negative charge is delocalized in a conjugate system involving phenyl group. After the proton transfer is completed, the removal of a chloride ion from **11** produces an allyl cation **12** which is also stabilized by the phenyl group. The results that the products **2**, **3**, **4**, **5**, and **6** consist of 82% of the whole products strongly suggest that the carbon atom having phenyl and ethoxyl group in **12** is preferentially attacked by ethoxide ion to produce **5**. These results agree with those obtained in the case of metallocene derivatives of **1**.

The formation of **2**, **3**, **4**, and **5** may be explained by a mechanism in which a transposition of the carbon side chain resulting in the exchange of 1- and 3-positions is involved. However, this mechanism is excluded by the experiment using 1,1,1-trichloro-3-ethoxy-3-(3-ethylferrocenyl)propane. When it was refluxed with potassium hydroxide in ethanol at 80 °C for 18 h, only 3-ethyl ferrocenyl ethynyl ketone was obtained and no product *via* carbon side chain transposition, such as 2-ethylferrocenyl ethynyl ketone or 1′-ethylferrocenyl ethynyl ketone was obtained.

The authors are grateful to Professor Naoki Inamoto for helpful discussions. We also thank Dr. Hideyuki Matsumoto for sending us spectral data of **1** and **13**.

## References

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5) a) H. Matsumoto, private communication; b) T. Asahara and C. Wu, *Kogyo Kagaku Zasshi*, **72**, 1516 (1969).

6) H. Matsumoto, private communication. IR (neat) 3070, 3040, 2970, 1505, 1460, 1420, 1205, 970, 760, and 699 cm$^{-1}$. $^1$H NMR ($CCl_4$) $\delta$=3.05—3.29 (4H, m, $-C\underline{H}_2-CHCl-C\underline{H}_2CCl_3$), 4.20—4.58 (1H, m, $-C\underline{H}Cl-$), and 7.21 (5H, s, $C_6H_5-$). Found: *m/e* 269.9538. Calcd for $C_{10}H_{10}Cl_4$: M, 269.9539.

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10) The only product which has molecular weight less than 300 could be identified by GC-MS (OV-1, 110 °C, 23 eV). The parent peak ($M^+$, *m/e* 208, $M^+ + 2/M^+ = 0.335$) and fragment pattern suggest the presence of 1-chloro-3-ethoxy-4-phenyl-1-butyne.