Onium Ions. XIV.¹ Evidence for the Formation of Benzochlorophenium Ions²

George A. Olah* and Yorinobu Yamada^{1c}

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received November 6, 1974

Benzochlorophenium ions were previously unknown. We have now studied, in the case of the 2-chlorobenzochlorophenium and 2-chloro-3-methylbenzochlorophenium ions, their possible preparation through the thermal dediazonation of $o \cdot (\beta,\beta$ -dichloroethenyl)phenyl- and $o \cdot (\alpha$ -methyl- β,β -dichloroethenyl)phenyldiazonium hexafluorophosphate. Whereas the desired benzochlorophenium ions could not be isolated, formation of $o \cdot (\beta$ -chloroethenyl)chlorobenzene in the case of the former, as well as of 1-chloro-1-fluoro-2-(o-chlorophenyl)propen-1-ol and 1-chloro-1-(o-chlorophenyl)-2-fluoropropene-1 in the case of the latter, clearly indicates the intermediacy of the related benzochlorophenium ions.

Cyclic dibenzohalophenium ions (1), particularly dibenziodophenium ions, were previously prepared and studied.² Besides dibenzohalophenium ions (1), 2-phenyl-3-butyl-



benziodophenium (2) and tetraphenyliodophenium ions (3a) were among others synthesized by Beringer et al.³ They reported that the iodophenium ion 2 underwent attack by nucleophiles, such as chloride, iodide, and methoxide ions, exclusively at the 2 position to give a mixture of trans and cis isomers (eq 1).



The intermediacy of the 2,5-diphenylchlorophenium ion **3b** was recently also shown in the silver ion assisted solvolysis of halobutadienes.⁴ The cyclic halophenium ions bear possible aromatic character, and their chemical reactivity is also of substantial interest.



Results and Discussion

In an attempt to prepare and study the previously unknown class of benzochlorophenium ions, $o - (\beta,\beta$ -dichloroethenyl)phenyl- (**5a**) and $o - (\alpha$ -methyl- β,β -dichloroethenyl)phenyl- (**5b**) diazonium fluorophosphate were used as precursors for synthesizing benzochlorophenium ions **4a** and **4b**, respectively. They were synthesized as shown in Scheme I.



Dichloro olefins (6) were prepared from the corresponding carbonyl compounds with triphenylphosphonium dichloromethylide [R = H, 36.7%, mp 49-50°; R = CH₃, 56.0%, bp 110° (0.4 mm)], and were reduced with zinc powder and ammonium chloride in acetone-water to give the aniline derivatives 7 [R = H, 95.8%, bp $85-90^{\circ}$ (0.03 mm); $R = CH_3$, 50%, bp 90° (1.3 mm)], which are, however, of only limited stability at room temperature. The aniline derivatives 7 were, therefore, immediately dissolved in acetonitrile, and were diazotized by using nitrosonium fluorophosphate in carbon tetrachloride to give the corresponding diazonium compounds 5 (R = H, 44.8%, mp $117-120^{\circ}$ dec; $R = CH_3$, 28.4%, mp 99–100° dec).⁵ Subsequently, we attempted the preparation of the 2-chlorobenzochlorophenium ion 4a by the thermal decomposition of $o - (\beta, \beta)$ dichloroethenyl)phenyldiazonium fluorophosphate (5a) in refluxing benzene for 1.5 hr. The desired benzochlorophenium ion (4a) could not be isolated, but o-(β -chloroethinyl)chlorobenzene $(8)^6$ was obtained in 99.0% yield (eq 2). The formation of 8 clearly shows the intermediacy of 4a. which via ring opening and deprotonation gives 8 (eq 3). A concerted elimination process is considered less probable. 4a is not sufficiently stable to be isolated under the reac-



tion conditions. If the acidic proton at C₃ is absent in the benzochlorophenium ion, a different behavior is observed. The thermal decompositon of o-(o-methyl- β , β -dichloroethenyl)phenyldiazonium fluorophosphate (**5b**) in refluxing benzene (for 0.5 hr) gave a mixture⁷ of 1-chloro-1-fluoro-2-(o-chlorophenyl)propene-1 (**9a** and **9b**) and 1,1-dichloro-2-(o-fluorophenyl)propene-1 (**10**, 25.6%), 1-chloro-1-(o-chlorophenyl)-2-fluoropropene-1 (**11**,⁸ 24.5%), and 1,1-dichloro-2-(2-biphenyl)propene-1 (**12**, 46.5%)⁹ (Scheme II). In refluxing *n*-heptane, the decomposition of **5b** gives a mixture of **9** and **10** (45.6%)¹⁰ and **11** (34.2%).

In the reaction of 5b in benzene, two isomers (9a and 9b) of 1,1-chlorofluoro-2-(o-chlorophenyl)propene-1 were obtained. However, carrying out the reaction in refluxing *n*-heptane, only one isomer (9b) was obtained, and 12 was not found.

The formation of 9 and 11 shows the presence of 2chloro-3-methylbenzochlorophenium ion (4b) as the intermediate, since only ring opening of 4b can introduce chlorine into the ortho position of the phenyl ring. This result is quite different from that of the reaction of 4a. 10 and 12 arise from the incipient phenyl cation 13, which was generated not only by the loss of nitrogen of 5b, but also from 4b (equilibrium between 13 and 4b). If the phenyl cation 13 is generated from 5b it reacts with solvent benzene or fluoride ion to give the fluorinated product expected in the

Scheme II



Formation of Benzochlorophenium Ions

Schiemann reaction. The phenyl cation formed from 5a would also be expected to react in a similar fashion. However, the corresponding products 10 and 12 were not obtained in the reaction of 5. This means that the chlorophenium ion (4b) is relatively stable compared to the chlorophenium ion (4a), and has two ways to cleave, giving the phenyl cation 13 or vinyl cation 14. The vinyl cation 14 then reacts with fluoride anion to give 9a (trans) and 9b(cis). As the nucleophilicity of the hexafluorophosphate anion is low, the phenyl group of 14 can migrate to give the iomeric vinyl cation 15, which reacts with fluoride anion to give 11 (giving only one isomer). When *n*-heptane was used as the solvent the yields of these products (9, 10, 11) increase and only one isomer of 9b was obtained.

The differing behavior of 4b, giving in benzene transand cis-1-chloro-1-fluoro-2-(o-chlorophenyl)propene-1 (in a ratio of 1:3), whereas in n-heptane only the trans isomer is formed, can probably be explained by the effect of the solvent. In benzene (a better solvating agent than n-heptane) the vinyl cation intermediate is more stabilized through solvation than in n-heptane, and two isomers are formed. However, in *n*-heptane the vinyl cation is less stabilized (compared to benzene), and some participation between the chlorine atom and the open vinyl cation formed subsequently from the benzochlorophenium ion, is taking place. Therefore, only the trans isomer could be formed. As aryl migration occurs, a free (or near-free) vinyl cation should be formed, which is then quenched by fluoride ion. Of course, it should be kept in mind that since the reaction in benzene gives us the major product 12 (in 46.5% yield) formation of which liberates an equimolecular amount of HF-PF₅, geometric isomerism in 9 via protonation-rotation-deprotonation also is possible.

The behavior of studied benzochlorophenium ions is quite different from the previously studied benzoiodophenium ions (2). This is not only due to the differing behavior of the benzochlorophenium ion, but also to the low nucleophilicity of the hexafluorophosphate anion used in their preparation via the corresponding arenediazonium ions, which allows a longer lifetime of the cationic center.

Experimental Section

Melting points are uncorrected.

Column chromatography was carried out using Sargent-Welch grade 60-200 mesh silica gel; TLC was done on Merck precoated PLC plates (silica gel F-254, layer thickness 2 mm). The NMR spectra were recorded on a Varian A-56/60 spectrometer using Me₄Si and trichlorofluoromethane as external standards for proton and fluorine NMR spectra. The infrared spectra were determined on a Beckman IR-10 spectrometer.

 $o-(\alpha-Methyl-\beta,\beta-dichloroethenyl)$ nitrobenzene. Potassium tert-butoxide was freshly prepared for use. Potassium (4.0 g, 0.1 g-atom) was added to 100 ml of dry tert-butyl alcohol (freshly distilled over sodium) and stirred for 5 hr. After the potassium completely reacted with tert-butyl alcohol, excess alcohol was distilled off. In order to eliminate tert-butyl alcohol completely, n-heptane (300 ml) was added to the still viscous residue, and distilled as the azeotrope. Triphenylphosphine (26.2 g, 0.1 mol in ca. 300 ml of heptane) was added to the mixture at under 5°, and then chloroform (11.9 g, 0.1 mol) in 100 ml of *n*-heptane again below 5° to give a yellow-colored solution which subsequently, on a vacuum evaporator, was concentrated to about 200 ml. o-Nitroacetophenone (16.5 g, 0.1 mol) in 100 ml of benzene was added below 10° and stirred for 1 hr in the ice bath and subsequently at room temperature overnight. The resulting brown-colored suspension was filtered off to give a red-colored solution. The solvent was evaporated to give a viscous liquid, which was separated by column chromatography (on silica gel with benzene as solvent) to give o-(α methyl- β , β -dichloroethenyl)nitrobenzene (13.0 g, yield 56.0%): bp 110° (0.4 mmHg); NMR (CDCl₃) δ 2.70 (s, 3 H, -CH₃), 7.67-8.67 (m, 4 H, aromatic H).

Anal. Calcd for $C_9H_7Cl_2NO_2$: C, 46.58; H, 3.04; N, 6.04. Found: C, 46.19; H, 3.20; N, 6.29.

o-(α-Methyl-β,β-dichloroethenyl)aniline. o-(α-Methy-β,βdichloroethenyl)nitrobenzene (2.32 g, 0.01 mol) was mixed with 20 ml of acetone, 4 ml of water, and 1.0 g of ammonium chloride to give a homogeneous solution. Zinc powder (2.0 g) was added to the mixed solution below 55°, an additional 1.0 g of zinc powder was added, and the solution was refluxed for 30 min. After the reaction, the reaction mixture was filtered off to give a solution, which was evaporated off to give a yellow liquid. The resulting yellow liquid uid was extracted with ether, which was dried over anhydrous magnesium sulfate. The product was distilled to give o-(α-methylβ,β-dichloroethenyl)aniline (1.00 g, yield 50.0%): bp 90° (1.3 mmHg); NMR (CDCl₃) δ 2.67 (s, 3 H, -CH₃), 4.67 (s, 2 H, -NH₂), 7.07-7.80 (m, 4 H, aromatic H).

Anal. Calcd for C₉H₉Cl₂N: C, 53.49; H, 4.49; N, 6.93. Found: C, 53.20; H, 4.67; N, 6.71.

o-(α-Methyl-β,β-dichloroethenyl)phenyldiazonium Hexafluorophosphate. o- (α-Methyl-β,β-dichloroethenyl)aniline (0.530 g, 2.6 mmol) dissolved in 10 ml of acetonitrile was gradually added to the mixture of nitrosonium fluorophosphate (0.600 g, 3.4 mmol) and 15 ml of carbon tetrachloride below 0°, giving a brown-colored solution. After the reaction 2 ml of water was added to the reaction mixture, and the solvent was evaporated off to give a solid, which was washed with ether to give o-(α-methyl-β,β-dichlorethenyl)phenyldiazonium fluorophosphate (0.270 g, yield 28.4%): mp 99-100° dec; NMR (DMSO-d₆) δ 2.70 (s, 3 H, -CH₃), 8.33-9.33 (m, 4 H. aromatic H).

Anal. Calcd for $C_9H_7Cl_2F_6N_2P$: C, 30.11; H, 1.97; N, 7.80. Found: C, 30.11; H, 1.90; N, 7.73.

 $o-(\alpha-Methyl-\beta,\beta-dichloroethenyl)$ phenyl-Reaction of diazonium Fluorophosphate. $o - (\alpha - Methyl - \beta, \beta - dichloroethenyl)$ phenyldiazonium fluorophosphate (0.500 g, 1.39 mmol) was refluxed in 10 ml of benzene for 0.5 hr to give a brown-colored oil. It was separated by TLC to give a mixture of 1-chloro-1-fluoro-2-(ochlorophenyl)propene-1 (trans and cis isomers) and 1,1-dichloro-2-(o-fluorophenyl)propene-1 (73 mg, yield 25,6%), 1-chloro-1-(ochlorophenyl)-2-fluoropropene-1 (70 mg, 24.5%), and 1,1-dichloro-2-(2-biphenyl)propene-1 (170 mg, 46.5%). The mixture of 9a, 9b, and 10 could not be isolated. Their physical, spectral, and analytical data are as follows: bp 80° (1.0 mmHg); 9a (trans), δ 2.71 (d, J = 4.5 Hz), $\phi_{\rm F}$ 100.9 (q, J = 4.5 Hz); 9b (cis), δ 2.45 (d, J = 3.75 Hz), $\phi_{\rm F}$ 82.3 (q, J = 3.75 Hz); 10, δ 2.64, $\phi_{\rm F}$ 113.9 (m). The aromatic protons appear at δ 7.54–7.94. The ratio of the mixture was as follows: 9a:9b:10, 1:3:2.

Anal. Calcd for C₉H₇Cl₂F: C, 52.72; H, 3.64; F, 9.27. Found: C, 52.66; H, 3.33; F, 10.28.

Compound 11: bp 90° (2.0 mmHg); NMR (CDCl₃) δ 2.40 (d, J = 17.0 Hz, 3 H, -CH₃), 7.90 (s, 4 H); ϕ F 92.1 (q, J = 17.0 Hz).

Anal. Calcd for C₉H₇Cl₂F: C, 52.72; H, 3.44; Cl, 34.58. Found: C, 52.80; H, 3.63; Cl, 34.29.

Compound 12: mp 78-79° (*n*-hexane); NMR (CDCl₃) δ 2.40 (s, 3 H, -CH₃), 7.94 (s, 9 H, aromatic proton); mass spectrum (obtained on a Japan Electron Optics JMS-D100 spectrometermeter at the Tokyo Institute of Technology) *m/e* (rel intensity) 266 (3, M⁺ + 4), 264 (20, M⁺ + 2), 262 (32, M⁺), 229 (7), 227 (25), 212 (14), 193 (18), 192 (100), 191 (64), 190 (16), 189 (39), 176 (16), 165 (34), 164 (14), 152 (11), 151 (18), 150 (14), 149 (34), 139 (9), 133 (18), 125 (14), 116 (9), 115 (55), 91 (23), 89 (20), 87 (18), 77 (23), 75 (25), 63 (34), 51 (45), 50 (25); uv spectrum λ_{max} (EtOH) 240 nm (obtained on a Hitachi EPS-3T spectrometer).

Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.64; H, 4.60; Cl, 26.94. Found: C, 68.26; H, 4.49; Cl, 26.79.

The ratio of $M^+ + 4:M^+ + 2:M^+ = 1:6:9$ shows the presence of the two chlorine atoms in compound 12. The fragmentation of compound 12 is as follows.



The loss of two chlorines from compound 12 is very typical to the geminal dichloride compound. The λ_{max} of compound 12 is very similar to that of styrene ($\pi \rightarrow \pi^*$ 244 nm). In the case of stilbene the λ_{max} appear at 280 (cis isomer) and 295.5 nm (trans isomer).

Therefore, the structure is not that of a stilbene, but of a styrene derivative. That is, the phenyl cation formed from the diazonium salt reacts with benzene to give the styrene derivative (compound



12). The reaction of cyclic chloronium ion with benzene should not occur.

Reaction of 5b in *n***-Heptane.** o-(α -Methyl- β , β -dichloroethenyl)phenyldiazonium fluorophosphate (0.77 g, 2.14 mmol) was refluxed in 30 ml of n-heptane for 0.5 hr to give a pale yellow solution, which was separated in a similar manner to that described above to give a mixture of 9b and 10 (200 g, yield 45.6%) and 11 (150 mg, yield 34.2%). The ratio of 9b and 10 is 2:3.

 $o-(\beta,\beta-Dichloroethenyl)$ nitrobenzene. Triphenylphosphine (26.2 g, 0.1 mol) was added to the potassium tert-butoxide made by the same way as described above; chloroform (11.9 g, 0.1 mol) in 100 ml of *n*-heptane was added to the mixed solution below 5° , and o-nitrobenzaldehyde (15.1 g, 0.1 mol) in 100 ml of benzene was added to the resulting brown-colored suspension below 10° and it was treated in the same way to give $o - (\beta, \beta$ -dichloroethenyl)nitrobenzene (8.0 g, yield 36.7%): mp 49-50°; NMR (CCl₄) δ 7.25 (s, 1 H, olefinic H), 7.63 (m, 3 H, aromatic H), 8.10 (m, 1 H, aromatic H).

Anal. Calcd for C₈H₅Cl₂NO₂: C, 44.07; H, 2.31; N, 6.42; Cl, 32.25. Found: C, 44.18; H, 2.35; N, 6.36; Cl, 32.70.

 $o-(\beta,\beta-\text{Dichloroethenyl})$ aniline. $o-(\beta,\beta-\text{Dichloroethenyl})$ nitrobenzene (2.20 g, 0.01 mol) was mixed with 20 ml of acetone, 4 ml of water, and 1.0 g of ammonium chloride to give a homogeneous solution. Zinc powder (2.0 g) was added to the mixed solution below 55°, an additional 1.0 g of zinc powder was added, and the solution was refluxed for 30 min. After the reaction, the reaction mixture was treated in the same way as the case of o-(α -methyl- β , β -dichloroethenyl)aniline to give $o \cdot (\beta, \beta$ -dichloroethenyl)aniline (1.800 g, yield 95.8%): bp 85–90° (0.03 mmHg); NMR (CCl₄) δ 4.02 (s, 2 H, amine H), 7.16 (s, 1 H, olefinic H), 7.00–7.83 (m, 4 H, aromatic H). Anal. Calcd for C₈H₇Cl₂N: C, 51.09; H, 3.75; N, 7.45; Cl, 37.43.

Found: C, 50.91; H, 3.80; N, 7.55; Cl, 37.91.

o-(β , β -Dichloroethenyl)phenyldiazonium Hexafluorophosphate. $o - (\beta, \beta$ -Dichloroethenyl)aniline (1.46 g, 7.8 mmol) dissolved in 10 ml of acetonitrile was gradually added to the mixture of nitrosonium fluorophosphate (1.40 g, 8.0 mmol) and 15 ml of carbon tetrachloride below 0°, giving a brown-colored solution. After the reaction 2 ml of water was added to the reaction mixture and the solvent was evaporated off to give a solid, which was washed with ether to give $o - (\beta,\beta$ -dichloroethenyl)phenyldiazonium fluorophosphate (1.200 g, yield 44.8%): mp 117-120° dec; NMR (acetone-d₆) δ 7.60 (s, 1 H, olefinic H), 8.30 (m, 2 H, aromatic H), 8.70 (m, 2 H, aromatic H).

Anal. Calcd for C8H5Cl2F6N2P: C, 27.85; H, 1.46; N, 8.12; Cl, 20.29. Found: C, 28.09; H, 1.50; N, 8.15; Cl, 20.41

Reaction of $o-(\beta,\beta-Dichloroethenyl)$ phenyldiazonium Fluorophosphate. o-(2,2-Dichloroethenyl)phenyldiazonium fluorophosphate (0.100 g, 0.29 mmol) was refluxed in 10 ml of benzene for 0.5 hr, giving a brown-colord solution, which was distilled to give $o - (\beta$ -chloroethinyl)chlorobenzene (0.049 g, yield 99.0%): bp 38° (0.13 mmHg); NMR (CCl₄) δ 7.40-7.90 (m, aromatic H); ir (NaCl) 2220 cm⁻¹ (-C=C-).

Anal. Calcd for C₈H₄Cl₂: C, 56.18; H, 2.35; Cl, 41.17. Found: C, 55.97; H, 3.19; Cl, 40.98.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.-5a, 54143-10-1; 5b, 54142-99-3; 6a, 51991-50-5; 6b, 54143-00-9; 7a, 54143-01-0; 7b, 54143-02-1; 8, 54143-03-2; 9a, 54143-04-3; 9b, 54143-05-4; 10, 54143-06-5; 11, 54143-07-6; 12, 54143-08-7; o-nitroacetophenone, 577-59-3; triphenylphosphonium dichloromethylide, 6779-08-4; nitrosonium fluorophosphate, 16921-91-8; o-nitrobenzaldehyde, 552-89-6.

References and Notes

- (1) (a) Part XIII: G. A. Olah and J. L. Grant, J. Am. Chem. Soc., in press. (b) The naming dibenzoiodolium, -bromolium, and -chlorolium ions was used in the past. As the heteroaromatic ring system is analogous to thiophene, naming according to "halophenium ions" seems proper. (c) Postdoctoral Research Associate, 1973-1974, from the Tokyo Institute of Technology, Tokyo, Japan. (2) F. M. Beringer and L. L. Chang, *J. Org. Chem.*, **36**, 4055 (1971), and
- references cited therein.
- (3) F. M. Beringer, P. Ganis, G. Avitabile, and H. Jaffe, J. Org. Chem., 37, 879 (1972).
- 879 (1972). I. L. Reich and H. J. Reich, J. Am. Chem. Soc., **96**, 2654 (1974). **Compound 5a:** ir (KBr) 2280 (−N==N⁺) and 865–830 cm⁻¹ (PF₆⁻); NMR (acetone-d₆) 7.60 (s, 1 H), 8.30 (m, 2 H), and 8.70 ppm (m, 2 H). Anal. Calcd for C₈H₅Cl₂F₆N₂P: C, 27.85; H, 1.46; N, 8.12. Found: C, 28.09; H, 1.50; N, 8.15. **Compound 5b:** ir (KBr) 2280 (−N==N⁺) and 800–900 cm⁻¹ (PF₆⁻); NMR (DMSO-d₆) 2.70 (s, 3 H), and 9.33–8.33 ppm (m, 4 H). Anal. Calcd for C₉H₇Cl₂F₆N₂P: C, 30.11; H, 1.97; N, 7.80. Found: C, 30.11; H, 1.90; N, 7.80. All other new compounds were fully character-ized by their spectral and analytical properties. (5)ized by their spectral and analytical properties. **Compound 8:** bp 38° (0.13 mm); ir 2220 cm⁻¹ (C=C); NMR (CDCl₃) δ
- 7.40-7.90 ppm (m). Anal. Calcd for C₈H₄Cl₂: C, 56.18; H, 2.35. Found: 55.97; H, 3.19.
- The mixture of **9a**, **9b**, and **10** could not be separated by preparative TLC (silica gel), bp 80° (1.0 mm). By the coupling constants of fluorine, isomer **9a** is probably the trans form and isomer **9b** is the cis isomer: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1968, p 912. The NMR spectra of the methyl proton and fluorine are as follows: **9a** (trans), $\delta 2.71$ (d, J = 4.5 Hz), $\phi_F 100.9$ ppm (q, J = 4.5 Hz); **9b** (cis), $\delta 2.45$ (d, J = 3.75 Hz), $\phi_F 82.3$ ppm (q, J = 3.75 Hz); **10**, $\delta 2.64$ (s), $\phi_F 113.9$ ppm (m). Their aromatic protons appear at $\delta 7.54$ – 7.94 ppm. The ratio of the mixture is as follows: **9a:9b:10**, 1:3:2. Anal. Calcd for C₉H₇Cl₂F: C, 52.72; H, 3.64; Cl, 34.58; F, 9.27. Found: C, 52.66; H, 3.33; Cl, 34.28; F, 9.57.
- **Compound 11:** bp 90° (2.0 mm); NMR (CDCl₃) δ 2.40 (d, J = 17.0 Hz, 3 H), 7.90 ppm (s, 4 H), ϕ_F 92.1 ppm (q, J = 17.0 Hz). Anal. Calcd for $C_9H_7Cl_2F$; C, 52.72; H, 3.44; Cl, 34.58; F, 9.27. Found: C, 53.05; H,
- C₉H₇Cl₂F: 0, 52.72, n, 5.44, 0, 64.66, 7, 51.27, 74.66, 7, 51.27, 74.67, 75.75,
- (10) The ratio of the mixture is as follows: 9b:10, 2:3