two diastereotopic methyl groups of the tertiary rhodium alkyl intermediate is suggested by the absence of deuterium incorporation in the methyl group β to the hydroxyl.

Caution is unquestionably warranted when extrapolating to a much broader range of compounds those conclusions drawn from careful study of one particular substrate for a given reaction. We have found that the relative rates of the elementary steps in the hydroboration catalytic cycle are highly substrate dependent.[17] Thus, the alcohol regioselectivity-determining step is different for 1-decene and styrene (Scheme III).

An important prologue to the development of meaningful rationales for observed selectivity is the elucidation of the selectivity-determining step for the specific reaction of interest. Relevant in this regard are the many models proposed in order to rationalize diastereoselective addition reactions to chiral olefins. Frequently, the tacit assumption is made that the product stereochemistry is defined by irreversible complexation of the alkene to the reagent, as in the recent case of Burgess and Ohlmeyer in their analysis of the rhodium-catalyzed hydroboration reaction.[2c] Clearly, this need not be the case for multistep processes (e.g., oxymercuration[18] or hydrogenation[19]). Our observation that olefin binding to the rhodium catalyst, as well as subsequent hydride migration, is indeed reversible for certain substrates undergoing catalyzed hydroboration serves to underscore this caveat. Further studies probing the mechanism of the rhodium-catalyzed olefin hydroboration reaction are in progress.

Acknowledgment. Support has been provided by the National Institutes of Health and Merck. The NIH BRS Shared Instrumentation Program 1 S10 RR01748-01A1 is acknowledged for providing NMR facilities.

(17) For labeling studies of other rhodium-catalyzed olefin hydrometalation reactions, see: (a) Hydroformylation (leading references): Lazzaroni, R.; Uccello-Barretta, G.; Benetti, M. *Organometallics* **1989**, *8*, 2323-2327. (b) Hydrosilation: Ryan, J. W.; Speier, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 895-898. Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84*, 1863-1868.

(18) For leading references, see: Chamberlin, A. R.; Mulholland, R. L., Jr.; Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 672-677.

(19) For example, see: Halpern, J. *Science* **1982**, *217*, 401-407.

Preparation of the 5,6-Arene Oxide of 3,3',4,4'-Tetrachlorobiphenyl. Decarboxylative Elimination as an Effective Last Step

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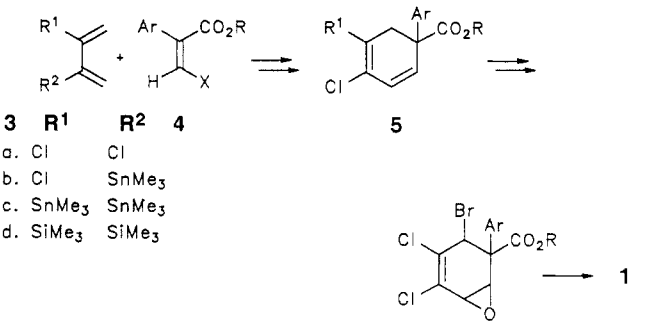
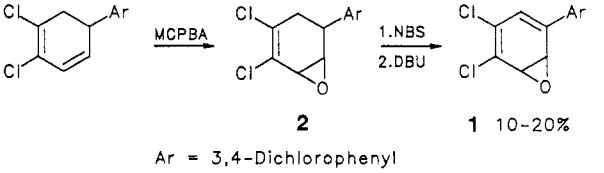
Summary: The 5,6-arene oxide of 3,3',4,4'-tetrachlorobiphenyl was prepared by a sequence in which two of the double bonds were introduced by decarboxylations. The first involved a Barton decarboxylative selenation and selenoxide elimination, the second a decarboxylative elimination.

The principal challenge in the synthesis of arene oxides is the introduction and manipulation of functionality in molecules that are on the verge of irreversible aromatization. This problem is exacerbated with halogenated biphenyl oxides, of interest as potential metabolites of polychlorinated biphenyls,[1] since highly halogenated intermediates have unusual reactivities and additional opportunities for aromatization compared to hydrocarbon analogues. Traditionally the synthesis of arene oxides, including halogenated ones,[2] has proceeded from a diene by epoxidation and bromination, with dehydrobromination as the final double bond forming step.[3] This method when applied to the 5,6-epoxide of 3,3',4,4'-tetrachlorobiphenyl

Scheme I



(1) gave only low and irreproducible yields due to extensive epoxide opening and aromatization during the bromination of **2**.[4]



Ar = 3,4-Dichlorophenyl

We report here a much more effective synthetic procedure for the preparation of arene oxide 1 using a bromodecarboxylative elimination as the final double bond forming step. The strategy is similar to that employed by Ganem[5] in a synthesis of senepoxide, in which thermal

(1) Kimbrough, R.; Buckley, J.; Fishbein, L.; Flamm, G.; Kasza, L.; Marcus, W.; Shibko, S.; Teske, R. *Environ. Health Perspect.* **1978**, *24*, 173. Forgue, S. T.; Preson, B. D.; Hargraves, W. A.; Reich, I. L.; Allen, J. R. *Biochem. Biophys. Res. Commun.* **1979**, *91*, 475. Stadnicki, S. S.; Lin, F. S. D.; Allen, J. R. *Res. Commun. Chem. Pathol. Pharmacol.* **1979**, *24*, 313. Stadnicki, S. S.; Allen, J. R. *Bull. Environ. Contam. Toxicol.* **1979**, *23*, 788. Preston, B. D.; Miller, E. C.; Miller, J. A. *Carcinogenesis* **1985**, *6*, 451. Yoshimura, H.; Yonemoto, Y.; Yamada, H.; Koga, N.; Oguri, K.; Saeki, S. *Xenobiotica* **1987**, *17*, 897.

(2) Reich, I. L.; Reich, H. J. *J. Org. Chem.* **1981**, *46*, 3721. Selander, H. G.; Jerina, D. M.; Piccolo, D. E.; Berchtold, G. A. *J. Am. Chem. Soc.* **1975**, *43*, 2711.

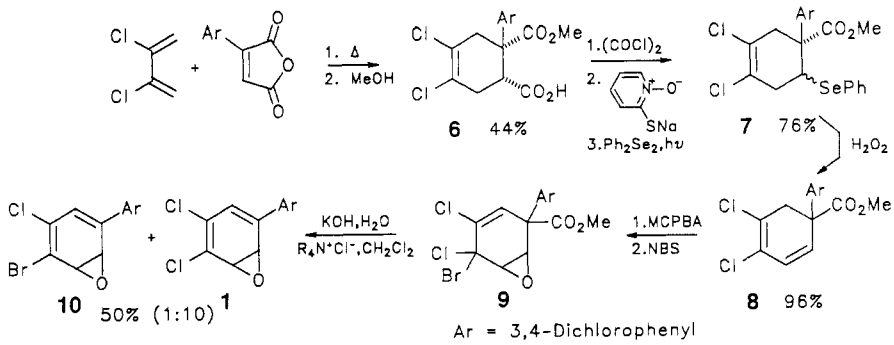
(3) Vogel, E.; Schubart, R.; Boll, W. A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 510. Vogel, E.; Gunther, H. *Ibid.* **1967**, *6*, 385. Rastetter, W. H.; Nummy, L. J. *J. Org. Chem.* **1980**, *45*, 3149. Watabe, T.; Hiratsuka, A.; Aizawa, T.; Sawahata, T. *Tetrahedron Lett.* **1982**, *23*, 1185. McManus, M. J.; Berchtold, G. A.; Boyd, D. R.; Kennedy, D. A.; Malone, J. F. *J. Org. Chem.* **1986**, *51*, 2784.

(4) Use of several other allylic halogenating agents and the addition of oxiranes did not improve the results. Wiberg, N.; Raschig, F. *J. Organomet. Chem.* **1967**, *10*, 15.

(5) Ganem, B.; Holbert, G. W.; Weiss, L. B.; Ishizumi, K. *J. Am. Chem. Soc.* **1978**, *100*, 6483.

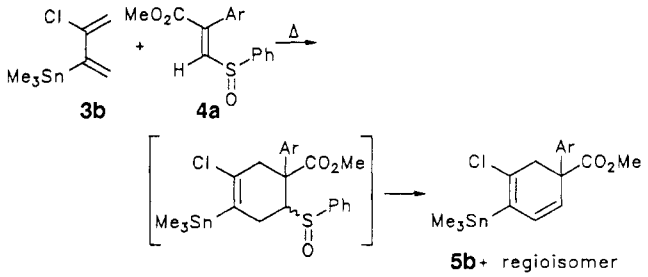
0022-3263/90/1955-2282$02.50/0

Scheme II



fragmentation of a β-lactone was used as the last step in the preparation of a benzene oxide intermediate. A Diels–Alder cycloaddition of 2,3-dichlorobutadiene **3a** or a synthetic equivalent (**3b–d**) with a dienophile **4** bearing an X group suitable for introduction of a double bond seemed a natural approach to the epoxide ring of **1** (Scheme I).

2,3-Dichlorobutadiene is a notoriously poor Diels–Alder diene,[6] and the dienophile **4** needed for the synthesis is trisubstituted. In fact, we are unable to obtain useful yields of cycloadducts between **3a** or the more reactive equivalent **3b**[7] and a number of dienophiles in which X is an oxidized sulfur or selenium group.[8] The best of these was the reaction of **4** (X = S(O)Ph) with **3b**, which gave **5b** in up to 20% yield.



This problem was solved with an approach in which X is a carboxy group (Scheme II). 3,4-Dichlorophenylmaleic anhydride (prepared by Meerwein arylation of dimethyl maleate[9]) reacted with the chloro stannyl diene **3b** in high yield, and even with 2,3-dichlorobutadiene in acceptable yield.[10] Base-catalyzed methanolysis of the anhydride differentiated the two carboxyl functions through exclusive attack (>95%) at the more hindered carbonyl group (**6**).[11]

Conversion of the carboxy group to an olefin or olefin precursor was achieved with the excellent *N*-hydroxy-2-pyridinethione procedure of Barton et al.[12,13] which produced a 1:1 diastereomeric mixture of selenides (**7**) in 76% yield. Oxidative elimination was quantitative. Epoxidation[14] and *N*-bromosuccinimide bromination of **8** gave a good yield of a mixture of six isomers, of which the major regioisomer was assigned structure **9**. Similar epoxidation–bromination of the analogue of **8** lacking the carbomethoxy group (**2**) could only be performed in low and variable yield.

The crucial decarboxylative elimination step was successful only in nonpolar solvents. Treatment of **9** with Na_2CO_3/CH_3OH, for example, gave largely phenolic products. However, $KOH/H_2O/CH_2Cl_2$ with benzyltriethylammonium chloride as phase-transfer catalyst caused saponification and decarboxylative elimination at room temperature in 50% yield from **8** with no detectable aromatization.

Not unexpectedly, the reaction also produced 7–12% of the bromo compound **10** by a chlorodecarboxylative elimination.[15] Pure **1** could be prepared by allylic chlorination of **8**. This proceeded in significantly lower yield than the bromination and after saponification and elimination led to only 15–20% yield of the arene oxide.[16] The procedure developed here should be applicable to the synthesis of a variety of related arene oxides.

Acknowledgment. We thank the National Institutes of Health (NIEHS) for financial support. We would like to thank Donald M. Sperbeck for technical assistance.

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(7) Reich, H. J.; Yelm, K. E.; Reich, I. L. *J. Org. Chem.* **1984**, *49*, 3438. Compounds **3c** and **3d** were much *less* reactive than **3a**.

(8) Sulfoxide substituted dienophiles have been used for similar purposes by Danishefsky, S.; Hirama, M. *J. Am. Chem. Soc.* **1977**, *99*, 7740. Alexandre, C.; Rouessac, F.; Tabti, B. *Tetrahedron Lett.* **1985**, *26*, 5453.

(9) Doyle, M. P.; Siegfried, B.; Elliot, R. C.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2431.

(10) Levy, L. A. *J. Org. Chem.* **1978**, *43*, 3068.

(11) Bloomfield, J. J.; Lee, S. L. *J. Org. Chem.* **1967**, *32*, 3919. Bailey, D. M.; Johnson, R. E. *J. Org. Chem.* **1970**, *35*, 3575. Kayser, M. M.; Wipff, G. *Can. J. Chem.* **1982**, *60*, 1192.

(12) Lead tetraacetate decarboxylations proceeded in marginal yields. Treatment of carboxylic acid **6** with $Pb(OAc)_4$ in the presence of LiCl (Sheldon, R. A.; Kochi, J. K. *Org. React.* **1972**, *19*, 279) gave a 60:40 mixture of two diastereomeric chlorides one of which (minor) could not be eliminated without decomposition. Attempts using procedures which provide olefin directly ($PbOAc_4$, $CuOAc_2$, Py) also gave poor yields of **8**. Hanessian, S.; Sahoo, S. P. *Tetrahedron Lett.* **1984**, *25*, 1425.

(13) Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Heterocycles* **1987**, *25*, 449.

(14) Epoxidation with MCPBA in CCl_4 gave a 78:22 mixture of diastereomers. The major one can be crystallized, mp 129–130 °C. Anal. Calcd for $C_{14}H_{10}Cl_4O_3$: C, 45.68; H, 2.74. Found: C, 46.12; H, 2.94. NMR 200 MHz ($CDCl_3$): δ 2.95 (dd, *J* = 17, 2 Hz, 1 H) 3.16 (d, *J* = 17 Hz, 1 H), 3.76 (d, *J* = 4 Hz, 1 H), 4.14 (dd, *J* = 4, 2 Hz, 1 H), 7.13 (dd, *J* = 8.5, 2.5 Hz, 1 H), 7.39 (d, *J* = 2.5 Hz, 1 H), 7.46 (d, *J* = 8.5 Hz, 1 H).

(15) Characteristic NMR signals (200-MHz, $CDCl_3$) of **10** are: δ 4.48 (d, *J* = 3.8 Hz) and 6.63 (d, *J* = 2.5 Hz).

(16) The arene oxide was purified by TLC using 20% ether–hexane containing 1% triethylamine. The crude TLC product is generally >95% pure. The oxide was crystallized from CH_2Cl_2–hexane (1% triethylamine), mp 128–131 °C. Some aromatization may occur during the recrystallization. Neither the crystallization nor TLC purification removed **10**. NMR of **1**: (200 MHz, $CDCl_3$) δ 4.33 (dd, *J* = 4.0, 2.5 Hz, 1 H), 4.39 (d, *J* = 4 Hz, 1 H); 6.65 (d, *J* = 2.5 Hz, 1 H), 7.42 (dd, *J* = 8.5, 2 Hz, 1 H), 7.52 (d, *J* = 8.5 Hz, 1 H), 7.68 (d, *J* = 2 Hz, 1 H). Pure **1** was converted to the phenol acetate 3,3′,4,4′-tetrachloro-6-acetoxybiphenyl (TsOH, CH_2Cl_2; Ac_2O, Py), mp 155–6 °C. Anal. Calcd for $C_{14}H_8Cl_4O_2$: C, 48.00; H, 2.31. Found: C, 47.94; H, 2.55.