

## The Synthesis of 1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane

S. W. CHOW, L. A. PILATO, AND W. L. WHEELWRIGHT

Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805

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1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane was prepared by pyrolyzing  $\alpha,\alpha'$ -bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene and  $\alpha,\alpha'$ -dihalo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene with steam as a diluent and condensing the pyrolysate in an organic solvent at 80–90°.

Since its first identification<sup>1</sup> and chemical synthesis,<sup>2</sup> the chemistry of the uniquely strained [2.2]paracyclophane has been the subject of extensive research. The transannular interaction between aromatic rings has been demonstrated by electrophilic substitution reactions,<sup>3</sup> spectral properties,<sup>4</sup> and  $\pi$ -base strengths.<sup>5</sup>

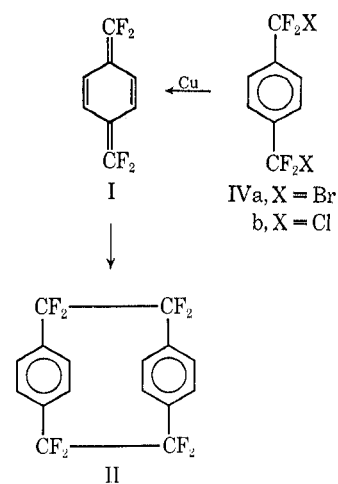
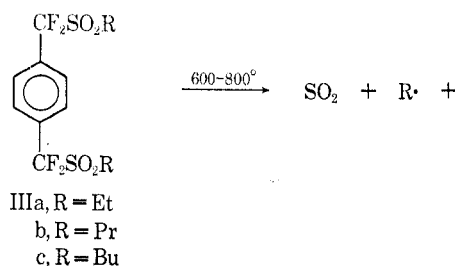
Recently, a new method for the preparation of a family of substituted *p*-xylylene polymers has been disclosed.<sup>6</sup> The method is based on the facile thermal cleavage of [2.2]paracyclophanes to yield an intermediate postulated to be *p*-xylylene. This latter species polymerizes rapidly in the condensed phase.

1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane<sup>7</sup> (II) is of interest because the polymer derived from this compound possesses no readily oxidizable groups, and hence should exhibit greatly improved oxidative and thermal stability. We now wish to report the synthesis of this compound II.

Synthetic methods for the preparation of [2.2]paracyclophane have involved either the Wurtz–Fittig coupling of 4,4'-dibromoethylbibenzyl or the dimerization of *p*-xylylene. The dimerization reaction of *p*-xylylene, in general, gave superior yields. *p*-Xylylene can be generated as a transient intermediate by the decomposition of *p*-xylyltrimethylammonium hydroxide<sup>8</sup> or by the pyrolysis of *p*-xylene at 900–1000°. <sup>9–11</sup>

Thus, it was expected that, if  $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene (I) could be generated under conditions which favor its dimerization, octafluoro[2.2]paracyclophane should result. Two methods were developed which led to the preparation of II. These were the pyrolysis of  $\alpha,\alpha'$ -bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene and the pyrolysis of  $\alpha,\alpha'$ -dihalo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene.

$\alpha,\alpha'$ -Bis(alkylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene was pyrolyzed at 600–800° with steam as diluent. After the pyrolysate was condensed in an organic solvent such as toluene according to the method of Pollart,<sup>10</sup> isolation and purification of II was readily accomplished by evaporation, recrystallization, and sublimation. Variation of the alkyl groups in III from ethyl to butyl exhibited no significant difference in



yields or in pyrolysis conditions. The fate of the alkyl radicals has not been elucidated.

Compound II is a white crystalline solid, mp 262° (sealed capillary), with an elemental composition of  $\text{C}_{16}\text{H}_8\text{F}_8$ . Its ultraviolet spectrum is very similar to [2.2]paracyclophane. The absorption at the 244-m $\mu$  region has been ascribed to *trans*-spatial overlap of the  $\pi$  orbitals of the two benzene rings, while the absorption at the 300-m $\mu$  region is attributable to the puckering of benzene rings.<sup>2,4,12</sup> The infrared spectrum exhibited a strong absorption at 718  $\text{cm}^{-1}$  characteristic of compounds in the [2.2]paracyclophane family.<sup>13</sup> The nmr spectrum of I showed only aromatic protons with a chemical shift of 7.3 ppm (60 Mcps, TMS). The structure of II is further substantiated by the formation of poly( $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) on pyrolysis according to the method of Gorham.<sup>6</sup> The preparation of poly( $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) will be reported elsewhere.

Steam-diluted pyrolysis of  $\alpha,\alpha'$ -dihalo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene (IV) under similar conditions also

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- (2) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).
- (3) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *ibid.*, **81**, 5977 (1959), and previous references.
- (4) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).
- (5) L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).
- (6) W. F. Gorham, *J. Polym. Sci., Part A-1*, **4**, 3027 (1966).
- (7) The numbering system is that proposed by W. M. Schubert, W. H. Sweeney, and H. K. Lactourette, *J. Amer. Chem. Soc.*, **76**, 5462 (1954).
- (8) N. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).
- (9) D. F. Pollart, U. S. Patent 3,149,175 (1964).
- (10) D. F. Pollart, *Petrol. Chem. Preprints*, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 175.
- (11) A. Errede, R. S. Gregorian, and J. M. Hoyt, *J. Amer. Chem. Soc.*, **82**, 5218 (1960).

(12) More recently, Filler and Choe, through the study of ring-fluorinated [2.2]paracyclophanes, have suggested that the absorption at the 300-m $\mu$  region is associated with donor-acceptor-type electronic transition while that at the 240-m $\mu$  region arises from transannular repulsive forces of the rings: R. Filler and E. W. Choe, *J. Amer. Chem. Soc.*, **91**, 1862 (1962).

(13) The origin of this absorption has not been elucidated. However, a number of substituted [2.2]paracyclophanes prepared in this laboratory by W. F. Gorham and coworkers all exhibited absorption in this region. This absorption is absent in the poly(*p*-xylylene) prepared by pyrolysis of [2.2]paracyclophane: W. F. Gorham and coworkers, unpublished results.

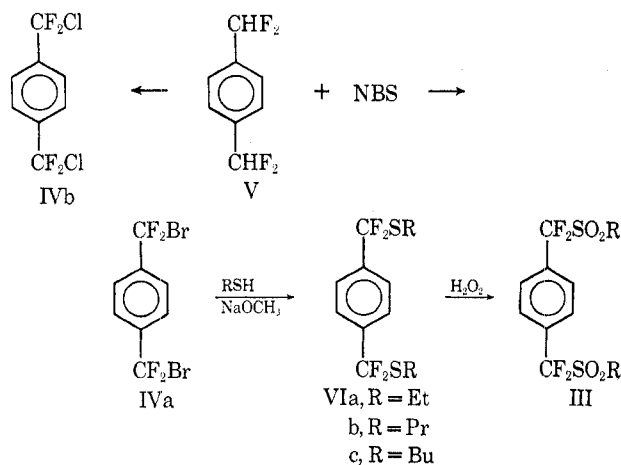
yielded II. Optimum yields were obtained when the pyrolysis chamber was packed with copper mesh. In most experiments, toluene was used as the quench diluent because of convenience. Other organic diluents, such as chlorobenzene and *p*-xylene, have been examined, and no adverse effect on the yield of II was observed.

Various metals have been used to transform  $\alpha,\alpha'$ -dihalo-*p*-xylene to poly(*p*-xylylene). Hertler<sup>14</sup> pyrolyzed IV (X = Br) over zinc or zinc-copper couple at 330° and obtained a low yield of poly( $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene). Gilch<sup>15</sup> reported the transformation of  $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene into the monomeric species  $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*p*-xylylene and the corresponding polymer by conducting the reaction with either copper metal or electrolysis.

Various products are obtained during the steam-diluted dimerization of *p*-xylylene to [2.2]paracyclophane.<sup>2,3,16</sup> These products are similar to the materials isolated and identified by Errede and coworkers.<sup>11</sup> The highly reactive *p*-xylylene yields a variety of linear and cyclic oligomers during dimerization.<sup>16</sup> In the copper-catalyzed pyrolysis, IV (X = Br or Cl) was completely transformed, since no dihalo compound could be detected in the toluene solution of the pyrolysate by gas chromatography. Presumably similar linear and cyclic  $\alpha$ -perfluoro oligomers are formed during dimerization of I to II. Consequently, these oligomers, as well as attendant solvolyses, limit the yield of II to ca. 30%. The  $\alpha$ -perfluoro by-products were not examined.

Currently, the chemistry of II is under investigation. These results will be published shortly.

The required III was prepared by a sequence of reactions shown below.



The bromination of  $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene is considerably more difficult than of simple benzylic compounds. In refluxing carbon tetrachloride, using ultraviolet light (through a Pyrex filter) as a catalyst and as a heat source, 20 hr were required for the consumption of N-bromosuccinimide. Bromination with 1–2 equiv of N-bromosuccinimide persistently gave a mixture of monobromo and dibromo compounds. However, IVa can be obtained free from  $\alpha$ -bromo-

$\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene by using an excess of N-bromosuccinimide.

The compound  $\alpha,\alpha'$ -bis(alkylthio)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene was prepared by the action of sodium mercaptide on IVa in dimethyl sulfoxide solution in about 75% yield. The thio ether was smoothly converted into the sulfone by oxidation with 30% hydrogen peroxide in acetic acid solution in yields of 60–80%.

### Experimental Section

**1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane (II).**—A solution of  $\alpha,\alpha'$ -bis(ethylsulfonyl)- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene (IIIa, 5.0 g, 0.0138 mol) in 75 ml of toluene was introduced dropwise over 2 hr into a quartz tube heated at 750° by means of a Hevi-Duty furnace. Steam generated from distilled water (300–400 g/hr) was admixed with the solution before entering the pyrolysis zone. The pyrolysate was condensed into a bath of 1.5 l. of toluene maintained at 85 ± 5°. Separation of the organic layer and evaporation of the toluene solution gave 0.36 g of a product which, on recrystallization from chloroform–hexane followed by sublimation, gave 0.22 g (9.1%) of II, mp 263° (sealed capillary). The nmr spectrum of II showed only aromatic protons with a chemical shift of 7.3 ppm (TMS, 60 Mcps). The ultraviolet spectrum of II had  $\lambda_{\text{max}}^{\text{EtOH}}$ ,  $m\mu$  (log  $\epsilon$ ), 215 (4.08), 248 (3.0), 274 (2.89), 280 (3.03), and 3.07 (2.2).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_8\text{F}_8$ : C, 54.55; H, 2.29; F, 43.15; mol wt, 352. Found: C, 54.63; H, 2.33; F, 43.36; mol wt, 317.

In addition to IIIa, IIIb and IIIc were also pyrolyzed in a similar manner and yields of II ranging from 4 to 10% were obtained.

**Pyrolysis of  $\alpha,\alpha'$ -Dihalo- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene.**—Similar experimental equipment for the steam-diluted, organic solvent quenched pyrolyses was used as described previously.

A total of 61.7 g (0.189 mol) of  $\alpha,\alpha'$ -dibromo- $\alpha,\alpha,\alpha',\alpha'$ -*p*-xylylene (IVa) was metered into the pyrolysis zone along with 8270 ml of water or 134:1 weight ratio of water to dibromo material. The quartz pyrolysis tube was packed with copper mesh and maintained at 650°. The pyrolysate vapors were quenched by passage into a 5-l., three-neck flask containing 2.5 l. of toluene at its azeotropic temperature (84°). The three-neck flask was equipped with a bottom take-off stopcock which was used to remove water during the experiment. The toluene solution was washed with three 500-ml portions of water, dried over  $\text{MgSO}_4$ , and evaporated to yield 28.7 g of crude product. The impure material was recrystallized from hexane to yield 9.6 g (28.8%) of II, mp 263° (sealed capillary).

The pyrolysis of  $\alpha,\alpha'$ -dichloro- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene was analogous to the pyrolysis of the dibromo compound. Optimum yields (15%) were obtained at a pyrolysis temperature of 750° and a weight ratio of steam to IVb of about 150–180:1.

**$\alpha,\alpha'$ -Dichloro- $\alpha,\alpha,\alpha',\alpha'$ -Tetrafluoro-*p*-xylene (IVb).**—A solution of  $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene<sup>17</sup> (17.8 g, 0.1 mol) in 200 ml of carbon tetrachloride was irradiated at reflux with a Hanovia utility lamp through a Pyrex filter. Chlorine was bubbled into the solution until the green color of  $\text{Cl}_2$  persisted. Ca. 33.0 g (0.46 mol) of chloride had been added. Argon was then bubbled through the reaction medium to displace the excess chlorine. The concentrated product was distilled to yield 20.7 g (81%) of  $\alpha,\alpha'$ -dichloro- $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene, bp 57–59° (11 mm). Vapor phase chromatographic analysis of distilled product on silicone rubber column at 150° with helium as carrier indicated a purity of 99%.

*Anal.* Calcd for  $\text{C}_8\text{H}_4\text{F}_4\text{Cl}_2$ : C, 38.90; H, 1.63; F, 30.77; Cl, 28.70. Found: C, 39.18; H, 1.55; F, 30.43; Cl, 28.51.

**Bromination of  $\alpha,\alpha,\alpha',\alpha'$ -Tetrafluoro-*p*-xylene (V).**—A mixture of  $\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylene (178 g, 1 mol) and N-bromosuccinimide (480 g, 2.7 mol) in 2 l. of carbon tetrachloride was irradiated at reflux with a Hanovia utility ultraviolet lamp (through a Pyrex filter). Succinimide was removed by filtration and the product was isolated by distillation. The purity of the product was ascertained by vapor phase chromatography on a silicone rubber column at 150° and helium as carrier gas.

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(15) (a) H. G. Gilch, *Angew. Chem.*, **77**, 592 (1965). (b) H. G. Gilch, *J. Polym. Sci., Part A-1*, **4**, 1351 (1966).

(16) D. F. Pollart, L. A. Pilato, and O. M. Garty, unpublished results.

(17) S. A. Fuqua, R. M. Parkhurst, and R. M. Silverstein, *Tetrahedron*, **20**, 1625 (1964).

The product,  $\alpha, \alpha'$ -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene, bp 104–108° (29 mm), was obtained in 50–80% yield.

*Anal.* Calcd for  $C_8H_4F_4Br_2$ : C, 28.60; H, 1.20; F, 22.62; Br, 47.58. Found: C, 28.85; H, 1.34; F, 22.87; Br, 47.85.

$\alpha, \alpha'$ -Bis(ethylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIa).—To a solution of 2.53 g (0.11 mol) of sodium in 40 ml of methanol was added 6.2 g (0.1 mol) of ethyl mercaptan. The solution was then diluted with 100 ml of dimethyl sulfoxide. After 15.1 g (0.045 mol) of  $\alpha, \alpha'$ -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was added, the solution was heated at 50–60° for 2 hr, stirred at room temperature for 16 hr, and poured into ca. 750 ml of water. The product separated and was isolated from the aqueous mixture by extraction with three 300-ml portions of methylene chloride. Removal of methylene chloride by evaporation followed by distillation gave 10.2 g (75%) of the thio ether: bp 90–110° (0.2 mm); mp 70–78°.

$\alpha, \alpha'$ -Bis(propylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIb).—This compound was prepared by the same procedure described for VIa.

From 7.6 g (0.1 mol) of propyl mercaptan and 15.1 g (0.045 mol) of  $\alpha, \alpha'$ -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 11.8 g (76%) of the thio ether, bp 123–140° (0.5–1 mm).

$\alpha, \alpha'$ -Bis(butylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIc).—This compound was prepared by the same procedure described for VIa.

From 10.0 g (0.1 mol) of butyl mercaptan and 15.1 g (0.045 mol) of  $\alpha, \alpha'$ -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 12.0 g (75%) of this ether, bp 130–140° (0.2 mm).

$\alpha, \alpha'$ -Bis(ethylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIa).—To a stirred solution of 24.8 g (0.083 mol) of  $\alpha, \alpha'$ -bis(ethylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIa) in 300 ml of 1:1 acetic acid–acetic anhydride cooled at 0–5° was added dropwise 57 ml

(0.5 mol) of  $H_2O_2$  of 30% hydrogen peroxide over 1–2 hr. The reaction mixture was allowed to warm to room temperature gradually over 3–4 hr, stirred for 24 hr, and poured into water (ca. 500 ml). The bissulfone separated and was filtered and washed successively with water, 5% sodium carbonate, and water. Recrystallization from chloroform–hexane gave 24 g (80%) of the bissulfone, mp 163–164°.

*Anal.* Calcd for  $C_{12}H_{14}F_4S_2O_4$ : C, 39.77; H, 3.89; F, 20.97; S, 17.7. Found: C, 39.73; H, 3.91; F, 20.74; S, 17.50.

$\alpha, \alpha'$ -Bis(propylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIb).—This compound was prepared by the procedure described for IIIa.

From 26.2 g (0.08 mol) of  $\alpha, \alpha'$ -bis(propylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 20.2 g (65%) of the sulfone, mp 162–163°.

*Anal.* Calcd for  $C_{14}H_{18}F_4S_2O_4$ : C, 43.11; H, 4.65; F, 19.48; S, 16.44. Found: C, 43.16; H, 4.91; F, 19.78; S, 16.25.

$\alpha, \alpha'$ -Bis(butylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIc).—This compound is prepared by the procedure described for IIIa.

From 35.4 g (0.1 mol) of  $\alpha, \alpha'$ -bis(butylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 21 g (50%) of the sulfone IIIc, mp 163–166°.

*Anal.* Calcd for  $C_{16}H_{22}F_4S_2O_4$ : C, 45.02; H, 5.32; F, 18.16; S, 15.32. Found: C, 45.28; H, 5.33; F, 18.36; S, 15.58.

**Registry No.**—II, 3345-29-7; IIIa, 3200-21-3; IIIb, 3200-22-4; IIIc, 3200-23-5; IVa, 651-12-7; IVb, 2629-68-7; VIa, 3200-26-8; VIb, 3200-28-0; VIc, 3200-13-3.

## Stereospecific Coupling Reactions between Organolithium Reagents and Secondary Halides<sup>1</sup>

LEO H. SOMMER<sup>2</sup> AND W. D. KORTE

*Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, and University of California, Davis, California 95616*

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In sharp contrast to simple alkylolithium reagents, which give largely racemized products in their coupling reactions with optically active organic halides, the present study shows that charge-delocalized organolithium reagents couple with optically active secondary halides with predominant inversion of configuration. The organolithium reagents studied were benzyl-, allyl-, and benzhydryllithium. Optically active secondary halides studied were 2-bromobutane, 2-bromooctane, 2-chlorooctane, and  $\alpha$ -phenylethyl chloride. It is of considerable interest for dynamic stereochemistry that the present finding of good inversion stereospecificity for reactions of charge-delocalized RLi reagents parallels the situation for certain poor leaving groups on asymmetric silicon, which actually give retention of configuration with simple alkylolithium reagents. The tendency for charge-delocalized RLi to give inversion thus appears to be fairly general.

Reaction of an optically active secondary halide with an alkylolithium reagent gives a low yield of coupled product and proceeds with predominant racemization (98%) of the asymmetric center.<sup>3</sup> Analogous reactions utilizing organosodium<sup>4,5</sup> and Grignard reagents<sup>5–8</sup> show considerable variation in stereospecificity and yield. In several cases, condensation reactions using charge-delocalized organosodium and Grignard reagents, where the charge on the carbanion is partially dispersed through a  $\pi$  system, proceed with almost 100% inversion of configuration at the asymmetric

carbon bearing the halogen. Both pyrrolylmagnesium bromide<sup>7</sup> and benzyllithium<sup>4,9</sup> coupled with 2-bromobutane without apparent loss of optical activity.<sup>10</sup>

The latter results and the observation that the stereochemical pathway in organosilicon coupling reactions is influenced to a great extent by the degree of charge delocalization in organometallic reagents<sup>12</sup> indicated that some types of organolithium reagents might couple with optically active organic halides with a high degree of stereospecificity.

### Results

Charge-delocalized organolithium reagents coupled with optically active secondary halides with a stereo-

(1) We acknowledge the generous support of the Dow Corning Corp. and a NSF Summer Fellowship to W. K.

(2) To whom all correspondence should be addressed: Department of Chemistry, University of California, Davis, California 95616

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