

## Formation of Carbocations from Bornan-2-*exo*-ol and Its Derivatives and their Reactions with Some Nucleophiles

By Nobuhisa Kitagawa, Masatomo Nojima, and Niichiro Tokura,\* Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

The reactions of bornan-2-*exo*-yl chloride and its isomers with carbon monoxide, acetonitrile, and water in antimony pentachloride-sulphur dioxide give bornan-2-*exo*-yl derivatives selectively. The reactions of bornan-2-*exo*-ol and its isomers with thionyl chloride showed marked dependence on the solvent used. The reactions of the alcohols with sulphuryl chloride are also reported.

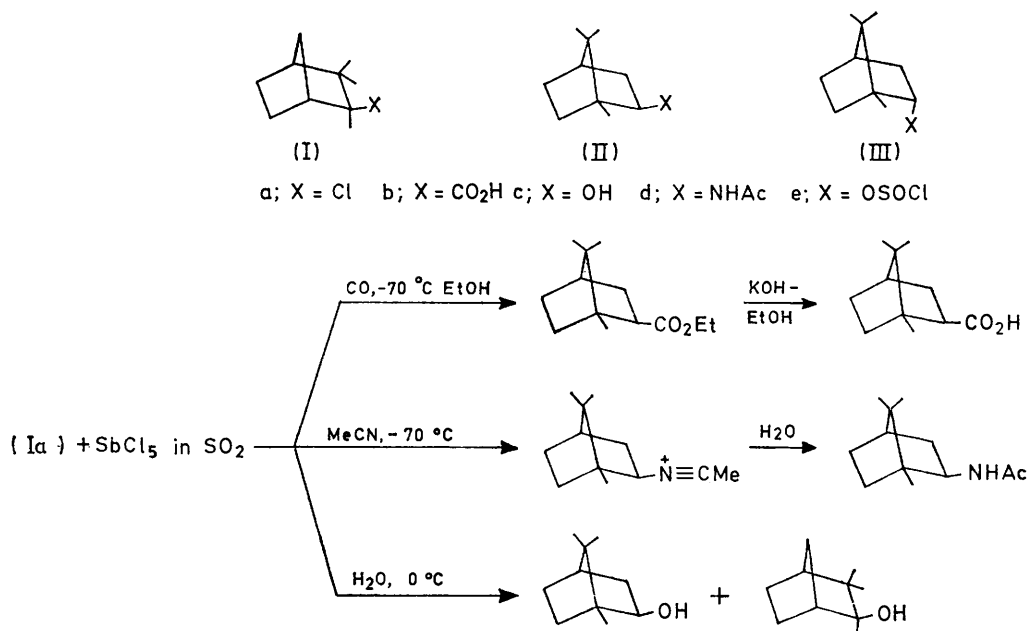
THE carbonylation of alkyl chlorides and their derivatives with carbon monoxide has been reported to be conveniently performed in liquid sulphur dioxide-antimony pentachloride.<sup>1</sup> From norbornan-2-*exo*- and -*endo*-ols and their 2-methyl derivatives, norbornane-2-*exo*-carboxylic acid and 2-*endo*-methylnorbornane-2-*exo*-carboxylic acid, respectively, were obtained selectively by use of this reagent system, and steric hindrance by the 6-*endo*-hydrogen atom was considered to play an important role in effecting selective *exo*-attack of the carbon monoxide.<sup>2</sup>

We were interested in the corresponding reactions of bornan-2-*exo*-yl chloride and its isomers for the following

oxylic acid was obtained from 2-methylnorbornan-2-ol selectively;<sup>2</sup> 2,3,3-trimethylnorbornyl derivatives are well known to be unstable under acidic conditions, rearranging to bornan-2-*exo*-yl and finally to bornan-2-*endo*-yl derivatives.<sup>4</sup> We also considered that the carbonylation of carbocations might be a good way of quenching solutions of ions without allowing the temperature of the system to rise.

### RESULTS AND DISCUSSION

*Carbonylation Reactions of Bornan-2-*exo*-yl Chloride and Its Isomers.*—When bornan-2-*exo*-yl chloride and its isomers were treated with carbon monoxide in antimony



reasons. Brown *et al.*<sup>3</sup> found that the 7-methyl groups exerted considerable steric hindrance to *exo*-attack for cyclic addition to 7,7-dimethylnorborn-2-ene. On the other hand, for non-cyclic addition, *i.e.* addition involving open transition states or intermediates, a preference for *exo*-reaction was found. Also, the possibility of the concomitant formation of 2,3,3-trimethylnorbornane-2-carboxylic acid could not be excluded, since 2-*endo*-methylnorbornane-2-*exo*-carb-

onylic acid (IIc) was obtained selectively. To ascertain whether the high selectivity of formation of the bornan-2-*exo*-yl derivative is characteristic of this system, reactions with acetonitrile and water were performed under similar conditions. The results (Table 1) show the preference for the formation of bornan-2-*exo*-yl derivatives in these reactions also, and the illustrated Scheme is suggested to account for this.

<sup>1</sup> M. Nojima, K. Tatsumi, and N. Tokura, *Bull. Chem. Soc. Japan*, 1971, **44**, 2001.

<sup>2</sup> M. Yoshimura, M. Nojima, and N. Tokura, *Bull. Chem. Soc. Japan*, 1973, **46**, 2164.

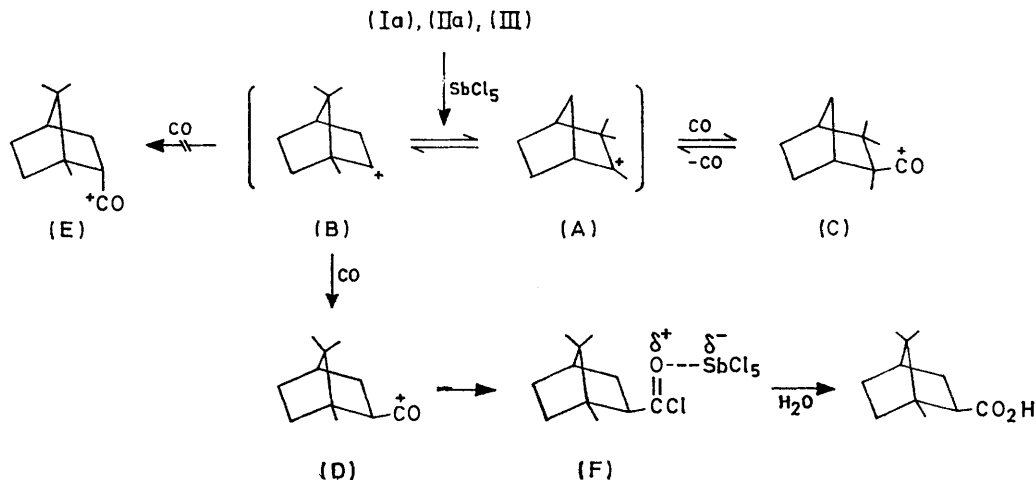
<sup>3</sup> H. C. Brown, J. H. Kawamura, and K. T. Liu, *J. Amer. Chem. Soc.*, 1973, **95**, 2209.

<sup>4</sup> T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1939, 1188.

*Reactions with Thionyl Chloride.*—The reactions of alcohols with thionyl chloride have been investigated by many workers,<sup>5</sup> and the effect of solvent upon the mechanism is well defined.<sup>6</sup> To ascertain the effect of

presence of pyridine. The results (Table 2) can be explained in terms of the ionizing powers of the solvents.

*Reactions with Sulphuryl Chloride.*—The reactions of the isomeric alcohols (Ic), (IIc), and (IIIc) with sulphuryl



SCHEME

reaction conditions upon product distribution, the reactions of bornan-2-*exo*-ol and its isomers with thionyl

chloride in the absence and in the presence of pyridine were examined (Table 3). The results are very similar

TABLE 1

Products (%) of reactions of chlorides with carbon monoxide, acetonitrile, and water in  $\text{SbCl}_5\text{-SO}_2$  <sup>a, b</sup>

Starting material	Nucleophile					
	CO <sub>2</sub>		MeCN		H <sub>2</sub> O	
	(Ia)	(IIb) (91)	(IIc) (81)	(IIc) (25), (Ic) (2.0)		
(IIa)	(IIb) (75)	(IIc) (89)	(IIc) (11), (Ic) (2.3)			
(IIIa)	(IIb) (90)	(IIc) (89)	(IIc) (14), (Ic) (1.6)			

<sup>a</sup> Conditions are described in the Experimental section.

<sup>b</sup> The by-products are the isomeric chlorides (Ia), (IIa), and (IIIa).

TABLE 2

Products (%) of reactions of alcohols with thionyl chloride under various conditions <sup>a</sup>

Starting material	Solvents			
	CCl <sub>4</sub> <sup>b</sup>	CHCl <sub>3</sub> <sup>b</sup>	SO <sub>2</sub> <sup>c</sup>	C <sub>5</sub> H <sub>5</sub> N <sup>d</sup>
(Ic)	(Ia) (94)	(Ia) (73), (IIa) (24)	(IIa) (88)	(IIa) (44)
(IIc)	(Ia) (98)	(Ia) (76), (IIa) (23)	(IIa) (93)	(IIa) (81)
(IIIc)	(Ie) (74) <sup>e</sup>	(Ie) (48) <sup>e</sup>	(Ie) (62) <sup>e</sup>	(IIa) (95)

<sup>a</sup> Camphene was the sole by-product. <sup>b</sup> At 0 °C for 2 h. <sup>c</sup> At -40 °C for 2 h. <sup>d</sup> Treatment with thionyl chloride (1.4 mol. equiv.) and pyridine (1.1 mol. equiv.) in carbon tetrachloride. <sup>e</sup> Bornan-2-*endo*-ol was recovered along with the chlorosulphite.

chloride were performed in carbon tetrachloride, chloroform, sulphur dioxide, and carbon tetrachloride in the

<sup>5</sup> D. J. Cram, *J. Amer. Chem. Soc.*, 1953, **75**, 332.

<sup>6</sup> C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, New York, 1969, p. 537.

<sup>7</sup> D. V. Banthorpe and D. G. Morris, *J. Chem. Soc. (B)*, 1971, 687.

TABLE 3

Products (%) of reactions of alcohols with sulphuryl chloride <sup>a</sup>

Starting material	CCl <sub>4</sub> <sup>b</sup>			CCl <sub>4</sub> -C <sub>5</sub> H <sub>5</sub> N <sup>c</sup>		
	(Ia)	(IIa)	(IIIa)	(Ia)	(IIa)	(IIIa)
(Ic)	4	6	38	12	20	1.6
(IIc)	15	38	3	11	20	3.0
(IIIc)	33	30	5.7	18	37	1.0

<sup>a</sup> As by-products, camphene and other products not identified were obtained. <sup>b</sup> The alcohol (1.0 mmol) was treated with sulphuryl chloride (1.4 mmol) in carbon tetrachloride at 0 °C for 2 h. <sup>c</sup> A mixture of the alcohol (1 mmol), sulphuryl chloride (1.4 mmol), and pyridine (1.1 mmol) in carbon tetrachloride (25 ml) was kept at 0 °C for 2 h.

to those obtained in the deamination of bornan-2-*endo*-ylamine and its isomers,<sup>7</sup> suggesting the formation of active carbocations from alkyl chlorosulphates.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were obtained with a Nippon Denshi LNM 3H-60 spectrometer, i.r. spectra with a Hitachi 215 spectrometer, and mass spectra with a Hitachi RMU-6E spectrometer.

Bornan-2-*endo*-yl chloride,<sup>8</sup> bornan-2-*exo*-yl chloride,<sup>9</sup> and camphene hydrochloride<sup>10</sup> were prepared according to reported methods. Camphene hydrate was obtained by the oxymercuration of camphene.<sup>11</sup> Bornan-2-*endo*- and -*exo*-ols were obtained from Wako Pure Chemical Co. (Osaka, Japan).

<sup>8</sup> M. Hanack and R. Hahnle, *Chem. Ber.*, 1962, **95**, 193.

<sup>9</sup> T. J. Floutt and W. F. Erman, *J. Amer. Chem. Soc.*, 1963, **85**, 3212.

<sup>10</sup> W. Huckel and P. Rieckmann, *Annalen*, 1959, **625**, 1.

<sup>11</sup> H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.

*Reaction of Bornan-2-exo-yl Chloride with Carbon Monoxide in Antimony Pentachloride-Sulphur Dioxide.*—In a flask fitted with a stirrer, an addition funnel, a gas inlet tube, and a reflux condenser equipped with calcium chloride tube were placed antimony pentachloride (30 g, 0.1 mol) and liquid sulphur dioxide (50 ml). The flask was kept in a solid CO<sub>2</sub>-methanol bath at -70 °C during the reaction. A solution of bornan-2-exo-yl chloride (3.4 g, 0.02 mol) in dichloromethane (10 ml) was added over 30 min, while a current of dry carbon monoxide was bubbled through the mixture. Bubbling was continued with stirring for a further 30 min. Then ethanol (30 ml) was added and the mixture was poured onto ice-cold aqueous sodium hydroxide, and extracted with three portions of ether. The combined ether layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated and the products were analysed with a Hitachi K-53 g.l.c. apparatus (flame ionization detector; SE 30 and PEG-6000 columns).

Hydrolysis of products with alcoholic potassium hydroxide gave bornane-2-exo-carboxylic acid as the sole acidic product (2.7 g, 75%), m.p. 80–81° (lit.,<sup>12</sup> 81–81.5°), showing physical data identical with those of an authentic sample.<sup>13</sup>

*Reaction of Bornan-2-exo-yl Chloride with Acetonitrile in Antimony Pentachloride-Sulphur Dioxide.*—To a mixture of antimony pentachloride (30 g, 0.1 mol) and sulphur dioxide (50 ml) was added the chloride (0.02 mol) in acetonitrile (50 ml) over 30 min; the reaction was then continued for 30 min. The mixture was treated as in the preceding experiment. The n.m.r. spectrum of the crude product showed the formation of *N*-(bornan-2-exo-yl)acetamide contaminated with a small amount of a mixture of isomeric chlorides. Recrystallization from methanol gave the pure amide (II<sub>d</sub>), m.p. 142–143° (lit.,<sup>14</sup> 142–143°),  $\tau$  9.20 (6 H), 9.08 (3 H), 8.08 (3 H), and 6.20 (1 H).

*Reaction of Bornan-2-exo-yl Chloride with Water in Antimony Pentachloride-Sulphur Dioxide.*—A solution of the chloride (0.02 mol) and antimony pentachloride (0.1

mol) in sulphur dioxide (50 ml) was kept at -70 °C for 1 h, then poured onto ice-water. The products were isolated as before and analysed by g.l.c. on a PEG-6000 column at 170 °C.

*Reactions of Alcohols with Thionyl Chloride in Carbon Tetrachloride.*—To a mixture of thionyl chloride (1.4 mmol) and carbon tetrachloride (20 ml) a solution of the alcohol (1 mmol) in carbon tetrachloride (5 ml) was added at 0 °C during 1 h, and stirring was continued for an additional 1 h while nitrogen was bubbled through the solution. After removal of solvent, the mixture was analysed by n.m.r. and i.r. spectroscopy. From bornan-2-endo-ol, bornan-2-endo-yl chlorosulphite was obtained,  $\nu_{\max}$  1 200s, 1 000s, and 860m;  $\tau$  9.18 (3 H), 9.13 (6 H), and 5.5 (1 H). Attempts to purify the sulphite failed, but by refluxing in aqueous potassium hydroxide bornan-2-endo-ol was recovered quantitatively.

The reaction in chloroform was performed under the same conditions, and that in liquid sulphur dioxide was carried out at -40 °C.

For the reaction in the presence of pyridine, to a solution of thionyl chloride (1.4 mmol) and pyridine (1.1 mmol) in carbon tetrachloride (20 ml), a mixture of alcohol (1.0 mmol) and carbon tetrachloride (5 ml) was added during 1 h at 0 °C. The mixture was refluxed for 2 h, and the products were isolated by the usual method, and analysed by g.l.c. and n.m.r. spectroscopy.

*Reaction of Alcohols with Sulphuryl Chloride.*—Sulphuryl chloride (1.4 mmol) and the alcohol (1.0 mmol) in carbon tetrachloride (25 ml) were kept at 0 °C for 2 h under the conditions used for the reaction with thionyl chloride, and the products were analysed by g.l.c. and n.m.r. spectroscopy. The reaction of an alcohol (1.0 mol) with sulphuryl chloride (1.4 mmol) in the presence of pyridine (1.1 mmol) was performed at 0 °C for 2 h, and the products were isolated and analysed by the same procedure.

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<sup>12</sup> M. de Botton, *Bull. Soc. chim. France*, 1958, 372.

<sup>13</sup> G. E. Gream and D. Wege, *Tetrahedron Letters*, 1967, 505.

<sup>14</sup> J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, 1948, **70**, 4045.