## A New Route to Chiral Diaryldiacetylenic Liquid **Crystals.** Preparation of Iodonium Salts Bearing **Chiral Alkynyl Ligands and Utility for Chiral Alkynyl Transfer Agents**

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1.4-Disubstituted diacetylenes display liquid-crystalline and nonlinear optical properties.<sup>1</sup> The extensive conjugation and polarity of these diacetylenes are associated with high nonlinear optical coefficients.<sup>2</sup> Long-chain alkyl groups play an important role in the generation of such properties and are essential for the molecular assembly that is useful for crystal engineering and molecular devices.<sup>3</sup> Moreover, introduction of chiral units into liquid-crystalline materials creates new functionality; the generation of ferroelectricity is especially important for highspeed display devices. In view of the increasing importance of chiral materials, we thought that chiral alkynylphenyliodonium salts might be suitable transfer agents of chiral alkynyl components and applicable to the synthesis of novel chiral diaryldiacetylenes which are potent ferroelectric liquid crystals. We report here the novel chiral alkynylphenyliodonium tosylates 1 and their application as chiral alkynyl transfer agents for the synthesis of chiral diaryldiacetylenic liquid crystals.

 $\mathbf{R}^* = \mathbf{C}_2\mathbf{H}_5\mathbf{C}^*\mathbf{H}(\mathbf{C}\mathbf{H}_3)\mathbf{C}\mathbf{H}_2\mathbf{O}, \ \mathbf{C}_2\mathbf{H}_5\mathbf{C}^*\mathbf{H}(\mathbf{C}\mathbf{H}_3)\mathbf{C}\mathbf{H}_2\mathbf{O}\mathbf{C}\mathbf{O} \quad \mathbf{R}^-\mathbf{C} \equiv \mathbf{C}^{-1}\mathbf{P}\mathbf{h} \ \mathbf{X}^-$ 

Hypervalent iodine reagents are versatile reagents in oxidation and functionalization of organic compounds.<sup>4</sup> However, despite their potential utility for asymmetric synthesis, the preparation and use of iodanes with chiral ligands are still rare.<sup>5,6</sup> Reported studies include asymmetric oxidation of sulfides to sulfoxides with chiral organoiodanes<sup>5</sup> and the synthesis of organoiodanes bearing chiral binaphthyl ligands.<sup>6</sup>

Among hypervalent iodine compounds, the alkynylphenyliodonium salts 2 are especially valuable in organic reactions because they contain a synthetically significant carbon-carbon triple bond and can serve as synthons of alkynyl cations.<sup>4,7</sup> We have found that reactions of alkynyliodonium salts with organocopper reagents are useful for introduction of alkynyl components into various organosubstrates.<sup>8,9</sup> Selective synthesis of unsymmetrical diaryldiacetylenes is particularly important from the standpoint of synthesis of functionalized materials.

Chiral alkynylphenyliodonium salts 1 were prepared by the following two methods (Scheme 1). Method A was conducted according to the procedures of Koser<sup>10</sup> and Stang.<sup>11</sup> ((S)-(2-Methylbutoxy)phenyl)acetylene ( $[\alpha]_D^{27}$  +12.3° (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>)) was treated with [hydroxy(tosyloxy)iodo]benzene in CH<sub>2</sub>Cl<sub>2</sub> in the presence of a drying agent at room temperature. Evaporation of the solvent followed by trituration with hexane-ether afforded (((((S)-2-methylbutoxy)phenyl)ethynyl)phenyliodonium tosylate (1a) ( $[\alpha]^{27}_{D}$  +5.5° (c 0.40, CH<sub>2</sub>Cl<sub>2</sub>)) as crystals in 30% yield. Method B is a modification of the procedure of Bachi and Stang.<sup>12</sup> 1-[4-[((S)-(2-Methylbutoxy)carbonyl]phenyl]-2-(trimethylsilyl)acetylene was treated with  $\mu$ -oxobis[((trifluoromethylsulfonyl)oxy)phenyliodine], prepared in situ from PhIO and triflic anhydride in  $CH_2Cl_2$ . However, the desired [[4-[((S)-2-methylbutoxy)carbonyl]phenyl]ethynyl]phenyliodonium triflate could not be obtained as crystals and was unstable. The CH<sub>2</sub>Cl<sub>2</sub> solution of the crude iodonium triflate was then treated with aqueous NaOTs and stirred vigorously. Extraction with CH<sub>2</sub>Cl<sub>2</sub> gave [[4-[((S)-2-methylbutoxy)carbonyl]phenyl]ethynyl]phenyliodonium tosylate (1b) as crystals in 38% yield. The chiral alkynylphenyliodonium tosylates 1 were stable to air and moisture and used without any special precautions.

Reactions of the chiral alkynyliodonium salts 1 with the alkynylcopper reagents 3 were conducted under argon (Scheme 2). Addition of the chiral alkynyliodonium tosylate 1a to solutions of the lithium alkynylcuprates 3, prepared from lithium arylacetylides and CuCN, in THF at -70 °C and workup of the reaction mixture gave chiral diaryldiacetylenes (4) in good isolated yields (54-58%) after separation by column chromatography on silica gel or by recrystallization from ethanol. The lithium alkynylcuprates 3 bearing electron-withdrawing groups provide the unsymmetrical diaryldiacetylenes 4 selectively. For

(7) Ochiai, M. Rev. Heteroat. Chem. 1989, 2, 92-111. Stang, P. J. Angew. Chem., Int. Ed. Engl. 1992, 31, 274-285. Stang, P. J. Supplement C2: The Chemistry of Triple-bonded Functional Groups, Patai, S., Ed.; John Wiley & Sons: Chichester, 1994; Chapter 20. Koser, G. F. Supplement D2: The Chemistry of Halides, Pseudo-Halides and Azides; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1995; Chapter 21.

 (8) Stang, P. J.; Kitamura, T. J. Am. Chem. Soc. 1987, 1990, 7561–7563.
 Stang, P. J.; Kitamura, T. Org. Synth. 1991, 70, 215–225. Kitamura, T.; Tanaka, T.; Taniguchi, H.; Stang, P. J. J. Chem. Soc., Perkin Trans. 1 1991, 2892-2893.

(9) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Matsumoto, M.; Sano, Y. J. Org. Chem. 1994, 59, 8053-8057. Kitamura, T.; Lee, C. H.; Taniguchi, Y.; Fujiwara, Y.; Matsumoto, M.; Sano, Y. Mol. Cryst. Liq. Cryst. 1996, 287, 93-100.

(10) Rebrovic, L.; Koser, G. F. J. Org. Chem. 1984, 49, 4700-4702.
(11) Stang, P. J.; Surber, B. W. J. Am. Chem. Soc. 1985, 107, 1452-1453. Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. J. Am. Chem. Soc. 1987, 109, 228-235.

(12) Bachi, M. D.; Bar-Ner, N.; Crittell, C. M.; Stang, P. J.; Williamson, B. L. J. Org. Chem. 1991, 56, 3912-3915.

<sup>(1)</sup> Wand, M. D.; Monahan, S. SPIE 1993, 1911, 29-38. Wu, S. T.; Margerum, J. D.; Hsu, C. S.; Lung, S. H. Appl. Phys. Lett. 1992, 61, 630-632. Stiegman, A. E.; Graham, E.; Perry, K. J.; Khundkar, L. R.; Cheng, L.-T.; Perry, J. W. J. Am. Chem. Soc. **1991**, 113, 7658–7666. Milburn, G. H. W.; Campbell, C.; Shand, A. J.; Werninick, A. R. Liq. Cryst. **1990**, 8, 623-637. Fouquey, C.; Lehn, J.-M.; Malthete, J. J. Chem. Soc., Chem. Commun. 1987, 1424-1426. Vincett, P. S.; Roberts, G. G. Thin Solid Films **1980**, 68, 135–171. Grant, B. *Mol. Cryst. Liq. Cryst.* **1978**, 48, 175–181. Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, 27, 647–678.

<sup>(2)</sup> Tsibouklis, J.; Werninck, A. R.; Shand, A. J.; Milburn, G. H. W. *Liq. Cryst.* **1988**, *3*, 1393–1400. (3) Van Der Veen, J.; De Jeu, W. H.; Grobben, A. H.; Boven, J. *Mol.* 

Cryst. Liq. Cryst. 1972, 17, 291-301.

<sup>(4)</sup> For recent reviews, see: Varvoglis, A. Chem. Soc. Rev. 1982, 10, 377-407. Umemoto, T. Yuki Gosei Kagaku Kyokai Shi 1983, 41, 251-265. Koser, G. F. The Chemistry of Functional Groups, Supplement D; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapters 18 and 25. Varvoglis, A. Synthesis 1984, 709–726. Moriarty, R. M.; Prakash, O. Acc. Chem. Res. 1986, 19, 244–250. Ochiai, M.; Nagao, Y. Yuki Gosei Kagaku Kyokai Shi 1986, 44, 660–673. Merkushev, E. B.
 Russ. Chem. Rev. (Eng. Transl.) 1987, 56, 826–845. Moriarty, R. M.; Vaid,
 R. K. Synthesis 1990, 431–447. Moriarty, R. M.; Vaid, R. K.; Koser, G.
 F. Synlett 1990, 365–383. Varvoglis, A. The Organic Chemistry of Polycoordinated Iodine; VCH Publishers: New York, 1992. Kita, Y.; Tohma, H.; Yakura, T. Trends Org. Chem. 1992, 3, 113–128. Prakash, O.; Singh, P. S. Aldrichimica Acta 1994, 27, 15–23. Prakash, O.; Saini, N.; Sharma, P. K. Synlett 1994, 221–227. Kitamura, T. Yuki Gosei Kagaku Varkai Sti 1005 52, 802–005. Strong, P. L. Zhdankin, V. Y. Cham, Peru Kyokai Shi 1995, 53, 893-905. Stang, P. J.; Zhdankin, V. V. Chem. Rev. 1996, 96, 1123-1178.

<sup>(5)</sup> Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskalchuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G. Zh. Org. Khim. 1975, 11, 1259–1263. Imamoto, T.; Koto, H. Chem. Lett. 1986, 967–968. Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. J. Org. Chem. 1990, 55, 315-318. Ray, D. G., III; Koser, G. F. J. Am. Chem. Soc. 1990, 112, 5672-5673.

<sup>(6)</sup> Ochiai, M.; Takaoka, Y.; Masaki, Y.; Nagao, Y.; Shiro, M. J. Am. Chem. Soc. **1990**, 112, 5677–5678.

Scheme 1. Preparation of Chiral Alkynylphenyliodonium Salts 3 and 4



Method B:



Scheme 2. Preparation of Chiral Diaryldiacetylenes



the alkynylcuprates **3** with electron-donating groups, however, the homocoupling products **5** derived from the copper reagents **3** were also formed in 23-38% yields. Table 1 shows the yields of the chiral diaryldiacetylenes **4** and their specific rotations. The formation of the chiral diaryldiacetylenes **4** indicates that the chiral alkynylphenyliodonium salt **1a** acts as a chiral alkynyl transfer agent.

Similar coupling reactions of the chiral alkynyliodonium tosylate **1b** with the alkynylcopper reagents **3** gave only 17-19% yields of chiral diaryldiacetylenes and did not provide satisfactory results. Further improvements are required for future work.

The chiral diaryldiacetylenes **4** are mostly mesogenic. The mesomorphic temperatures are listed in Table 2. The calorimetric curves were recorded on a differential scanning calorimeter (DSC) during heating and cooling. The heating rate was 5 °C/min. The observed mesophases were identified by the textures observed with a polarizing microscope. The most mesogenic diaryldiacetylenes **4** were enantiotropic liquid crystals and display smectic or nematic phases. Most importantly, a chiral smectic C phase was observed with the diaryldiacetylene **4f**, which showed a characteristic striated fan-shaped texture.

**Table 1.** Chiral Diaryldiacetylenes from Coupling Reaction of 1awith  $3^a$ 

	diaryldi yiel	acetylene d (%) <sup>b</sup>	$\left[\alpha\right]_{D}^{27}$ (CH <sub>2</sub> Cl <sub>2</sub> )
Y	4	5	(deg) of 4
NO <sub>2</sub> CF <sub>3</sub> CN CH <sub>3</sub> <i>n</i> -C <sub>8</sub> H <sub>17</sub> O <i>n</i> -C <sub>12</sub> H <sub>25</sub> O	54 ( <b>4a</b> ) 54 ( <b>4b</b> ) 57 ( <b>4c</b> ) 57 ( <b>4d</b> ) 54 ( <b>4e</b> ) 58 ( <b>4f</b> )	trace (5a) trace (5b) trace (5c) 23 (5d) 32 (5e) 38 (5e)	c +21.6 +12.9 +16.5 +8.6 c

<sup>*a*</sup> A solution of **1a** (0.75 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added dropwise to a stirred solution of **3** prepared from a lithium acetylide (3 mmol) and CuCN (1.5 mmol) in THF (30 mL) at -70 °C, and the reaction mixture was allowed to warm to room temperature. <sup>*b*</sup> Diaryldiacetylenes were isolated by column chromatography on silica gel or by recrystallization. <sup>*c*</sup> Not measured.

**Table 2.** Liquid Crystal Phase and Transition Temperatures of Chiral Diaryldiacetylenes  $4^{a}$ 

<b>4</b> a	к	172.0 Sp	174.0
	••	160.0	162.0
4b	K	114.0	
		110.0	
4c	v	165.0	
	v	158.0	
4d	к	87.3 N	90.0
		70.5	102.0
10	v	51.2	96.9
40	ĸ	50.7 SA	96.7
45	v	63.2	70.2 s * <u>85.0</u> S <u>101.5</u> I
-41	v	47.5	$51.7$ $S_{\rm C}$ $80.0$ $S_{\rm A}$ $100.9$

<sup>*a*</sup> Key: K, crystal;  $S_1$ , higher order smectic;  $S_A$ , smectic A;  $S_B$ , smectic B;  $S_C^*$ , chiral smectic C; N, nematic; I, isotropic.

In summary, we have developed a new chiral alkynyl transfer agent, the chiral alkynylphenyliodonium salt 1. Novel chiral liquid-crystalline diaryldiacetylenes 4 have been synthesized by using the chiral alkynyliodonium salts 1. A chiral diaryldiacetylenic ferroelectronic liquid crystal was prepared for the first time by the present procedure. We suggest that the present reactions can be utilized for the synthesis of chiral diaryldiacetylenic liquid crystals that are applicable to liquid crystal display devices, electronic, and nonlinear optical materials.<sup>1–3</sup>

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Supporting Information Available: Spectral data of chiral alkynyliodonium salts 1 and chiral diaryldiacetylenes 4a-f (2 pages). See any current masthead page for ordering and Internet access instructions.

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