

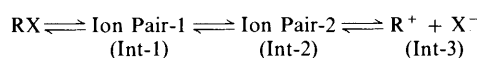
## Number and Structure of Solvolysis Intermediates. Part 1. A Comparison of Nucleophilic Reactions on *in situ* Generated Carbocations with Solvolysis Reactions for 2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl Cation

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2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl cation has been generated by treatment of the corresponding chloride with AgSbF<sub>6</sub> in SO<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> (20% CD<sub>2</sub>Cl<sub>2</sub>) at -98 °C and its <sup>13</sup>C NMR spectrum observed. The reactions of the generated carbocation with methanol or phenol give products with a rearranged carbon atom skeleton and non-rearranged products with complete racemization, as expected for a typical carbocation reaction, whereas the solvolysis of the corresponding *p*-nitrobenzoate in phenol affords exclusively the non-rearranged products with partial retention of configuration. Such distinctions between generated carbocation reactions and the solvolysis reactions indicate that no dissociated (free) carbocation intermediate intervenes even in this solvolysis system, *i.e.*, it is one of a few systems which have been hitherto confirmed to proceed *via* multiple intermediate stages.

Although it has already been explained that the S<sub>N</sub>1 solvolysis proceeds *via* multiple intermediate stages (Scheme 1),<sup>1,2</sup> *i.e.*, two kinds of ion-pair intermediates (Int-1 and Int-2)‡ and the dissociated (free) carbocation intermediate, we can find no example involving one thoroughly studied system in which all three intermediates exist as solvolysis intermediates. While, in contrast to the general explanation,<sup>1,2</sup> many examples of solvolyses are found to proceed *via* a single ion-pair intermediate stage,<sup>5</sup> only a few examples of solvolysis provide experimental evidence for the existence of multiple solvolysis intermediate stages.§<sup>3a,5-8</sup> Such examples include the phenolyses of the 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl<sup>3a,5</sup> and 1-(*p*-methoxyphenyl)ethyl systems<sup>5,6</sup> and the acetolyses of the 2-(*p*-methoxyphenyl)-1-methylpropyl system.¶<sup>5,7,8</sup> However, no information is available to distinguish directly the intermediacy of the dissociated carbocation intermediate (the third solvolysis intermediate) in solvolysis systems with multiple intermediate stages.||<sup>5</sup>



Scheme 1

A comparison of the nucleophilic reactions on enforcedly-generated carbocations with solvolysis reactions might contribute to an elucidation of the intermediacy of the dissociated carbocation intermediate in the solvolysis system,

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‡ Although Int-1 (the first ion-pair intermediate) and Int-2 signify a contact (tight or intimate) and a solvent-separated ion-pair intermediate, respectively, in the Winstein ion-pair mechanism,<sup>1,2</sup> various other types of model have been experimentally found<sup>3</sup> or proposed<sup>4</sup> for the structure of ion-pair intermediates, especially for that of Int-2.

§ For solvolyses which contained single and multiple solvolysis intermediate stages, 21 and three examples were determined, respectively.<sup>5</sup> Recently, an additional seven examples for the former have been found in the acetolyses.<sup>9</sup>

¶ For this system, the intermediacy of the dissociated carbocation intermediate was refuted on the grounds that no common ion rate depression was observed.<sup>2,10</sup>

though the reaction conditions are not identical in each case. Many examples have been reported for the generation and the direct spectrometric observation of carbocation species,<sup>12</sup> whereas only a few reports can be found for the reactions of a dissociated carbocation with nucleophiles<sup>13</sup> and for a comparison of solvolyses with other liberated carbocation reactions.<sup>14</sup>

In this paper, we wish to report an examination of the possibility of the involvement of the dissociated (free) carbocation intermediate in the solvolysis of the 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl system, which has a chiral reaction centre and no neighbouring group participation and which tends to undergo a rearrangement of the carbon atom skeleton after ionization.<sup>15,16</sup> We concentrated on a comparison of the rearrangement and the stereochemistry for the solvolysis products with those for the reaction products of the carbocation, which was generated by a well-known method<sup>12</sup> using phenol or methanol.

### Results and Discussion

**Generation and <sup>13</sup>C NMR Spectrum of the Carbocation.**—2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl chloride (RCl) was mixed with AgSbF<sub>6</sub><sup>12,17</sup> (1.5 equiv.) in SO<sub>2</sub>-CH<sub>2</sub>Cl<sub>2</sub> (containing 20% CD<sub>2</sub>Cl<sub>2</sub>) (1:1, v/v) maintained at -98 °C in an NMR sample tube to yield a red solution. The <sup>13</sup>C NMR spectrum of the solution suggested that the product was a mixture of two kinds of carbocation, 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl cation (R<sup>+</sup>) and 1,2-dimethyl-1-(*p*-methoxyphenyl)propyl cation (R'<sup>+</sup>) as a major and a minor species, respectively, under conditions employed (Table 1). Each signal of the spectrum was assigned by using the spectral data for *p*-methoxyphenylmethyl cations,<sup>18</sup> aryl- and cyclopropylmethyl cations with methyl substituents on the 1-position<sup>18,19</sup> and *p*-methoxybenzoyl[bis(*p*-methoxyphenyl)]methyl cation.<sup>20</sup>

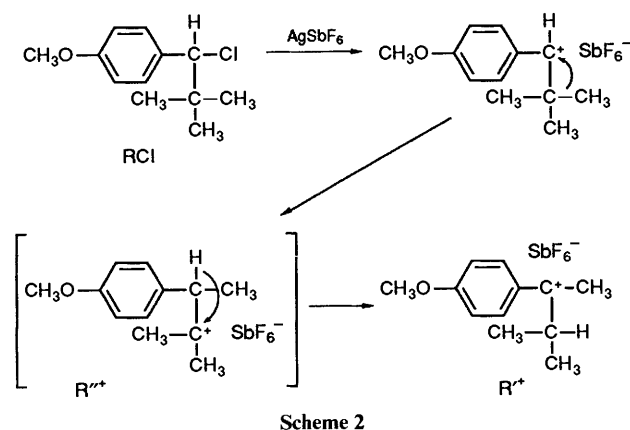
This cation rearrangement most probably occurred *via* a

|| Although it has been proposed that the observation of a common ion rate depression provides strong evidence for the intermediacy of the dissociated carbocation intermediate in the S<sub>N</sub>1 solvolysis,<sup>10</sup> a novel example of the rate depression arising at the ion-pair intermediate stage has been found in the phenolysis of the 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl system.<sup>11</sup>

**Table 1**  $^{13}\text{C}$  NMR spectral data for the carbocation species generated from 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (RCl) with  $\text{AgSbF}_6$  in  $\text{SO}_2\text{-CH}_2\text{Cl}_2$  (20%  $\text{CD}_2\text{Cl}_2$ , 1:1 by vol.) at  $-98^\circ\text{C}$  and related compounds<sup>a</sup>

| Compound                   | Formula | $-\text{C}^+-$ | $\text{CH}_3\text{O}-$      | $\text{CH}_3-\text{C}$   | $-\text{C}-\text{CH}_3$ | $-\text{CH}-$ | $\text{C}=\text{C}$          | Ar   |
|----------------------------|---------|----------------|-----------------------------|--|-------------------------|---------------|------------------------------|--|
| $\text{R}^+$               |         | 204.4 (d, 6)   | 59.2 (q, 1)                 | 28.0 (q, 8)  | 42.3 (s, 7)             |               |                              | 182.0 (s, 2)<br>115.0 (d, 3)<br>142.6 (d, 4)<br>130.8 (s, 5) |
| $\text{R}'^+$              |         | 225.5 (s, 6)   | 58.1 (q, 1)                 | 20.4 (q, 8)<br>20.7 (q, 8)   |                         | 36.8 (d, 7)   |                              | 180.1 (s, 2)<br>117.9 (d, 3)<br>143.8 (d, 4)<br>130.8 (s, 5) |
| RCl                        |         |                | 53.9 (q, 1)                 | 26.8 (q, 8)  | 37.1 (s, 7)             | 74.2 (d, 6)   |                              | 158.9 (s, 2)<br>112.8 (d, 3)<br>129.6 (d, 4)<br>131.7 (s, 5) |
| $\text{R}'\text{OMe}$      |         |                | 53.2 (q, 1)<br>51.6 (q, 10) | 16.6 (q, 8) <sup>b</sup><br>15.9 (q, 9) <sup>b</sup>                             | 82.4 (s, 6)             | 38.0 (d, 7)   |                              | 156.0 (s, 2)<br>112.0 (d, 3)<br>127.0 (d, 4)<br>134.4 (s, 5) |
| AnMeC=<br>$\text{CMe}_2^c$ |         |                | 55.1 (q, 1)                 | 20.0 (q, 8) <sup>d</sup><br>20.5 (q, 8) <sup>d</sup><br>20.8 (q, 9) <sup>d</sup> |                         |               | 129.4 (s, 6)<br>126.8 (s, 7) | 157.4 (s, 2)<br>113.2 (d, 3)<br>129.3 (d, 4)<br>137.5 (s, 5) |

<sup>a</sup> 25 MHz;  $\delta$  values calculated based on  $\delta = 53.1$  ppm for  $\text{CH}_2\text{Cl}_2$  unless otherwise noted. <sup>b</sup> Interchangeable. <sup>c</sup> In  $\text{CDCl}_3$  at  $24^\circ\text{C}$ ;  $\delta$  values calculated based on  $\delta = 77.0$  ppm for  $\text{CDCl}_3$ . <sup>d</sup> Interchangeable.



Wagner-Meerwein rearrangement<sup>15,16</sup> of  $\text{R}^+$  to a rearranged cation  $\text{R}'^+$ , which successively underwent a rapid 1,2-hydride shift<sup>21</sup> to form cation  $\text{R}'^+$  (Scheme 2). The rate of rearrangement of the cation  $\text{R}^+$  to  $\text{R}'^+$  can be estimated to be  $1.1 \times 10^{-3} \text{ s}^{-1}$  at  $-98^\circ\text{C}$  using the same conditions as for the NMR spectroscopic measurements. Above  $-78^\circ\text{C}$ , the signals corresponding to the cation  $\text{R}^+$  disappeared and only those for the cation  $\text{R}'^+$  were observed. The intermediary cation  $\text{R}'^+$  was not detected. The rearranged cation  $\text{R}'^+$  was stable for more than one week at  $-78^\circ\text{C}$  and then changed to 2-(*p*-methoxyphenyl)-3-methylbut-2-ene and its polymers at ambient temperature in the solution.

**The Reaction of the Carbocation with Methanol.**—To the red carbocation solution, generated from RCl and  $\text{AgSbF}_6$  as mentioned above, was added methanol (12 equiv. to RCl), in an NMR sample tube at  $-98^\circ\text{C}$ , yielding a  $^{13}\text{C}$  NMR spectrum corresponding to 1,2-dimethyl-1-(*p*-methoxyphenyl)propyl methyl ether ( $\text{R}'\text{OMe}$ ; Table 1). It is reasonable to assume that the aralkyl methyl ether is derived from the rearranged cation  $\text{R}'^+$  (Scheme 2). When this reaction mixture was brought to ambient temperature and then worked-up with water, the

aralkyl methyl ether was not obtained but rather 2-(*p*-methoxyphenyl)-3-methylbut-2-ene (Table 1; 27% yield) and its polymeric products.

On the other hand, the addition of  $\text{AgSbF}_6$  to a solution of RCl in  $\text{SO}_2\text{-CH}_2\text{Cl}_2$  (20%  $\text{CD}_2\text{Cl}_2$ ) (1:1, v/v) containing methanol (3 equiv. to RCl) and 2,6-di-*tert*-butyl-4-methylpyridine (the hindered pyridine; 1.2 equiv.)\* at  $-72^\circ\text{C}$  produced  $\text{R}'\text{OMe}$ <sup>3a</sup> and a trace amount of the rearranged products. Without  $\text{AgSbF}_6$ , RCl did not react with methanol under identical conditions. Hence the products formed arose from the reaction of the generated carbocation species. Apparently, the methyl ether is cleaved to alkene by  $\text{HSbF}_6$  in the absence of the hindered pyridine.

**The Reaction of the Carbocation with Phenol.**— $\text{AgSbF}_6$  was added to a solution of RCl in  $\text{SO}_2\text{-CH}_2\text{Cl}_2$  (20%  $\text{CD}_2\text{Cl}_2$ ) (1:1, v/v) containing phenol (3 equiv. to RCl;  $0.75 \text{ mol dm}^{-3}$ , ca. 6 vol%) and the hindered pyridine\* (1.2 equiv.) in an NMR sample tube at  $-78^\circ\text{C}$ . After being kept at  $-63^\circ\text{C}$  for 1 h, the reaction mixture was allowed to warm to room temperature then washed with water to produce the rearranged polymeric products (33.0%) in addition to ordinary non-rearranged phenolysis products,<sup>3a</sup> i.e.,  $\text{ROPh}$ , *o*- and *p*- $\text{RC}_6\text{H}_4\text{OH}$  (94.1:0.1:5.8; 67.0%; Table 2). Each rearranged product contained an isopropyl group and was estimated to come from the rearranged cation  $\text{R}'^+$  as described above (Scheme 2). However, the substitution products from  $\text{R}'^+$  were not detected.

The reaction of the carbocation generated from the optically active chloride and  $\text{AgSbF}_6$  in  $\text{SO}_2\text{-CH}_2\text{Cl}_2$  containing phenol and the hindered pyridine\* at  $-70^\circ\text{C}$  produced the completely racemized aralkyl phenyl ether with a non-rearranged carbon atom skeleton (Table 3).

In the absence of  $\text{AgSbF}_6$ , RCl did not react with phenol at all under the reaction conditions. Although the carbocation species

\* The hindered pyridine was added in order to neutralize the liberated acid, which caused cleavage of the methyl ether to alkenes or the rearrangement of the aralkyl phenyl ether to the aralkylphenols.<sup>3,22</sup>

**Table 2** Product distribution for the reaction of carbocation ( $R^+$ ) generated from 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (RCl) and  $AgSbF_6$  with phenol in  $SO_2-CH_2Cl_2$  (20%  $CD_2Cl_2$ ) and the solvolysis of the corresponding *p*-nitrobenzoate (ROPNB) in phenol

| Substrate |                                | Solvent                    | Product distribution (%) <sup>c</sup> |  |                   |                 |      |   |   |                                     |
|-----------|--------------------------------|----------------------------|---------------------------------------|--|-------------------|-----------------|------|---|---|-------------------------------------|
| Nature    | Conc./<br>mol dm <sup>-3</sup> | Composition                | [PhOH]/<br>mol dm <sup>-3</sup>       | [HPy] <sup>a</sup> /<br>mol dm <sup>-3</sup> | T/°C <sup>b</sup> | t/h             | ROPh | <i>o</i> -RC <sub>6</sub> H <sub>4</sub> OH | <i>p</i> -RC <sub>6</sub> H <sub>4</sub> OH | Rearranged<br>polymeric<br>products |
| $R^+$     | 0.25 <sup>d</sup>              | $SO_2-CH_2Cl_2$ e-<br>PhOH | 0.75                                  | 0.30   | -78               | 1               | 63.0 | 0.07  | 3.9   | 33.0                                |
|           | 0.25 <sup>d</sup>              | $SO_2-CH_2Cl_2$ e-<br>PhOH | 1.5                                   | 0.30   | -78               | 1               | 65.4 | 0.09  | 4.5   | 30.0                                |
| ROPNB     | 0.100                          | PhOH                       | 11.4                                  | 0.105  | 75                | 22 <sup>c</sup> | 88.5 | 0.8   | 10.7  | 0.00                                |

<sup>a</sup> HPy: 2,6-di-*tert*-butyl-4-methylpyridine (see the footnote of the text). <sup>b</sup> Accurate to within  $\pm 1$  °C for the carbocation reactions and  $\pm 0.1$  °C for the solvolysis reaction. <sup>c</sup> Determined by GLPC; (ROPh + *o*-RC<sub>6</sub>H<sub>4</sub>OH + *p*-RC<sub>6</sub>H<sub>4</sub>OH + rearranged products) % = 100%. <sup>d</sup> The concentration of RCl from which  $R^+$  was synthesized. <sup>e</sup> 1:1 v/v, containing 20%  $CD_2Cl_2$ . <sup>f</sup> Eleven half-lives.

**Table 3** The stereochemical course for the non-rearranged products of the reaction of carbocation ( $R^+$ ) generated from 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (RCl) and  $AgSbF_6$  with phenol in  $SO_2-CH_2Cl_2$  and the solvolysis of the corresponding *p*-nitrobenzoate (ROPNB) in phenol

| Substrate<br>(Conc./<br>mol dm <sup>-3</sup> ) | Solvent   | [HPy] <sup>a</sup> /<br>mol dm <sup>-3</sup> | T/°C <sup>b</sup> | t/h             | Net stereochemical course (%) <sup>c</sup> {[ $\alpha$ ] <sub>D</sub> <sup>d</sup> } |   |   |
|--|---|--|-------------------|-----------------|--|---|---|
|  |   |  |                   |                 | ROPh   | <i>o</i> -RC <sub>6</sub> H <sub>4</sub> OH | <i>p</i> -RC <sub>6</sub> H <sub>4</sub> OH |
| $R^+$ e<br>(0.25 <sup>f</sup> )                | $SO_2-CH_2Cl_2$ (1:1,<br>v/v)-PhOH <sup>g</sup> | 0.30   | -70               | 2               | 100.0 Rac. <sup>j</sup><br>( $\pm 0.002$ )<br>{0.000<br>( $\pm 0.002$ )}             | —   | —   |
| ROPNB <sup>h</sup><br>(0.0973)                 | PhOH  | 0.105  | 75                | 22 <sup>i</sup> | 1.09 Ret. <sup>k</sup><br>( $\pm 0.13$ )   | 20.4 Ret<br>( $\pm 5.1$ )                   | 3.57 Ret<br>( $\pm 0.29$ )                  |

<sup>a</sup> HPy: 2,6-di-*tert*-butyl-4-methylpyridine (see the footnote in the text). <sup>b</sup> Accurate to within  $\pm 1$  °C for the carbocation reaction and  $\pm 0.1$  °C for the solvolysis reaction. <sup>c</sup> Calculated on the basis of the optical purity of the starting RCl, from which  $R^+$  was synthesized: the maximum specific rotations for RCl and ROPh are taken to be  $\geq 68.4^\circ$  ( $\pm 0.2^\circ$ ) and  $45.0^\circ$  ( $\pm 0.2^\circ$ ), respectively [cited from ref. 3(a)]. <sup>d</sup> In  $CHCl_3$ . <sup>e</sup> Synthesized *in situ* from (*R*)-(+)-RCl, {[ $\alpha$ ]<sub>D</sub><sup>20</sup> + 19.45  $\pm$  0.03 (*c* 6.38 in  $CHCl_3$ )}. <sup>f</sup> The concentration of RCl from which  $R^+$  was synthesized. <sup>g</sup> 3 equiv. (0.75 mol dm<sup>-3</sup>) to RCl. <sup>h</sup> Cited from ref. 3(a). <sup>i</sup> Eleven half-lives. <sup>j</sup> Racemic. <sup>k</sup> Retention.

was not observed in the presence of phenol by NMR spectroscopy, the generation of the carbocation species was confirmed by the occurrence of the reaction with the nucleophile.

*The Solvolysis Reaction of the Corresponding p-Nitrobenzoate in Phenol.*—Racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) was solvolyzed in phenol in the presence of the hindered pyridine\* at 75 °C under identical conditions as those employed in the previous work, with the exception of added base.<sup>3a</sup> The product distribution was determined, especially for the rearranged products, by means of both isolation and GLPC methods. Solvolysis produced only the ordinary phenolysis products,<sup>3a</sup> *i.e.*, a major amount of ROPh, a trace amount of *o*-RC<sub>6</sub>H<sub>4</sub>OH, and a small amount of *p*-RC<sub>6</sub>H<sub>4</sub>OH (Table 2). No product containing a rearranged carbon atom skeleton was detected, similar to the phenolysis of ROPNB in the presence or the absence of the other bases,<sup>3a</sup> indicating little  $\sigma$ -participation<sup>15</sup> by a methyl group in the neopentyl moiety in the solvolysis medium. However, some other solvolyses of neopentyl systems proceed with rearrangement to yield substitution and elimination products from the pentyl cation species.<sup>16,17</sup> The solvolyses of RCl in 2,2,2-trifluoroethanol (TFE)<sup>23</sup> and 2,2-dimethyl-1-phenylpropyl systems in acetic acid<sup>16</sup> and in phenol<sup>24</sup> also produce small amounts of rearranged products other than the usual non-rearranged products.

All the products of the solvolysis reaction of optically active ROPNB in phenol have a partially retained configuration

(Table 3).<sup>3a</sup> As regards the stereochemical course of the other solvolyses of 1-aryl-2,2-dimethylpropyl systems containing a neopentyl group, the competing solvolysis of ROPNB in a PhOH-MeOH solvent<sup>3a</sup> and the acetolyses of 2,2-dimethyl-1-phenylpropyl systems<sup>16</sup> proceed with partial inversion, whereas RCl is solvolyzed in 80% aqueous ethanol with partial retention.<sup>25</sup> This stereochemical outcome suggests that, for the product-forming ion-pair intermediates (Int-1 or Int-2), which are generated from these substrates with a neopentyl group, a nucleophile can attack both from the front and the rear side of the solvolysis intermediate depending on the reaction conditions.

*The Carbocation Reactions and the Solvolysis Reactions.*—The following distinct differences are found when comparing generated carbocation reactions with solvolysis reactions.

(a) The rearranged products were produced by the generated carbocation reactions. On the other hand, no rearranged products were detected in the solvolysis reaction of ROPNB in phenol.

(b) The generated carbocation reaction afforded the non-rearranged product with complete racemization, whereas all the non-rearranged products which were obtained in the solvolysis of ROPNB in phenol took place not with complete racemization but with partial retention of configuration (Table 2).<sup>3a</sup>

The phenolysis of ROPNB was determined to proceed *via* multiple ('virtually' two) solvolysis intermediates by the  $k_p-k_t$  pattern analysis method.<sup>3a,5</sup> However, no definitive description could be provided in the previous papers<sup>3a,5</sup> for the further dissociation of Int-2 into a dissociated carbocation intermediate. Although the reaction conditions for the generated carbocation

\* See footnote, p. 102.

reactions and the solvolysis reactions are different from each other, a comparison of both reactions can shed light on the structure of the product-forming intermediate in the solvolysis of ROPNB in phenol as follows.

The rearranged products, which were produced by the generated carbocation reactions, were not detected in the solvolysis of ROPNB in phenol.<sup>3a</sup> On the other hand, the solvolyses of RCl in TFE<sup>23</sup> and 2,2-dimethyl-1-phenylpropyl systems in acetic acid<sup>16</sup> and in phenol<sup>24</sup> produce small amounts of rearranged product in a manner similar to the other solvolyses of neopentyl systems.<sup>15,16</sup> The phenolysis of the 2,2-dimethyl-1-phenylpropyl system proceeds through a less stable ion-pair intermediate stage,\* than the intermediate stages in the phenolysis of ROPNB,<sup>5</sup> showing that the rearrangement in solvolysis could occur at a stage of formation of the ion-pair intermediate other than that of the dissociated carbocation intermediate. To summarize, the rearrangement can occur in these cases: (a) solvolysis in a low nucleophilic solvent such as TFE, (b) solvolysis of a substrate which gives a relatively unstable intermediate and (c) when a dissociated carbocation is involved. The fact that no rearrangement was observed in the solvolysis of ROPNB in phenol indicates most probably that no intervention of a dissociated carbocation intermediate in the solvolysis system takes place. The difficulty of rearrangement may be attributed to the structure of the solvolysis ion-pair intermediate with high stability, *i.e.*, the rear-side shielded ion-pair intermediate.<sup>3a</sup>

In conclusion, it is probable that no dissociated carbocation intermediate intervenes, even in the solvolysis of ROPNB in phenol, one of a few systems which have been confirmed to proceed *via* multiple solvolysis intermediate stages.

## Experimental

<sup>13</sup>C and <sup>1</sup>H NMR spectra were taken using JEOL JNM FX-100 25 MHz and FX-90Q 90 MHz Fourier transform instruments, respectively. IR spectra were recorded with a Hitachi model 215 spectrophotometer. Optical rotations were measured with a JASCO model DIP-SL polarimeter. GLPC was performed with a Hitachi model 163 instrument. MPLC was done with a Chemco chromatograph system composed of a FMI model RP-SY-2 pump and a Merck silica gel 60 column. M.p.s were measured on a Yamato model MP-21 apparatus. Solvolysis products were identified by comparison of their IR, <sup>13</sup>C and <sup>1</sup>H NMR spectra, and chromatographic data with those of authentic samples.<sup>3a</sup>

**Materials.**—2,6-Di-*tert*-butyl-4-methylpyridine was prepared by a known method.<sup>26</sup> 2,2-Dimethyl-1-(*p*-methoxyphenyl)propan-1-ol was synthesized and resolved in the manner previously reported.<sup>3a</sup> Optically active and racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chlorides were prepared by the usual method.<sup>3a</sup> Sulfur dioxide was prepared by the decomposition of sodium hydrogen sulfite by sulfuric acid and dried over P<sub>2</sub>O<sub>5</sub>. All other organic reagents were analytical grade and were dried and fractionated prior to use.

**Generation and Observation of <sup>13</sup>C NMR Spectra of the Carbocation.**—Racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (225 mg, 1.06 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.80 cm<sup>3</sup>) and CD<sub>2</sub>Cl<sub>2</sub> (0.20 cm<sup>3</sup>) were placed in a <sup>13</sup>C NMR sample tube (10 mm<sup>φ</sup>). Sulfur dioxide (1 cm<sup>3</sup>, as a condensed liquid) was introduced into the sample tube which was cooled in a dry ice-methanol bath. To the sample tube cooled to  $-110 \pm 1$  °C with

a liquid nitrogen-methanol bath was added AgSbF<sub>6</sub><sup>12,16</sup> (560 mg, 1.63 mmol; dried at ambient temperature/4 mmHg for 2 h) in one portion. The sample tube was immediately placed in the probe of the <sup>13</sup>C NMR spectrometer which was kept at  $-98.0 \pm 0.5$  °C and the <sup>13</sup>C NMR spectra were recorded. The NMR spectral data are summarized in Table 1.

**The Reaction of the Carbocation with Methanol.—Method A.** To the carbocation solution prepared as mentioned above was added methanol (0.50 cm<sup>3</sup>, 400 mg, 12.5 mmol), dropwise, using a 1 cm<sup>3</sup> syringe at  $-98 \pm 1$  °C, and the <sup>13</sup>C NMR spectrum was recorded under the same conditions (*vide supra*); only signals corresponding to 1,2-dimethyl-1-(*p*-methoxyphenyl)propyl methyl ether were observed (Table 1). An additional 2 cm<sup>3</sup> of methanol was then added at  $-98$  °C and the mixture was stored in a dry ice-methanol bath overnight. After work-up with diethyl ether-5% aqueous NaHCO<sub>3</sub>, the products were separated by preparative TLC (SiO<sub>2</sub>) to afford 2-(*p*-methoxyphenyl)-3-methylbut-2-ene (50 mg, 27% yield) and a mixture of four components (by GLPC) of polymeric product (25 mg). One (15 mg) component was isolated.

2-(*p*-Methoxyphenyl)-3-methylbut-2-ene. <sup>13</sup>C NMR data are tabulated in Table 1;  $\delta_{\text{H}}$ (90 MHz, CCl<sub>4</sub>) 1.57 (s, 3 H), 1.77 (s br, 3 H), 1.90 (s br, 3 H), 3.70 (s, 3 H) and 6.57–6.97 ppm (m, 4 H);  $\nu_{\text{max}}$ (CCl<sub>4</sub>)/cm<sup>-1</sup> 830, 1040, 1180, 1250, 1360, 1460, 1510, 1610, 2900, 2950 and 3030 (Found: C, 81.95; H, 9.1. C<sub>12</sub>H<sub>16</sub>O requires C, 81.77; H, 9.15).

One of the polymeric products. <sup>13</sup>C NMR  $\delta_{\text{C}}$ (25 MHz, CDCl<sub>3</sub>) 20.5 (q), 22.1 (q), 26.1 (q), 28.1 (q), 19.7 (?), 33.7 (t), 53.8 (q), 55.0 (q), 57.1 (s), 91.6 (d), 109.8 (?), 111.4 (?), 112.2 (d), 112.7 (d), 113.5 (?), 126.9 (?), 129.3 (d), 130.0 (d), 130.6 (d), 133.6 (s), 134.5 (s), 136.8 (s) and 157.4 (s);  $\delta_{\text{H}}$ (90 MHz, CDCl<sub>3</sub>) 1.51–1.98 (m), 3.63 (s), 3.68 (s) and 6.55–6.95 ppm (m) (9:1:2:4).

**Method B.** AgSbF<sub>6</sub> (253 mg, 0.740 mmol) was added in one portion at  $-72 \pm 1$  °C to a solution of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (111 mg, 0.520 mmol) in CH<sub>2</sub>Cl<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (4:1 v/v; 1 cm<sup>3</sup>) and SO<sub>2</sub> (1 cm<sup>3</sup> as a liquid) containing methanol (51.0 mg, 1.59 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (134 mg, 0.650 mmol) in an NMR sample tube. The <sup>13</sup>C NMR spectrum was taken at  $-72.0 \pm 0.5$  °C. The temperature was raised to  $-63$ ,  $-50$ ,  $-37$  and  $-25$  °C at *ca.* 1 h intervals and the reaction was followed by recording the <sup>13</sup>C NMR spectrum of the mixture. After the usual work-up with diethyl ether and water at ambient temperature, 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl methyl ether<sup>3a</sup> was obtained.

**The Reaction of the Carbocation with Phenol.—From the racemic chloride.** A solution of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (110 mg, 0.520 mmol) was prepared in CH<sub>2</sub>Cl<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (4:1 v/v; 1 cm<sup>3</sup>) and SO<sub>2</sub> (1 cm<sup>3</sup> as a liquid) containing phenol (150 mg, 1.59 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (132 mg, 0.640 mmol) in an NMR sample tube at  $-78.0 \pm 0.5$  °C. To the solution was added AgSbF<sub>6</sub> (240 mg, 0.70 mmol) at  $-78$  °C and the reaction was monitored by NMR spectroscopy. The reaction mixture was kept in a dry ice-methanol bath for 1 day before being worked-up with diethyl ether-water to afford 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl phenyl ether (82.4 mg, 63.0% yield), *o*-[2,2-dimethyl-1-(*p*-methoxyphenyl)propyl]phenol (0.1 mg, 0.07% yield), *p*-[2,2-dimethyl-1-(*p*-methoxyphenyl)propyl]phenol (5.1 mg, 3.9% yield), and polymeric products (26 mg, 28% yield).

The product distribution data are shown along with the data in the presence of the duplicate amount of phenol in Table 2.

**From the optically active chloride.** Optically active 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride (638 mg, 3.00 mmol),  $\{[\alpha]_{\text{D}}^{25} +19.45 \pm 0.030$  (*c* 6.38 in CHCl<sub>3</sub>) $\}$ , was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>) containing phenol (847 mg, 9.00

\* It is suggested that the single intermediate stage should be composed of a rear side-shielded and a rear side-open (contact) ion pair.<sup>24</sup>

mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (765 mg, 3.72 mmol) with stirring. Sulfur dioxide (6 cm<sup>3</sup> as liquid) was introduced into the solution, which was cooled to  $-70 \pm 1^\circ\text{C}$  with a dry ice-methanol bath. To the yellow solution was added AgSbF<sub>6</sub> (1.29 g, 3.80 mmol) in one portion with cooling and stirring. After 2 h, diethyl ether (100 cm<sup>3</sup>) was added to the reaction mixture and the ethereal solution was washed with cold 10% aqueous NaOH, cold 10% aqueous HCl and cold 10% aqueous NaCl before being dried and concentrated to give a yellow oil (688 mg). The products were separated by preparative TLC to afford 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl phenyl ether (243 mg, 30% yield),  $\{[\alpha]_D^{20} 0.000 \pm 0.002^\circ (c 2.43 \text{ in } \text{CHCl}_3)\}$ . The stereochemical data are shown in Table 3.

*Product Distribution Analysis for Solvolysis.*—Product distribution for the solvolysis of ROPNB in phenol was analysed by GLPC in a similar manner to those reported earlier.<sup>27</sup> All the products were isolated and confirmed according to the previous procedures.<sup>3a</sup> The result is summarized in Table 2.

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