2,3-Bis(methoxycarbonyl)-9,10-bis(methylene)-5,6,7,8-tetramethyl-1,4,9,10-tetrahydroanthracene (17). The pyrolyzate from 250 mg of 8 in 5 mL of $CDCl_3$ was stirred at room temperature with excess (300 mg) dimethyl acetylenedicarboxylate for 2 h, after which reaction was complete (NMR). The solvent was removed under reduced pressure and the solid residue was triturated with petroleum ether (bp 30–60 °C) and filtered. Recrystallization from hexane–benzene gave 160 mg (52% based on 8) of 17 as light yellow crystals: mp 278–280 °C; IR (KBr) 2960 (m), 1735 (m), 1265 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.27 (6 H, s, aromatic methyls), 2.44 (6 H, s, aromatic methyls), 3.40 (4 H, s, methylene), 3.80 (6 H, s, methoxyl), 5.30 and 5.51 (each 2 H, br s, vinyl); mass spectrum, m/e (relative intensity) 378 (100), 345 (28), 331 (26), 319 (67), 287 (29), 260 (66); high-resolution mass spectrum, calcd for $C_{24}H_{26}O_4$ 378.18311; found 378.18393.

Reaction of 9 with Sulfur Dioxide. Sulfur dioxide was bubbled into a solution containing approximately 60 mg of 9 in 2 mL of $CDCl_3$ at −30 °C for 2 min. The solution was poured into 50 mL of petroleum ether (bp 30–60 °C) and the resulting precipitate was filtered and recrystallized from hexane–tetrahydrofuran to give 53 mg (49%) of 18: no melting point (decomposes on heating); NMR ($CDCl_3$) δ 2.23 (6 H, methyls), 2.40 (6 H, s, methyls), 4.10 (4 H, s, methylenes), 5.26 and 5.36 (2 H each, br s, vinyls).

When the same reaction was carried out at room temperature with excess sulfur dioxide, or when a chloroform solution of 18 was similarly treated, the product isolated as above was 19, as small white crystals from chloroform–hexane: mp >300 °C (the solid became red at about 280 °C); IR (KBr) 3025 (m), 2990 (m), 2935 (m), 2870 (m), 1400 (w), 1322 (m), 1318 (s), 1268 (m), 1245 (m), 1220 (m), 1148 (s), 1110 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.36 (6 H, s, methyls), 2.55 (6 H, s, methyls), 4.23 (4 H, s, methylenes), 4.83 (4 H, s, methylenes); mass spectrum, m/e (relative intensity) 364 (22), 300 (22), 236 (100); high-resolution mass spectrum, calcd for $C_{18}H_{20}O_4S_2$ 364.08029, found 364.08118.

2,6-Bis(chloromethyl)-1,4,5,8-tetramethylnaphthalene (15). A mixture of 1,4,5,8-tetramethylnaphthalene[22] (0.92 g, 5 mmol), paraformaldehyde (1.70 g), glacial acetic acid (36 mL), and concentrated hydrochloric acid (20 mL) was heated with stirring at 85–90 °C for 6 h and then allowed to stand at room temperature for 12 h. The mixture was poured into ice water (200 mL) and filtered. The solid was dissolved in ether (50 mL), washed successively with water, 10% aqueous sodium bicarbonate, and water, and then dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue from hexane–ethyl acetate gave 604 mg (43%) of 15 as white crystals: mp 174–175 °C; ^1H NMR (CCl_4) δ 2.69 (12 H, s, methyls), 4.63 (4 H, s, methylenes), 6.98 (2 H, br s, aromatic); ^{13}C NMR ($CDCl_3$) δ 136.94, 134.01, 133.31, 132.75, 131.09 (aromatic), 45.62 (methylene), 26.87, 19.36 (methyls); mass spectrum, m/e (relative intensity) 282 (53), 280 (82), 247 (35), 245 (100), 210 (20), 195 (23), 179 (35).

4,8-Dimethylnaphtho[1,2:5,6]dicyclobutene (16). Pyrolysis of 100 mg (0.355 mmol) of 15 at 640 °C (10^{-4} torr) gave, after purification by sublimation, 35 mg (47%) of pure 16 as colorless crystals: mp 196–197 °C; ^1H NMR ($CDCl_3$) δ 2.65 (6 H, s, methyls), 3.18 (4 H, t, J = 0.2 Hz), 3.58 (4 H, t, J = 0.2 Hz), 6.97 (2 H, s, aromatic); ^{13}C NMR ($CDCl_3$) δ 140.95, 139.68, 133.21, 129.25, 122.11 (aromatic), 32.81, 29.63 (methylenes), 20.81 (methyl); mass spectrum, m/e (relative intensity) 208 (100), 193 (53), 178 (29), 165 (19); high-resolution mass spectrum, calcd for $C_{16}H_{16}$ 208.12520, found 208.12578.

X-ray Structure of 16. Crystals of 16 are monoclinic; space group $P2_1/c$; a = 8.304 (3), b = 5.060 (2), c = 13.510 (7) Å, β = 101.60 (3)°; Z = 2; M = 208.30; ρ_c = 1.244 g cm^{-3}. Lattice dimensions were determined by using a Picker FACS-I diffractometer and Mo $K\alpha_1$ (λ = 0.709 26 Å) radiation.

Intensity data were measured by using Mo $K\alpha$ radiation ($2\theta_{max}$ = 50°), yielding 978 total unique data points and, based on $I > 2\sigma(I)$, 804 observed data points. The data were reduced;[28] the structures were solved by direct methods.[29] The refinement was by full-matrix least-squares techniques.[30] The final R value was 0.047. The final difference Fourier map showed densities ranging from +0.20 to −0.21, with no indication of missing or incorrectly placed atoms except a possible disorder of the methyl hydrogen atoms. The occupancy ratio of the possible alternate set of hydrogen positions to the reported set would appear to be less than 0.3.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE 77-05956) for financial support of this research.

Registry No. 3, 69153-84-0; 4, 62571-60-2; 5, 69153-86-2; 6, 69153-85-1; 8, 39654-48-3; 9, 74420-19-2; 10, 74420-20-5; 15, 74420-21-6; 16, 74420-22-7; 17, 74420-23-8; 18, 74420-24-9; 19, 74420-25-0; 1,4,5,8-tetramethylnaphthalene, 2717-39-7.

Supplementary Material Available: Data for the X-ray structure of 16 are available as Table I, positional and thermal parameters and standard deviations; Table II, anisotropic thermal parameters and standard deviations; Table III, distances; Table IV, angles; Table V, observed structure factors, standard deviations, and differences (8 pages). Ordering information is given on any current masthead page.

---

[28] Wei, K.-T.; Ward, D. L. *Acta Crystallogr., Sect. B.* **1976**, *32*, 2768.

[29] Main, P. "MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data," University York, England, 1978.

[30] Zalkin, A., 1974, private communication.

Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides in the Presence of Organoantimony Compounds as Novel Catalysts

Ryoki Nomura,* Akira Ninagawa, and Haruo Matsuda

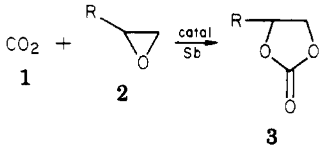
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

Received December 27, 1979

The reactions of carbon dioxide (1) with epoxides 2 to form cyclic carbonates 3 were carried out in the presence of organoantimony compounds as catalysts. Pentavalent organoantimony compounds, especially tetraphenylstibonium bromide (**4b**) and triphenylantimony dibromide (**4d**), are found to be more active catalysts than trivalent compounds, and the reactivity of compounds 2 seems to be in the following order: propylene oxide (**2b**) > styrene oxide (**2d**) > ethylene oxide (**2a**) > (chloromethyl)ethylene oxide (**2c**). The ring-opening polymerizations of **2b** and **2d** are also examined by using **4b** and **4d**, and it is found that they have no effect on the polymerization. On the basis of the results obtained, a reasonable scheme is proposed for the reaction.

There has been much attention given to synthetic utilization of carbon dioxide (1) along with various organometallic compounds. For example, alternating copolymers of 1 and epoxides 2 were synthesized by the use of orga-

Scheme I[a]



[a] **a**, R = H; **b**, R = CH_3; **c**, R = CH_2Cl; **d**, R = C_6H_5.

nozinc[1a] and organoaluminum[1b] compounds and cobalt acetate[1c] under mild conditions, while organotin alkoxides were effective for the direct synthesis of alkyl carbonates by reaction with **1**.[2]

In these reactions, it has been reported that the corresponding cyclic carbonates (**3**) were obtained directly from **1** and **2** in the presence of various catalysts[3] such as Lewis acids alone, Lewis acid–base systems, ammonium or phosphonium salts, etc. However, it is also known that these reactions need to be carried out under severe conditions and are accompanied by problems in purification of products in many cases. In addition, it has been found that transition-metal complexes in group 8 are effective for fixation of **1**.[4]

Recently, we found that organotin compounds, e.g., methyltin tribromide and butanestannoic acid, had a good catalytic effect for the reaction of **1** and **2a** to form ethylene carbonate **3a** under comparatively mild conditions[5] and that pentavalent organoantimony compounds more effectively catalyze the reaction than the tin compounds (Scheme I). The preliminary results of these catalytic reactions have been reported.[6]

This paper reports the results of the reaction of **1** with **2b** in the presence of the pentavalent organoantimony compounds Ph_5Sb (**4a**), Ph_4SbBr (**4b**), Ph_3SbCl_2 (**4c**), Ph_3SbBr_2 (**4d**), Me_3SbBr_2 (**4e**), and Ph_3SbO (**4f**) and trivalent compounds Ph_3Sb (**4g**), Ph_2SbCl (**4h**), and $SbCl_3$. We have studied the reactivity of four epoxides and the catalytic ability of **4b** and **4d** for ring-opening polymerization of **2b** and **2d**. From these results, a reaction scheme is proposed.

Results and Discussion

Reaction of 1 with 2. The reactions of **1** with **2b** catalyzed by organoantimony compounds to afford propylene carbonate **3b** are summarized in Table I. The yields of **3b** were approximately quantitative in the reactions catalyzed by the pentavalent organoantimony compounds, but the reaction time[7] was strongly dependent on the catalysts employed, 8–150 min in the presence of 1.0 mol % of catalyst at 120 °C. Among the pentavalent compounds, **4b** and **4d** exhibited the highest catalytic activity. For examination of the catalytic scheme, the reactions of **1** with **2b** which had been previously heated with catalysts (preheating reaction) were carried out, but no significant differences in the yield of **3b** or the reaction time were apparent in comparison with the reactions in Table I. The trivalent compounds did not seem to catalyze the reaction.

Table I. Reaction of 1 with 2b Catalyzed by Organoantimony Compounds[a]

catalyst	(concn)[b]	T, °C	t,[c] min	yield[d] of **3b**, %
Ph_5Sb, **4a**	(1.0)	120	130	87[e]
Ph_4SbBr, **4b**	(1.0)	120	8	92[f]
	(1.0)[g]	120	9	93[f]
	(1.0)[h]	120	9	93[f]
	(1.0)	100	20	98[f]
	(1.0)	80	60	93[f]
	(1.0)	60	120	93[f]
	(0.5)	120	40	99[f]
	(0.1)	120	480	88[f]
Ph_3SbCl_2, **4c**	(1.0)	120	150	96[f]
Ph_3SbBr_2, **4d**	(1.0)	120	16	97[f]
	(1.0)	100	50	92[f]
	(1.0)	80	100	96[f]
	(1.0)	60	390	97[f]
	(1.0)[g]	60	390	95[f]
	(1.0)	*k*	7200	95[f]
	(0.1)	120	840	92[f]
Me_3SbBr_2, **4e**	(1.0)	120	60	94[e,f]
Ph_3SbO, **4f**	(1.0)	120	120	94[i]
Ph_3Sb, **4g**	(1.0)	120	360[j]	7
Ph_2SbCl, **4h**	(1.0)	120	360[j]	5[e]
$SbCl_3$	(1.0)	120	360[j]	4[i]

[a] **2b**, 0.1 mol; **1**, ca. 50 kg/cm². [b] Mole % with respect to **2b**. [c] The time, t, is defined in ref 7. [d] With respect to **2b**. [e] The crude products were light brown. [f] The catalysts were able to be recovered in good yields. [g] **2b** and catalysts were preheated at 120 °C for 2 h prior to the reaction. [h] Recovered **4b** was employed. [i] The crude products were light brown. [j] Decreasing of pressure was not observed. [k] Room temperature.

Stibonium salt **4b** showed a large catalytic effect which was superior to the ammonium and phosphonium salts:[3b] in 8 min, a 92% yield of **3b** was obtained at 120 °C in the presence of 1.0 mol % of **4b**; quantitative yields were obtained at low reaction temperature or at lower concentrations of **4b**. It is interesting that **4d** as a covalent-type compound[8] displayed almost the same catalytic activity as **4b**.

The catalysts which contained halogen atoms and phenyl substituents are more active than those containing no halogen atom and methyl substituents, respectively. Bromides are more active than chlorides. Thus the increasing order of catalytic activity was as follows: **4b** > **4d** > **4e** > **4a**, **4c**, **4f** ≫ the trivalent compounds. Catalysts **4b–e** were recovered in good yields from the crude products. However, **4a** and **4f** could not be recovered, and the crude products were light brown and light yellow, respectively. These phenomena might be due to instability of these catalysts.

The reactions of **1** with epoxides **2a**, **2c**, and **2d** were carried out at 120 °C in the presence of the organoantimony compounds, and the corresponding cyclic carbonates, **3a**, **3c**, and **3d**, were obtained in good yields. In these runs, **4b** and **4d** also showed good catalytic activities, but in the reactions with **2d**, small amounts of poly(styrene oxide) were obtained as a byproduct, and a trace of poly-

---

(1) (a) S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B*, 7, 287 (1969); *Makromol. Chem.*, **130**, 210 (1969); (b) H. Koinuma and H. Hirai, 32nd Spring Meeting of the Chemical Society of Japan, Apr 1975, p 91; (c) K. Soga, K. Uenishi and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 415 (1979).

(2) S. Sakai, T. Fujinami, T. Yamada, and S. Furusawa, *Nippon Kagaku Kaishi*, 1789 (1975).

(3) (a) Various catalysts have been reported and patented since the references were reviewed in the following literature, and the direct preparation of cyclic carbonates from CO_2 and epoxides has been carried out on an industrial scale; however, the reaction conditions were severe, i.e., temperature 180–to 200 °C and pressure of CO_2 ca. 100 kg/cm². (b) W. J. Pepple, *Ind. Eng. Chem.*, **50**, 767 (1958).

(4) (a) R. J. De Pasquale, *J. Chem. Soc., Chem. Commun.*, 157 (1973); (b) H. Koinuma, H. Kato, and H. Hirai, *Chem. Lett.*, 517 (1977).

(5) H. Matsuda, A. Ninagawa, R. Nomura, and T. Tsuchida, *Chem. Lett.*, 573 (1979).

(6) H. Matsuda, A. Ninagawa, and R. Nomura, *Chem. Lett.*, 1261 (1979).

(7) After equilibrium of the temperature in the autoclave, the reaction time was clocked until the pressure fell to a constant value.

(8) (a) That R_3SbX_2-type compounds have covalent Sb–X bonds is well-known. (b) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds", Wiley, New York, 1957, p 215.

Table II. Reaction of **1** with **2a**, **2c**, and **2d** at 120 °C[a]

catalyst	epoxide	t,[b] min	yield[c] of **3**, %
4a	**2a**	330	82[d]
4b	**2a**	15	96
	2c	24	97[e]
	2d	15	91[e,f]
4c	**2a**	180	99
4d	**2a**	40	95
	2c	80	94[e]
	2d	24	82[e,g]
4e	**2a**	15	72[h]
4f	**2a**	960	74[d,i]
4g	**2a**	540	86
	2c	240	34[e]
	2d	600[j]	0[k]

[a] **2**, 0.1 mol; **1**, ca. 50 kg/cm^2; catalyst, 1.0 mol % with respect to **2**. [b] The time, t, is defined in ref 7. [c] With respect to **2**. [d] The crude product was light brown. [e] Yields after distillation. [f] A trace amount of poly(styrene oxide) was obtained. [g] Poly(styrene oxide) was obtained in ca. 10% yield besides **3d**. [h] The crude product was light yellow. [i] A trace amount of poly(ethylene oxide) was confirmed by ^{1}H NMR analysis. [j] Decreasing of pressure was not observed. [k] **2d** was recovered nearly quantitatively.

Table III. Ring-Opening Polymerization of **2b** and **2d**[a]

catalyst	T, °C	t, h	yield,[b] %	
			poly-**2b**	poly-**2d**
4b	120	5	5	5
	80	24	3	
4d	120	5	8	12
	80	24	4	

[a] Epoxides, 0.1 mol; catalyst, 1.0 mol % with respect to epoxides. [b] With respect to epoxides. Poly-**2b** and poly-**2d** are the polymerized compounds.

(ethylene oxide) was formed in the reaction with **2a** catalyzed by **4f**.

As judged from the reaction time,[7] the reactivity of the epoxides in the reaction catalyzed by **4d** seems to be in the order **2b** > **2d** > **2a** > **2c**, i.e., the same order as the electron-donor ability of the epoxides in hydrogen bonding.[9]

As can be seen from Table II, it was found that the catalytic behavior of **4g** is very much lower than that of the pentavalent compounds. It should be noted that **4g** also does not promote the reactions of the more sensitive epoxides, **2b** and **2d**, in cationic reactions.[10] On the other hand, cyclic carbonates from **2a** and **2c** were obtained in 86 and 34% yields, respectively. Overall, the catalytic activity of **4g** and other trivalent compounds was inferior to that of pentavalent compounds.

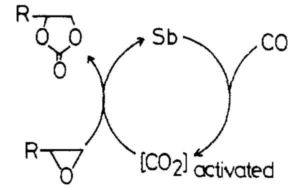
Ring-Opening Polymerization of 2b and 2d. Since it was important to investigate the interaction between epoxides and catalysts to reveal the reaction mechanism, the polymerizations of **2b** and **2d** initiated by **4b** or **4d** were carried out, and the results are shown in Table III. The yields of the polymer are rather low; the yields of poly(styrene oxide) are about the same as those obtained as a byproduct in the reaction of **2d** with **1** (Table II, footnote *g*).

Table IV. Lewis Acid Strength of **4** Measured by Hammett Indicators

catalyst	indicators and their color[a,b]				pK_a
	I	II	III	IV	
4a	B	B	B	B	~6.0
4b	B	B	B	B	~6.0
4c	A	B	B	B	6.0–4.8
4d	A	B	B	B	6.0–4.8
4e	A	B	B	B	6.0–4.8
4f	B	B	B	B	~6.0
4g	B	B	B	B	~6.0

[a] A represents acidic color and B basic color. [b] Indicators used here are as follows (pK_a at color change area): I, neutral red, (6.0); II, methyl red (4.8); III, naphthyl red (4.0); IV, butter yellow (3.3).

Scheme II



We had found that not only cationic polymerization of epoxides[11] but also formation of cyclic carbonates[5] was catalyzed by mono- or dialkyltin halides, but these pentavalent organoantimony compounds seem not to initiate the polymerization. This fact suggests that the strength of coordination of epoxides to central metal atoms is Sn > Sb.

Lewis Acid Strength of Organoantimony Compounds. The measurement of Lewis acid strength was carried out to obtain information about the coordination strength of the epoxide to the central metal atom of the catalysts.[12] The pK_a values of **4** were shown to be more than 4.8 based on the Hammett indicator and those of organotin compounds between 4.8 and 4.0[11c,d] (Table IV). The shifts of $\nu_{C=O}$ of xanthone caused by the complexation with the catalysts[12] were so small as to be undetectable. These facts led us to the consequence of weaker coordination ability of the organoantimony compounds relative to that of the organotin compounds.

Reaction Scheme. One possible path is that epoxides first coordinate to an Sb atom to interact with **1**. The catalytic activities of the pentavalent organoantimony compounds are superior to those of the tin compounds,[5,6] although the Lewis acid strength is observed to be Sn > Sb. Accelerative effects in the preheating reaction and polymerization of **2** besides the selective formation of **3**, both of which are inferred from the coordination, were not observed. No significant change in the IR and ^{1}H NMR spectra[13] occurred in the mixture of **2b** and the catalysts (1 mol % of solution of the catalysts in **2b**). These facts point out the absence of the coordination of the epoxides to the catalysts and of the formation of new catalytic species as in the organozinc catalysis.[14]

---

(9) S. Searles, M. Tamres, and E. R. Lippincott, *J. Am. Chem. Soc.*, **75**, 2775 (1953).

(10) (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) J. G. Princhard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 2667, 6008 (1956); (c) K. C. Frisch and S. L. Reeqen, Eds., "Ring-Opening Polymerization", Marcel Dekker, New York, 1969.

(11) (a) S. Matsuda, H. Matsuda, A. Ninagawa, and N. Iwamoto, *Kogyo Kagaku Zasshi*, **71**, 2054 (1968); (b) N. Iwamoto, M. Tanida, A. Ninagawa, H. Matsuda, and S. Matsuda, *ibid.*, **74**, 111 (1971); (c) N. Iwamoto, A. Ninagawa, H. Matsuda, and S. Matsuda, *ibid.*, **73**, 2429 (1970); **74**, 1400 (1971).

(12) (a) G. A. Olah, "Friedel–Crafts and Related Reactions", Wiley, New York, 1973; (b) H. A. Beneji, *J. Am. Chem. Soc.*, **78**, 5490 (1956); (c) D. Cook, *Can. J. Chem.*, **41**, 522 (1963).

(13) (a) G. G. Long, G. O. Doak, and L. D. Freedman, *J. Organomet. Chem.*, **4**, 82 (1965); (b) G. G. Long, C. G. Moreland, G. O. Doak, and M. Miller, *Inorg. Chem.*, **5**, 1358 (1966); (c) R. L. McKenney and H. H. Sisler, *ibid.*, **6**, 1178 (1967).

These results suggest that the organoantimony catalysts may activate 1; the cyclic mechanism shown in Scheme II is suggested.

Experimental Section

General Methods. IR spectra were recorded on a Hitachi EPI-G2 spectrophotometer and ^{1}H NMR spectra on a JEOL Model PS-100 spectrometer with tetramethylsilane as an internal standard. Gas chromatographic analyses (GC) were performed on a Shimadzu GC-4BT gas chromatograph with a FID detector connected to an Apiezon L grease coated 30 m × 0.25 mm capillary column.

Materials. The organoantimony compounds used as catalysts, pentaphenylantimony (**4a**),[15] tetraphenylstibonium bromide (**4b**),[16] triphenylantimony dichloride and dibromide (**4c** and **4d**),[17] trimethylantimony dibromide (**4e**),[18] triphenylstibine oxide (**4f**),[19] triphenylstibine (**4g**),[20] and chlorodiphenylstibine (**4h**),[21] were prepared from commercial $SbCl_3$ as reported in the literature and confirmed by elemental analysis.

Epoxides **2a–d** were purrified and dried by the general procedure.

Reaction of 1 with 2. (a) General Reaction Procedure. Measured quantities of **2b** and the catalyst were placed in a 100-mL, stainless-steel autoclave, and **1** was then introduced under a pressure of ca. 50 kg/cm^2. After the pressure in the autoclave fell to a constant value, the reaction was discontinued by cooling and decompression of the autoclave. The crude reaction product was found to consist of **3b** and the catalyst from the results of ^{1}H NMR, GC, and IR. Catalysts **4b–e** could be recovered in good yields. Fractional distillation under reduced pressure was necessary for the runs of **2c** and **2d** because of their high boiling points, and in the case of **2d**, a poly(styrene oxide)[22a] was obtained from the distillation residue.

(b) Preheated Reactions. After a mixture of measured quantities of **2b** and the catalyst sealed in a glass ampule was heated at 120 °C for 2 h, the ampule was placed in the autoclave, and **1** was then introduced. The reaction was then carried out as described in part a.

Ring-Opening Polymerization of 2b and 2d. The homopolymerizations of **2b** and **2d** were carried out in the autoclave at 120 °C or in a glass ampule at 80 °C. The polymers obtained were purified by reprecipitation (benzene/ether) and identified as poly(propylene oxide) and poly(styrene oxide), respectively, by their IR spectra.[22]

Measurements of Lewis Acid Strength. (a) Measurement with Hammett Indicator.[11c,12b] To 1–5 wt % solution of organoantimony compounds in benzene was added 1 drop of a 0.1 wt % solution of indicators in benzene, and the color change of the indicators was observed.

(b) Measurement with IR Spectra.[12c] According to the method reported in the literature, an attempt was made to observe the lower wavenumber shift of $\nu_{C=O}$ of xanthone caused by complexation with organoantimony compounds, but no shift was detected.

Registry No. **1**, 124-38-9; **2a**, 75-21-8; **2b**, 75-56-9; poly-**2b**, 25322-69-4; **2c**, 106-89-8; **2d**, 96-09-3; poly-**2d**, 25189-69-9; **3a**, 96-49-1; **3b**, 108-32-7; **3c**, 2463-45-8; **3d**, 4427-92-3; **4a**, 2170-05-0; **4b**, 21450-52-2; **4c**, 594-31-0; **4d**, 1538-59-6; **4e**, 5835-64-3; **4f**, 4756-75-6; **4g**, 603-36-1; **4h**, 2629-47-2; $SbCl_3$, 10025-91-9.

---

(14) S. Inoue, M. Kobayashi, H. Koinuma, and T. Tsuruta, *Makromol. Chem.*, **155**, 61 (1972).

(15) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **577**, 35 (1952).

(16) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1195 (1940).

(17) (a) A. Michaelis and A. Reese, *Justus Liebigs Ann. Chem.*, **233**, 50 (1886); (b) P. Pfeiffer, *Ber. Dtsch. Chem. Ges.*, **37**, 4621 (1904).

(18) H. Hibert, *Ber. Dtsch. Chem. Ges.*, **39**, 160 (1906).

(19) D. L. Venezky, C. W. Sink, B. A. Nevett, and W. F. Fortescue, *J. Organomet. Chem.*, **35**, 131 (1972).

(20) G. T. Morgan and F. M. G. Mickleitwait, *J. Chem. Soc.*, 2286 (1911).

(21) Netherlands Patent 6 505 216 (1965); *Chem. Abstr.*, **64**, 9766*d* (1966).

(22) (a) A. Kawasaki, J. Furukawa, T. Tsuruta, T. Saegusa, and G. Kakogawa, *Kogyo Kagaku Zasshi*, **63**, 871 (1960); (b) J. Furukawa, T. Tsuruta, R. Sakata, and T. Saegusa, *Makromol. Chem.*, **32**, 90 (1959).

Reaction of 3-Substituted Imidazo[1,2-*a*]pyridines with Br$^+$ and the Alleged 5-Bromo-Substituted Product

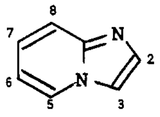
E. Smakula Hand and William W. Paudler*

Department of Chemistry, The University of Alabama, University, Alabama 35486

Received April 17, 1980

The reaction of 3-methylimidazo[1,2-*a*]pyridine with NBS was reinvestigated and is shown to give products formed by apparent *nucleophilic* substitution at the 2-position. NBS in $CHCl_3$ gave compounds **4** and **6**, while NBS in CCl_4 or Br_2 in $CHCl_3$ gave exclusively **4**. Mechanisms and differences in product formation are discussed; evidence that the previously reported NBS product was in fact 3-bromo-5-methylimidazo[1,2-*a*]pyridine, rather than the alleged 5-bromo-3-methyl derivative **3**, is presented. Compound **3** was prepared by diazotization of 5-amino-3-methylimidazo[1,2-*a*]pyridine in the presence of HBr and by condensation of 2-bromopropanal (or its acetal) with 2-amino-6-bromopyridine (**12**). This latter reaction of the weakly basic aminopyridine **12** is shown to follow the normal pattern in which the amino nitrogen condenses with the carbonyl carbon. Structures are established by infrared, mass, and ^{1}H NMR spectral analyses, mechanistic considerations, and diagnostic reactions. Experimental and computer-generated ^{1}H NMR spectra of compounds **3** and **13** are reproduced.

Electrophilic reagents react preferentially with the five-membered ring of imidazo[1,2-*a*]pyridines (**1**). Among the numerous electrophilic reactions which usually lead to exclusive substitution at the 3-position are halogenation,[1,2] nitration,[1,2] nitrosation,[1] condensation with aldehydes,[3] H/D exchange,[1] and the Mannich reaction.[1]



1

In contrast, conflicting data are reported in the literature for the few known reactions of imidazo[1,2-*a*]pyridines in

---

(1) Blewitt, H. L. *Chem. Heterocycl. Compd.* **1977**, *30*, 117 and references therein.

(2) Jacquier, R.; Lopez, H.; Maury, G. *J. Heterocycl. Chem.* **1973**, *10*, 755.

(3) Hand, E. S.; Paudler, W. W.; Zachow, S. *J. Org. Chem.* **1977**, *42*, 3377.