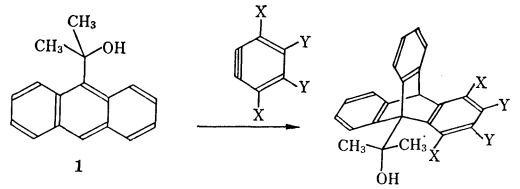
# Restricted Rotation Involving the Tetrahedral Carbon. XLIV. Atropisomers of 2,3-Dichloro-9-(1-hydroxy-1-methylethyl)-triptycene and Related Compounds[1)]

Michinori Ōki,* Yoshiyuki Tanaka, Gaku Yamamoto, and Nobuo Nakamura
*Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113*
(Received August 10, 1982)

Atropisomers of 2,3-dichloro-9-(1-hydroxy-1-methylethyl)triptycene were obtained as stable compounds at room temperature. The barrier to rotation (±*sc*→*ap*) was 34.0 kcal/mol at 153 °C. Other 9-(1-hydroxy-1-methylethyl)triptycenes carrying a substituent in the 1-position of the skeleton gave ±*sc* isomers only. Attempted isomerization of the ±*sc* forms failed because the free energy difference between the ±*sc* and *ap* forms is great due to the steric effect. ±*sc*-9-(1-Methoxy-1-methylethyl)-1,4-dimethyltriptycene was prepared in a hope that increasing the steric size of the hydroxyl group would help to produce an *ap*-isomer on heating. The *ap* isomer was detected but the population ratio *ap*/±*sc* was too small to isolate the *ap*.

Various triptycene derivatives were found to give stable rotational isomers at room temperature provided that the 9-substituent is tertiary and the triptycene skeleton carries a substituent which provides necessary breaking of the symmetry.[2)] However, the 9-substituent was confined to those carrying three carbons in the 1-position of the substituent so far. It may be of interest to see how the barriers to rotation and populations of rotamers are affected if one of the substituents in the 1-position of the 9-substituent is changed to a hetero atom. As the first of such investigations, we have undertaken the investigation on the case of a 9-(1-hydroxy-1-methylethyl) substituent. This paper is to report the results and to discuss implications therefrom.

The syntheses of the compounds were rather interesting. Although benzynes are known to react with hydroxylic compounds to give aromatic oxygen derivatives,[3)] 9-(1-hydroxy-1-methylethyl)anthracene (**1**) gave the desired triptycenes (**2**) when it was treated



1 2

**a**: X=Y=H
**b**: X=H, Y=Cl
**c**: X=$OCH_3$, Y=H
**d**: X=Y=Cl
**e**: X=$CH_3$, Y=H

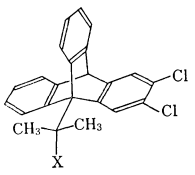
with benzynes. We believe that the result is caused because the anthracene moiety is strongly nucleophilic and the hydroxyl group is protected from the attack by the steric effect. The only exception to the normal cases was the reaction of tetrafluorobenzyne, which gave 9-isopropenylanthracene only as a product of the benzyne reaction. Since tetrafluorobenzyne is very strongly electrophilic, it seems to react with the oxygen of the alcohol (**1**) preferentially. In accordance with this explanation, other benzynes which are strongly electrophilic gave also 9-isopropenylanthracene to some extent.

The reaction, if proceeded as expected, gave ±*sc* conformational isomers of a desired compound as a sole product. This is reasonable in the sense that a methyl group is much larger than an oxygen group: the benzyne addition to 9-substituted anthracene is known to proceed from the less crowded side with great preference.[4)] The assignment of the stereostructure of the product is straightforward. The ±*sc* conformation should show two methyl signals in $^1$H NMR spectra because the environments of the two methyls are different in this conformation, whereas the environments of the methyls in the *ap* conformation are identical.

Table 1. Rates of isomerization (±*sc*→*ap*) and equilibrium constants in 2,3-dichloro-9-(1-hydroxy-1-methylethyl)triptycene (**2b**) in 1-chloronaphthalene

| Temperature/°C | $k$/s$^{-1}$ | $K$ (*ap*/±*sc*) |
|---|---|---|
| 212 | — | 0.30 |
| 165.6 | $8.63\times10^{-5}$ | 0.27 |
| 153.0 | $3.34\times10^{-5}$ | 0.29 |
| 144.6 | $1.69\times10^{-5}$ | 0.29 |
| 132.5 | $5.21\times10^{-6}$ | 0.31 |

The rate constants for isomerization of ±*sc*-**2b** are summarized in Table 1. The Eyring plot yielded $\Delta H^*$ 29.1±2.5 kcal/mol (1 cal=4.18 J) and $\Delta S^*$ −11.5± 6.0 e. u. (1 e. u.=4.18 J K$^{-1}$ mol$^{-1}$). If these activation parameters are compared with those of 2,3-dichloro-9-(1-methoxycarbonyl-1-methylethyl)triptycene (**3**) ($\Delta H^*$ 33.8 kcal/mol and $\Delta S^*$ −1.8 e. u.),[5)] 2,3-dichloro-9-(1-cyano-1-methylethyl)triptycene (**4**) ($\Delta H^*$ 39.4 kcal/mol and $\Delta S^*$ 6.5 e. u.),[5)] and 2,3-dichloro-9-(1,1-dimethyl-2-phenylethyl)triptycene (**5**) ($\Delta H^*$ 35.7



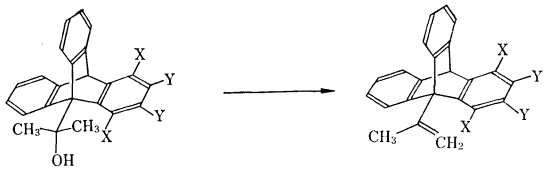
**3**: X=$COOCH_3$
**4**: X=CN
**5**: X=$CH_2C_6H_5$

kcal/mol and $\Delta S^*$ −9.3 e. u.),[4)] one notices that the enthalpy of activation of **2b** is definitely small. The results may be attributed to the small bulkiness of the oxygen group in **2b** relative to a methoxycarbonyl, cyano, or benzyl group. Namely, the lowering of the transition state energy is more effective than lowering of the ground state energy in determining the barrier

to rotation in **2b**.

The equilibrium constants ($ap/\pm sc$) of **2b** are smaller than the statistical value and are even smaller than those compounds cited above (**3**—**5**). Two possibilities emerge for the explanation. One is that the *ap* conformation of **2b** is destabilized relative to *ap* conformations of other compounds and the other is the special stabilization of the $\pm sc$ conformation of **2b**. The 1-H undoubtedly suffers from the buttressing effect of the 2-Cl group, thus it should be larger in effective size than other *peri*-hydrogens. Then probably the repulsive interaction between the 1-H and the flanking groups (two methyls) in the *ap* conformation is more severe than that between the 8(or 13) -H and two methyl groups in $\pm sc$ conformations. We believe this kind of steric effect is an important factor among others that favor the $\pm sc$ conformation of **2b** in the ground state, since no effect of stabilization of the $\pm sc$ form is apparent. Indeed, 2,3-dichloro-9-(1,1-dimethyl-2-phenylethyl)triptycene (**5**) gives $ap/\pm sc$ of 0.50,[4] which is the statistical value, because the effective sizes of the benzyl and the methyl groups are almost the same.

Other triptycenes (**2**) carrying (a) substituent in 1-position failed to give any sign of the presence of *ap* isomers, although their solutions were heated at 212 °C for a long time. Instead, they afforded compounds of which $^1$H NMR spectra are compatible with 9-isopropenyltriptycenes (**6**): indeed, 1,4-dimethyl derivative of **6** was characterized. Since this dehydration did not occur at 164 °C after 40 h, the dehydration is caused by heating at >200 °C. The results indicate that the *ap* conformation in these compounds are extremety unstable relative to the $\pm sc$, since the barriers to rotation in other analogous compounds[4,5] suggest that the internal rotation about the $C_9$–$C_{subst}$ bond must be occurring under the conditions of the heating. It is not clear at the moment at what conformation the dehydration takes place.



1 6

The $^1$H NMR spectra of isopropenyltriptycenes (**6**) indicate that the internal rotation about the $C_9$–$C_{ipr}$ bond in these compounds is fast on the NMR time scale. This is interesting, if one considers a very high barrier to rotation in 9-*t*-alkyltriptycenes. But there is a precedent of this instance: 9-*o*-tolyltriptycenes show rather low barriers to rotation.[6] If a 9-substituent has an $sp^2$-hybridized carbon in its 1-position, the ground state seems to be raised owing to the interaction of the triptycene skeleton with the trigonal group.

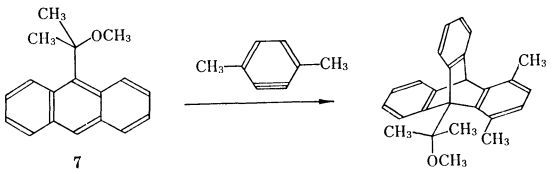
The great stability of the $\pm sc$ forms of **2c**—**e** relative to the *ap* must be attributed to the steric effect. If a 9-substituent in triptycenes contain a small group in its 1-position and the triptycene skeleton carries a *peri*-substituent, there is seen a strong preference of a conformation in which the small group gives the gauche interaction with the *peri*-substituent. If the 9-substituent is a secondary alkyl group, a conformation in which two bulky groups flank the *peri*-substituent is not usually detected.[7] Even in the tertiary alkyl cases, it is true: if a 1-substituent in the 9-substituent of triptycene is either trigonal or linear, the conformation in which the trigonal or linear group is $\pm sc$ to the *peri*-substituent is strongly favored.[5] The case of compound **2** is considered to be in the same line, since the OH group is much smaller than a methyl. The OH-*sc* conformation must be favored relative to the OH-*ap* conformation.

Hydrogen bonding between the OH group and the *peri*-substituent may be playing some role in stabilizing the $\pm sc$ conformation. Indeed, $^1$H NMR spectra show that the OH proton gives a sharp peak if there is a *peri*-substituent with lone pair electrons, whereas the OH proton signal either was broad or could not be detected in others. However, the effect of the hydrogen bond must be of minor importance, because even the 1,4-dimethyl compound (**2e**) gives only $\pm sc$ conformations.

This consideration suggests that, if the hydroxyl group is modified to make a larger group, there is a possibility that *ap* conformation exists. Thus ester formations and ether formations of both the anthracene–alcohol (**1**) and the triptycene–alcohol (**2**) were tried under various conditions. However, all the attempts failed because of the steric effect except for one case, that is the methylation of **1**.

Treatment of the methyl ether (**7**) with tetrachlorobenzyne did not afford a triptycene derivative but 9-isopropenylanthracene. It is not clear why the methyl ether (**7**) gives 9-isopropenylanthracene, whereas the hydroxy compound (**1**) gives a triptycene to some extent, since the oxygen in the methyl ether seems to be more protected than the hydroxylic oxygen on the steric ground. Probably the electronic effect and/or the steric deceleration of the attack of benzyne toward the anthracene ring, due to introduction of the methyl group to the hydroxyl, is important.

Tetrachlorobenzyne has been known to give an olefin if it reacts with an ether[8] because of its electrophilic nature. If we could lower the electrophilicity of a benzyne, there is a chance of obtaining a triptycene derivative. Thus we treated **7** with 3,6-dimethylbenzyne and indeed obtained *sc*-9-(1-methoxy-1-methylethyl)-1,4-dimethyltriptycene (**8**). Isomerization of **8**, however, gave only a minute amount of the *ap* isomer, of which isolation was not practical. The steric effect of a methoxyl group is indeed greater than a hydroxyl group, because we could detect the presence of the *ap* form of **8**, but is not great enough to give sizable amount of the *ap*.



7 8

## Experimental

*3,6-Dimethoxyanthranilic Acid.* To 90 mL of chilled nitric acid ($d$=1.38) was added portionwise 9.1 g (0.05 mol) of 2,5-dimethoxybenzoic acid[9] during the course of 30 min and the solution was stirred at 0—5 °C for 3 h. The mixture was poured into 300 mL of ice–water and the precipitate was collected by filtration. The product was shown to be a mixture (*ca.* 5:1) of 2,5-dimethoxy-6-nitrobenzoic acid and 2,5-dimethoxy-4(or 3)-nitrobenzoic acid by $^1$H NMR spectra. The mixture (10.4 g) was hydrogenated over Pd–C in ethyl acetate under normal pressure. Removal of the catalyst, evaporation of the solvent, and recrystallization of the residue from aqueous ethanol gave 3.4 g (38%) of the desired acid as white needles, mp 92—94 °C (lit,[10] mp 97 °C).

*9-(1-Hydroxy-1-methylethyl)anthracene (**1**).* A Grignard reagent was prepared from 1.42 g (60 mmol) of magnesium, 5.0 g (20 mmol) of 9-bromoanthracene[11] and 90 mL of ether. To the solution, 5 mL (68 mmol) of acetone in 20 mL of ether was added and the whole was stirred overnight. The mixture was decomposed with ice and aqueous ammonium chloride and the ether layer was separated. The ether layer was washed thoroughly and dried over magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from benzene. For further purification, the product was submitted to silica gel chromatography (hexane–dichloromethane eluent) to give 1.6 g of the desired product, mp 139.0—140.5 °C (lit,[12] mp 136 °C). $^1$H NMR ($CDCl_3$, $\delta$): 2.15 (6H, s), 7.1—7.6 (4H, m), 7.7—8.1 (2H, m), 8.28 (1H, s), 8.6—8.9 (2H, m).

*±sc-2,3-Dichloro-9-(1-hydroxy-1-methylethyl)triptycene (**2b**).* To a solution of 473 mg (2.0 mmol) of the alcohol (**1**) and 0.5 mL (3.8 mmol) of isopentyl nitrite in 40 mL of chlorobenzene, was added 828 mg (4.0 mmol) of 4,5-dichloroanthranilic acid[4] in 50 mL of chlorobenzene in *ca.* 2 h with stirring and heating. More isopentyl nitrite was added after *ca.* 1 h during the addition of the anthranilic acid. After heating for another hour, the solvents were evaporated *in vacuo* and the residue was taken up in dichloromethane. The solution was submitted to chromatography on silica gel with hexane–dichloromethane eluents (5:1—2:1) to give *±sc-***2b**, mp 193.5—195 °C, in 13% yield. Found: C, 72.22; H, 4.62; Cl, 18.47%. Calcd for $C_{23}H_{18}Cl_2O$: C, 72.45; H, 4.76; Cl, 18.60%. $^1$H NMR ($CDCl_3$, $\delta$): 2.20 (3H, s), 2.24 (3H, s), 5.16 (1H, s), 6.85—7.1 (4H, m), 7.2—7.45 (2H, m), 7.41 (1H, s), 7.55 (1H, m), 8.0 (1H, m), 8.15 (1H, s).

*Attempted Synthesis of 1,2,3,4-Tetrafluoro-9-(1-hydroxy-1-methylethyl)triptycene.* A similar treatment of the alcohol (**1**) and isopentyl nitrite in dichloromethane with tetrafluoroanthranilic acid[13] in tetrahydrofuran afforded anthraquinone and 9-isopropenylanthracene, mp 84.5—86.0 °C (lit,[14] mp 84.5—86 °C). $^1$H NMR ($CDCl_3$, $\delta$) of isopropenylanthracene exhibited the following signals: 2.15 (3H, d, $J$=1 Hz), 5.05 (1H, m), 5.63 (1H, m), 7.2—7.5 (4H, m), 7.7—7.9 (2H, m), 7.9—8.2 (2H, m), 8.18 (1H, s). No tetrafluorotriptycene derivative was detected.

*9-(1-Hydroxy-1-methylethyl)triptycene (**2a**),* mp 200—202 °C, was prepared similarly from **1** and isopentyl nitrite in dichloromethane and anthranilic acid in acetone in 75% yield. The original product was contaminated with a small amount of 9-isopropenylanthracene. The product was purified by recrystallization from tetrahydrofuran–hexane. Found: C, 88.64; H, 6.39%. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%. $^1$H NMR ($CDCl_3$, $\delta$): 2.31 (6H, s), 2.58 (1H, br s), 5.25 (1H, s), 6.8—7.5 (9H, m), 7.5—7.7 (1H, m), 7.9—8.1 (2H, m).

*±sc-1,2,3,4-Tetrachloro-9-(1-hydroxy-1-methylethyl)triptycene (**2d**),* mp 299—300.5 °C, was similarly prepared from the alcohol (**1**) and isopentyl nitrite in dichloromethane and tetrachloroanthranilic acid[15] in acetone in 11.2% yield. A fair amount of isopropenylanthracene was detected. Found: C, 61.06; H, 3.38; Cl, 31.31%. Calcd for $C_{23}H_{16}Cl_4O$: C, 61.36; H, 3.58; Cl, 31.50%. $^1$H NMR ($CDCl_3$, $\delta$): 2.12 (3H, s), 2.42 (3H, s), 4.33 (1H, s), 6.03 (1H, s), 6.9—7.25 (4H, m), 7.3—7.6 (2H, m), 7.6—7.8 (1H, m), 8.5—8.7 (1H, m).

*±sc-9-(1-Hydroxy-1-methylethyl)-1,4-dimethoxytriptycene (**2c**),* mp 272—273 °C, was prepared similarly from the alcohol and isopentyl nitrite in dichloromethane and 3,6-dimethoxyanthranilic acid in tetrahydrofuran in 14% yield. Found: C, 80.72; H, 6.46%. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.49%. $^1$H NMR ($CDCl_3$, $\delta$): 2.16 (6H, s), 3.77 (3H, s), 3.82 (3H, s), 5.86 (1H, s), 5.90 (1H, s), 6.55 (2H, s), 6.85—7.1 (4H, m), 7.25—7.55 (2H, m), 7.65 (1H, m), 8.4 (1H, m). On addition of benzene-$d_6$ to the chloroform-$d$ solution, the methyl proton signal at $\delta$ 2.16 was split into two.

*±sc-9-(1-Hydroxy-1-methylethyl)-1,4-dimethyltriptycene (**2e**),* mp 255—257 °C, was similarly prepared from the alcohol (**1**) and 3,6-dimethylanthranilic acid[16] in 50% yield. Found: C, 88.06; H, 7.01%. Calcd for $C_{25}H_{24}O$: C, 88.20; H, 7.10%. $^1$H NMR ($CDCl_3$, $\delta$): 2.22 (3H, s), 2.32 (3H, s), 2.46 (3H, s), 2.82 (3H, s), 5.57 (1H, s), 6.71 (2H, s), 6.85—7.1 (4H, m), 7.2—7.45 (2H, m), 7.6 (1H, m), 8.2 (1H, m).

*9-(1-Methoxy-1-methylethyl)anthracene (**7**).* To a solution of 718 mg (3.0 mmol) of the alcohol (**1**) in 100 mL of tetrahydrofuran was added 2 mL of 1.5 M butyllithium in hexane and the whole was stirred for 3 h. Methyl iodide (5 mL) was added and the mixture was stirred for 3 h. The solvent and the excess of methyl iodide were evaporated in vacuo and the residue was taken up in ether. The ethereal solution was washed and dried. Evaporation of the solvent followed by recrystallization of the residue from dichloromethane–hexane afforded 526 mg of the desired product, mp 107—108.5 °C. Found: C, 86.29; H, 7.06%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. $^1$H NMR ($CDCl_3$, $\delta$): 2.15 (6H, s), 2.80 (3H, s), 7.2—7.45 (4H, m), 7.85—8.05 (2H, m), 8.33 (1H, s), 8.6—8.95 (2H, m).

*±sc-9-(1-Methoxy-1-methylethyl)-1,4-dimethyltriptycene (**8**),* mp 251—252 °C, was prepared by treating **7** with 3,6-dimethylbenzyne as above. Found: C, 87.95; H, 7.15%. Calcd for $C_{26}H_{26}O$: C, 88.09; H, 7.39%. $^1$H NMR ($CDCl_3$, $\delta$): 2.09 (3H, s), 2.13 (3H, s), 2.46 (3H, s), 2.64 (3H, s), 3.55 (3H, s), 5.57 (1H, s), 6.69 (2H, s), 6.7—7.2 (4H, m), 7.2—7.4 (2H, m), 7.56 (1H, m), 8.00 (1H, m).

A 1-chloronaphthalene solution of *±sc-***8** showed the following $^1$H NMR signals (ppm from internal cyclododecane): 0.52 (6H, s), 1.16 (3H, s), 1.38 (3H, s), 1.87 (3H, s). When the solution was heated in a boiling-nitrobenzene bath, the following $^1$H NMR signals were observed: 0.72 (6H, s), 0.97 (3H, s), 1.91 (3H, s). Another signal for 1(or 4)-methyl protons is missing: it probably overlaps with one of the signals due to 1- and 4-methyls of the *±sc* form. The equilibrium was reached within 5 h at this temperature and the equilibrium constant (*ap*/*±sc*) was *ca.* 1/30. Prolonged heating of the solution caused decomposition of the solute.

*Determination of Barriers to Rotation.* A sample (55 mg) of *±sc-***2b** was dissolved in 1.4 mL of 1-chloronaphthalene and placed in NMR sample tubes, the solution being divided into 4 portions. The NMR sample tube was placed in an appropriate boiling-solvent bath and the isomerization rate was determined by $^1$H NMR spectroscopy. The temperature was directly read by a thermometer. The integration of the peak area was carried out 5 times and the

average of the middle three was taken for calculation of the rate constant. The conversion rate was treated assuming a reversible first-order reaction. The solvents used for the bath are nitrobenzene (212 °C), mesitylene (165.5 °C), anisole (153.0 °C), *o*-xylene (144.6 °C), and chlorobenzene (132.5 °C). The rate constants were put into the Eyring equation and the activation parameters were obtained.

*ap-2,3-Dichloro-9-(1-hydroxy-1-methylethyl)triptycene (**2b**).* The equilibrium mixture of ±*sc*- and *ap*-**2b**, obtained as a result of the isomerization experiments, was concentrated *in vacuo* and submitted to chromatography on alumina. After the solvent was eluted with hexane, a ±*sc*-*ap* mixture was obtained by elution with dichloromethane. The mixture was separated by TLC on silica gel (2:1 dichloromethane–hexane solvent). The *ap* form, mp 207—209 °C, had a smaller $R_f$ value than the ±*sc* form. High resolution mass spectrum showed molecular ion peaks at *m/e* 380.0775, 382.0759, and 384.0707, whereas $C_{23}H_{18}Cl_2O$ requires those at 380.0735, 382.0706, and 384.0676. The intensities of these peaks agreed well with those calculated from the natural abundance of $^{35}Cl$ and $^{37}Cl$. $^1H$ NMR ($CDCl_3$, $\delta$): 2.26 (6H, s), 5.17 (1H, s), 6.85—7.1 (4H, m), 7.2—7.45 (2H, m), 7.46 (1H, s), 7.59 (1H, s), 8.0 (2H, m).

*9-Isopropenyl-1,4-dimethyltriptycene (**6**: X=$CH_3$, Y=H).* A solution of ±*sc*-**2e** (20 mg) in 0.4 mL of 1-chloronaphthalene was heated in a boiling-nitrobenzene bath for 40 h. The solution was submitted to chromatography on alumina (hexane eluent) and the product was recrystallized from pentane to give 14 mg of the product, mp 149—150 °C. Found: C, 92.99; H, 6.84%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%. $^1H$ NMR ($CDCl_3$, $\delta$): 2.27 (3H, s), 2.44 (6H, s), 5.48 (1H, s), 5.79 (1H, br s), 5.93 (1H, br s), 6.63 (2H, s), 6.85—7.1 (4H, m), 7.2—7.6 (2H, m), 7.6—7.9 (2H, m).

*Determination of Spectra.* $^1H$ NMR spectra were obtained on a Varian EM 390 spectrometer.

## References


1) For Part XLIII, see M. Aoki, M. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **55**, 2512 (1982).
2) M. Ōki, *Angew. Chem., Int. Ed. Engl.*, **15**, 87 (1976).
3) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95**, 2718 (1962).
4) G. Yamamoto and M. Ōki, *J. Chem. Soc., Chem. Commun.*, **1974**, 713; *Bull. Chem. Soc. Jpn.*, **48**, 3686 (1975).
5) S. Otsuka, G. Yamamoto, T. Mitsuhashi, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **53**, 2095 (1980).
6) M. Nakamura and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 2106 (1975).
7) F. Suzuki, M. Ōki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **47**, 3114 (1974); M. Suzuki, G. Yamamoto, H. Kikuchi, and M. Ōki, *ibid.*, **54**, 2383 (1981); H. Kikuchi, S. Hatakeyama, G. Yamamoto, and M. Ōki, *ibid.*, **54**, 3832 (1981).
8) Reaction of diethyl ether with tetrachlorobenzyne to give ethyl tetrachlorophenyl ether and ethene is known: J. P. N. Brewer, H. Heaney, and J. M. Jablonski, *Tetrahedron Lett.*, **1968**, 4455.
9) P. K. Banerjee and D. N. Chandhbury, *J. Indian Chem. Soc.*, **36**, 257 (1959).
10) F. J. Villani and J. Laug, *J. Am. Chem. Soc.*, **72**, 2301 (1950).
11) D. C. Nonhebel, *Org. Synth.*, Coll. Vol. V, 206 (1973).
12) C. Jean and M. Ernest, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **286**, 169 (1978).
13) S. Hayashi and N. Ishikawa, *Nippon Kagaku Zasshi*, **91**, 1000, (1970).
14) E. G. E. Hawkins, *J. Chem. Soc.*, **1957**, 3858.
15) V. Villiger and L. Blangey, *Ber.*, **42**, 3549 (1909).
16) S. Gronowitz and G. Hansen, *Ark. Kemi*, **27**, 145 (1967).