Benzo[b]thiophene S-Oxides and Related Compounds from the Reactions of Arylalkynes and Antimony Pentafluoride in Sulfur Dioxide

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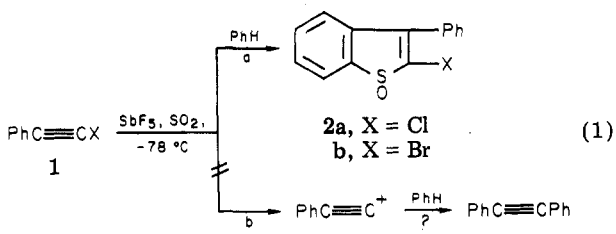
When treated with antimony pentafluoride and benzene in liquid sulfur dioxide, certain alkynes yield 2-X-3-phenylbenzo[b]thiophene S-oxides (X = Ph, Cl, Br) or 1,1-diphenyl-2-X-vinylsulfinic acids (X = H, Br). Though limited, this is a facile route to both types of compounds.

Although carbon–halogen bond cleavage was quite unlikely,[1] it seemed of interest to subject a *haloalkyne* to typical heterolysis conditions, namely antimony pentafluoride in liquid sulfur dioxide. Therefore, we treated 1-chloro- or 1-bromo-2-phenylethyne (**1a,b**) in this way: benzene was added as a scavenger of potential carbocations. The initial results are summarized in eq 1: 3-



(1)

phenylbenzothiophene S-oxides (**2**) were produced and there was no solvolysis. Subsequent examination of the products of such reactions turned up a variety of compounds, e.g., 1,1-diphenylvinylsulfinic acids (**3**) (see also eq 2 and 3 and Table I). Since this direct route to **2** and **3** is novel we investigated several alkynes in detail.

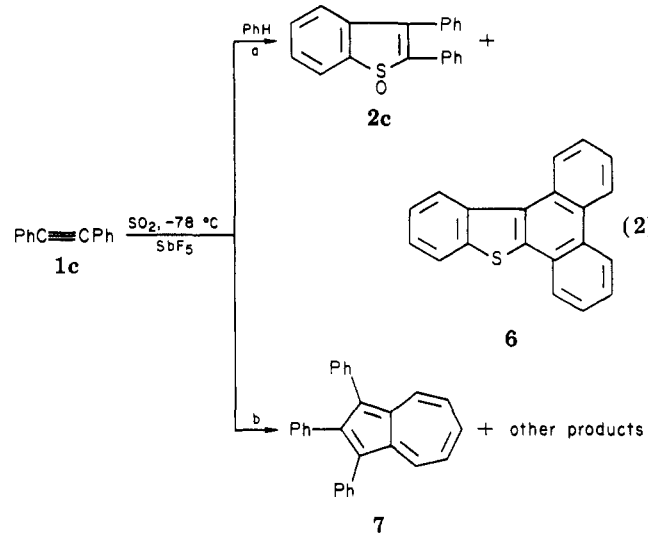
Some perspective on process 1a can be derived from the following observations. As a group the benzo[b]thiophene oxides (**2**) have not been readily accessible. Previously only indirect routes had been reported,[2] and it is only recently that several have been obtained by the selective oxidation of benzothiophenes.[3] As for the process that gave **2** and seemed unusual at first, there were analogies. Sulfinylation (and sulfonylation) of aromatic and unsaturated systems by sulfur dioxide facilitated by antimony pentafluoride[4] as well as electrophilic attacks on alkynes somewhat similar to eq 1, e.g., the reactions of alkyl or aryl halides with alkynes under Friedel–Crafts conditions, are known.[5-7] In fact, complexes formed by the addition of an aroyl chloride–aluminum chloride and alkynes yield β-chlorovinyl ketones and indenones, close analogues of the benzothiophene S-oxides.[7]

Our "standard" reaction conditions were those of eq 1 and 2a. When applied to diphenylethyne (**1c**), we obtained the expected sulfoxide (**2c**) as well as benzo[b]-phenanthro[9,10-d]thiophene (**6**). In the absence of benzene, tolan (**1c**) was converted into a "dimer", 1,2,3-

Table I. Products of the Reactions of Arylalkynes with Antimony Pentafluorine and Benzene in Liquid Sulfur Dioxide

alkyne (1)	yield sulfoxide (2), %	yield sulfinic acid (3), %	yield other, %
PhC≡CCl	64		
PhC≡CBr	16	67	
PhC≡CPh	~60		6 (10%)
PhC≡CPh[a]			7 (35%)
PhC≡CH		64	
4-MeOC$_6$H$_4$C≡CCOOH			4 (40%)

[a] Benzene was omitted.



(2)

triphenylazulene (**7**) and what appears to be a sulfonylated–sulfinylated tolan polymer (eq 2b). Here obviously was still another process or possibly a variant of eq 1. It is interesting that photolysis of tolan yields the "dimers" **7** and 1,2,3-triphenylnaphthalene,[8a,b] while treatment of tolan with lithium in ether produces some 1,2,3-triphenylnaphthalene.[8c]

In the case of phenylchloroethyne, the major product (64%) was the sulfoxide according to eq 1. Among the minor products with an unsatisfactory analysis was one that was somewhat analogous to a product from tolan in that it had a low R_f, broad IR absorption above 3000 cm^{-1}, low carbon content, and a relatively low m/e peak as the highest in the mass spectrum. We presume that such

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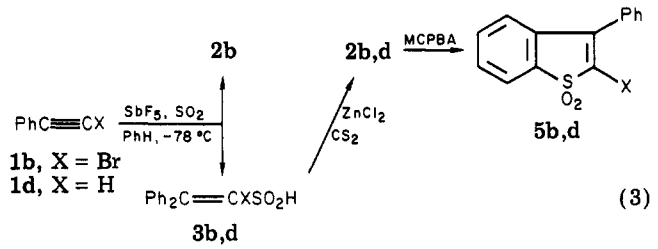
compounds have high molecular weights and "extra" S_xO_y relative to the sulfoxides.

With phenylbromoethyne, the sulfoxide (**2b**) was the minor product (16%) and 1-bromo-2,2-diphenylvinylsulfinic acid (**3b**) was the major (67%) product (eq 3). An

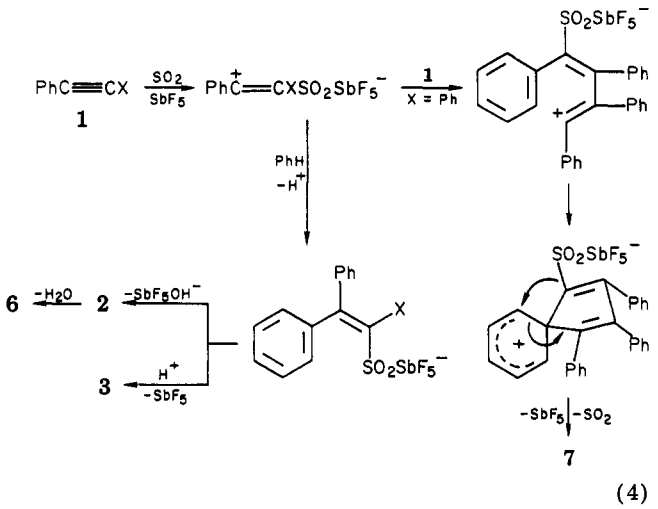


(3)

analogous acid (**3d**) was derived from phenylacetylene. Under mild Friedel–Crafts conditions ($ZnCl_2/CS_2$), the sulfinic acid could be converted to the ring sulfoxide (**2b**). Confirmation of these structures was obtained by their oxidation with *m*-chloroperbenzoic acid (MCPBA) to known sulfones **5b,d** (eq 3).

The appearance of the vinylsulfinic acids is of some interest. First they are rare, although not unknown.[9] Second, they *may* be intermediates in process 1 (see below eq 4). Third, they could lead to at least some of the observed complications found in our tests of process 1, since sulfinic acids disproportionate fairly readily. In water $ArSO_2H$ may yield some or all of the following: $ArSO_2SAr$, $ArSO_3H$, $ArS(O)SO_2Ar$, $ArSO\text{–}SO_2Ar$, and ArSOH.[10] We believe that such "side" reactions are partially responsible for the spectrum of products found under the conditions of eq 1.

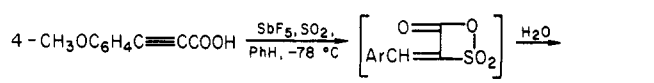
A plausible mechanism for the routes to the major products is given in eq 4 in abbreviated form. Fairly



(4)

typical carbocation processes appear to be involved so that paths to all products mentioned to this point are rationalized. Extensions of this scheme can explain two examples that follow.

Under the standard reaction conditions, (4-methoxyphenyl)propiolic acid yielded the sulfonic acid **4** (eq 5) and a large number of other materials that we could not characterize. The structure assigned to **4** was based on the familiar additivity rules for the chemical shift of olefinic



$4\text{-}CH_3OC_6H_4CH{=}C(COOH)SO_3H$ (5)

4

protons:[11] the *E* was somewhat favored over the *Z* isomer, and both were decisively favored over the compounds having aryl and SO_3H geminal. As for the origin of **4**, it obviously derives from the corresponding sulfinic acid. It is well known that sulfinic acids are readily oxidized and frequently disproportionate to sulfonic acids and other products.[10] It is also reasonable that antimony pentafluoride, a strong oxidizing agent,[4] could produce a precursor of **4**, e.g., the anhydride in eq 5.

Concluding Remarks. Almost every alkyne that we mentioned as well as a few other representative types that were used appeared to generate a different spectrum of products. It must be conceded that we have not found out how to control the selectivity of the reaction of alkynes with benzene, antimony pentafluoride, and liquid sulfur dioxide. On the other hand the products that have been found, i.e., the benzo[*b*]thiophene sulfoxides (**2**) and the sulfinic acids (**3**) are not easily available by other routes. Moreover, the conditions of process 1 are not normally those that might be considered as relevant to such products. Therefore we believe the several paths that we found, particularly eq 1 and 3, could provide fairly direct solutions for some special problems.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian T60 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained on a Varian MAT CH7 or the University of Illinois (Chicago) AEI MS 30 spectrometer. IR spectra were taken on a Pye Unicam 3-300 instrument. For the four benzo[*b*]thiophene sulfoxides, characteristic IR data for sulfoxide (1000–1100 cm^{-1}) and probable aryl C–H bending modes (700–800 cm^{-1}) will be listed. Eastman Chromagram sheet was used for TLC. Analyses were performed by MicroTech Laboratories, Skokie, IL, and Guelph Chemical Laboratories, Guelph, Ontario.

General Procedure for Reactions of Alkynes with Antimony Pentafluoride in Liquid Sulfur Dioxide. All the required glassware was dried in an oven and assembled, while warm, as the apparatus was swept with nitrogen. The reactor was a three-necked flask fitted with a gas inlet, gas outlet and oil bubbler, and a serum cap. Liquid sulfur dioxide (ca. 100 mL) was collected in the flask at ≥−78 °C. While a fast stream of prepurified nitrogen was passed into the flask, antimony pentafluoride was added through an open port. The opening was closed, and the flow of nitrogen was decreased. While the contents of the flask were agitated with a magnetic stirrer, a benzene solution of alkyne was added by syringe through the serum cap. Final workup consisted of pouring the colored reaction mixture into ca. 0.4 L of ice water, neutralizing with sodium carbonate, and extracting with ether or methylene chloride. Variations in the reaction temperature (−80 to −40 °C), in the reaction time, and in the warm-up period, if any, led to different proportions of products. Extended periods above −78 °C before workup led to darker solutions and more numerous products. Actual details for each of the preparations will be mentioned below.

Tolan Products (a). Tolan (1.78 g, 0.01 mol), antimony pentafluoride (5 g) and benzene (10–20 mL) were mixed in liquid SO_2 at −78 °C. The addition of tolan at −78 °C, and warm up to −40 °C took ca. 30 and 60 min, respectively. Workup yielded impure light yellow sulfoxide **2c** (1.04 g, 34%), mp 162–165 °C,

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as well as a similar quantity of material (30%), mp 146–152 °C. On repeated recrystallization, the first portion yielded a solid: mp 174–175 °C, from ether–methylene chloride; R_f (CH_2Cl_2, silica gel) 0.25; IR (KBr) 1068, 1040, 1032, 810, 775–740 (br), 705–699 (b) cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.6 (m, ~13 H), 7.9–8.4 (m, ~1 H).

Anal. Calcd for $C_{20}H_{14}OS$: C, 79.47; H, 4.70. Found: C, 79.84; H, 4.96.

TLC of the residual materials in the ether extracts indicated at least five compounds: those of R_f (CH_2Cl_2, silica gel) 0.8, 0.73, 0.69, and 0.03 were not investigated further. Liquid chromatography of a portion of the ether solution yielded benzo[*b*]phenanthro[9,10-*d*]thiophene (**6**) (ca. 10%) which was recrystallized from methylene chloride–heptane: mp 146.5–147.5 °C (lit.[12] mp 142 °C); a blood red picrate with mp 176–177 °C (lit.[12] mp 174 °C); NMR ($CDCl_3$) δ 7.3–7.9 (m, 6 H), 7.8–8.5 (m, 2 H), 8.5–9.3 (m, 4 H); MS, *m/e* 284 (parent $C_{20}H_{12}S$).

Anal. Calcd for $C_{20}H_{12}S$: C, 84.51; H, 4.23. Found: C, 83.88; H, 4.45.

Tolan Products (b). Tolan (3.56 g, 0.02 mol) was added in four portions over a period of 4 min to the mixture of antimony pentafluoride (18.5 g) and sulfur dioxide (ca. 100 mL)—no benzene was used. After 1 h, water was added slowly and then in large excess. The frozen mass was put aside to thaw overnight, after which it was neutralized with sodium carbonate and extracted with ether and methylene chloride. Attempted column chromatography on silica gel or celite was not effective in resolving the product mixture; besides, some decomposition occurred on the gel. Low-pressure liquid chromatography with a series of solvents yielded the major products. The first was dark blue 1,2,3-triphenylazulene (**7**) (ca. 35%): mp 209–210 °C (lit.[8b] 216–217 °C); R_f heptane, silica gel) 0.35, R_f (CH_2Cl_2, silica gel) 0.95; NMR ($CDCl_3$) δ 6.94 (br, ~6 H), 7.19 (br, ~12 H), 8.12 (br, ~1 H), 8.28 (br, ~1 H); MS, *m/e* 356 (parent $C_{28}H_{20}$).

Anal. Calcd for $C_{28}H_{20}$: C, 94.38; H, 5.62. Found: C, 93.92; H, 5.74.

The second component (ca. 35%) was an off-white component, which from its broad ^1H NMR absorption and high mp appeared to be polymeric; mp >340 °C dec; R_f (CH_2Cl_2, silica gel) 0, R_f (CH_3OH, silica gel) 0.7; IR (KBr) 3700–2800 (br), 1630 (br), 1443, 1220, 1183, 1025 (br), 965 (br), 700 cm^{-1}; NMR ($(CD_3)_2SO$) δ 6.4–7.6 (br); MS, *m/e* 356 ($C_{28}H_{20}$?).

Anal. Calcd for $(C_{14}H_{12}S_xO_{7-2x})_n$: C, 57.53; H, 4.11. Found: C, 57.88; H, 4.48.

Phenylchloroethyne Products. Alkyne (2.73 g, 0.02 mol),[13] SbF_5 (14.5 g, 0.067 mol), and C_6H_6 (5 mL) were used. Reaction time was ca. 1 h at −78 °C, after which the mixture was poured into cold water. From the ether extract a light yellow solid was obtained which on liquid chromatography on silica gel yielded sulfoxide with mp 108–112 °C (74%) or with mp 114–116 °C (64%). After another LC pass or on recrystallization from methylene chloride–heptane, the white 3-phenyl-2-chlorobenzo[*b*]thiophene (**2a**) sulfoxide had the following: mp 116–118 °C (lit.[14] mp 119–122 °C); R_f (CH_2Cl_2, silica gel) 0.5; IR (KBr) 1070, 1040, 800, 765, 752, 701 cm^{-1}; NMR ($CDCl_3$) δ 7.1, ~7.5 (m, 8 H), 7.7–8.0 (m, 1 H); MS, *m/e* 260 (parent $C_{14}H_9ClOS$).

Phenylbromoethyne Products (2b, 3b). Alkyne (5.43 g, 0.03 mol),[13] antimony pentafluoride (18 g), and benzene (5.5 g) were used. The mixing and reaction times were ca. 0.5 and 1 h, respectively, after which the reaction mixture was poured into ice water, neutralized, and extracted with ether. Workup of the ether layer yielded the 2-bromo-3-phenylbenzothiophene sulfoxide (**2b**) (1.46 g, 16%), from benzene–heptane: mp 128–130 °C; IR (KBr) 1072, 1035, 800, 770, 752, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.5 (m, ca. 3 H), 7.55 (br, ca. 5 H), 7.9–8.1 (m, 1 H); MS, *m/e* 304, 306 (parent $C_{14}H_9BrOS$).

Anal. Calcd for $C_{14}H_9BrOS$: C, 55.09; H, 2.95. Found: C, 55.25; H, 3.14.

The water layer from the original reaction was acidified with hydrochloric acid and extracted with ether. After several cycles involving treatment with base and then acid, extraction, and crystallization, the 1-bromo-2,2-diphenylvinylsulfinic acid (**3b**) (6.5 g, 67%), a white solid from ether–heptane, was obtained: mp 107–108 °C; IR (KBr) 3400 (br), 2950 ± 200 (br), 2390 (br), 1090 (br), 825 (br), 795, 765, 745, 700 cm^{-1}; NMR ($CDCl_3$); δ 7.0–7.45; MS, *m/e* 322 (parent $C_{14}H_{11}BrO_2S$).

Anal. Calcd for $C_{14}H_{11}BrSO_2$: C, 52.01; H, 3.4. Found: C, 51.87; H, 3.36.

Sulfoxide 2b from 1-Bromo-2,2-diphenylvinylsulfinic acid (3b). Finely ground zinc chloride (ca. 1 g) was kept under vacuum and heated with a flame. The cooled zinc chloride was dispersed in dry carbon disulfide (20 mL) by heating the mixture at reflux temperature for ca. 30 min. Compound **3b** (280 mg) was added to the stirred suspension at ca. 25 °C under nitrogen. After 30 min, the mixture was heated to reflux temperature for ca. 2 h, cooled, and treated with water and ether. The crude sulfoxide was recrystallized from ether and ether–heptane to yield colorless plates of **2b** (230 mg, 80%), mp 136–137 °C.

The sulfoxide was converted with *m*-chloroperbenzoic acid[14] in ether–chloroform (5:1 v/v) at ca. 25 °C (2 h) and at reflux temperature (2 h) to the colorless sulfone (**5b**) (75% yield), mp 121–122 °C (lit.[15] mp 121–123 °C), from ether–heptane: IR (KBr) 1315 (br), 1162 (br) cm^{-1}; NMR ($CDCl_3$) δ 7.18–7.7 (m, 8 H), 7.7–7.9 (m, 1 H).

Phenylethyne Products (3d). Alkyne (3.06 g, 0.03 mol), antimony pentafluoride (18 g), and benzene (10.4 g) were used. The mixing and reaction times were ca. 25 and 10 min, respectively, after which the reaction mixture was poured into ice water, treated with sodium carbonate, and extracted with ether. By TLC, the solids (0.65 g) in the ether contained at least eight compounds that were not resolved. Workup of the basic water layer yielded a white powder, 2,2-diphenylvinylsulfinic acid (**3d**) (4.69 g, 64%): mp 94–95 °C; IR (KBr) 3400–2200 (br), 1590, 1570, 1493, 1445–1365 (br), 1060–1050 (br), 1020–1000 (br), 942, 880–800 (br), 760, 730, 707, 692 cm^{-1}; NMR ($CDCl_3$) 7.1 (br, ca. 1 H), 7.39 (s, ca. 10 H); 7.8–8.1 (br, ca. 1 H).

Anal. Calcd for $C_{14}H_{12}SO_2$: C, 68.85; H, 4.92. Found: C, 68.53; H, 4.87.

3-Phenylbenzo[*b*]thiophene Oxide (2d) from 2,2-Diphenylvinylsulfinic Acid 3d. Following the procedure used for the bromo compound (**3b**), **3d**, (80 mg) was converted to colorless crystals of **2d** (125 mg, 84%): mp 82–83 °C (lit.[16] mp 83–85 °C); IR (KBr) 1603–1565 (br), 1086, 1060, 1030, 762, 735, 700 (lit.[16] 1560, 1030) cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.8 (9 H), 7.8–8.2 (1 H) (lit.[16] δ 7.52–8.20, 7.00).

The sulfoxide was converted with *m*-chloroperbenzoic acid in chloroform to the sulfone (**5d**) (75% yield), which was recrystallized from ether–petroleum ether; mp 154–157 °C (lit.[17] mp 158–160, 161–163 °C); IR (KBr) 1320, 1158 cm^{-1}; NMR ($CDCl_3$) δ 6.8–6.95 (m, 1 H), 6.95–7.7 (m, 8 H), 7.7–8.0 (m, 1 H).

(*E*)-1-Carboxy-2-(*p*-methoxyphenyl)vinylsulfonic Acid (4). (*p*-Methoxyphenyl)propiolic acid (3.16 g, 0.018 mol) in benzene (10 mL) was added to a mixture of antimony pentafluoride (12 g) and liquid SO_2 (ca. 50 mL) over a period of 30 min. After 30 min reaction, the dark mixture was poured into ice water. An orange solid (2.26 g) was obtained from this mixture by filtration, and more material (1.53 g) was obtained by extraction of the water solution with methylene chloride. A portion of the crude solid acid was dissolved in methylene chloride and then treated with aqueous sodium carbonate; the aqueous part was acidified with hydrochloric acid to regenerate **4** and then extracted repeatedly with ether. (By TLC it was evident that the residue, which was not further purified, had at least 12 components.) The sodium carbonate–hydrochloric acid cycle was repeated several times, after which a white solid (40% yield) was obtained: mp 185–187 °C; IR (KBr) 3300–2500 (br), 1675 (br), 1590, 1505, 1425, 1270–1255 (br), 1178, 1020, 998, 909, 825 cm^{-1}; NMR ($(CD_3)_2SO$) δ 8.08 (s, 1 H), 7.91 (d, 2 H), 7.05 (d, 2 H), 3.8 (s, 3 H). The chemical shift of the vinyl proton provides the basis of the structural assignment.[11]

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Registry No. 1a, 1483-82-5; **1b**, 932-87-6; **1c**, 501-65-5; **1d**, 536-74-3; **2a**, 39561-64-3; **2b**, 81423-90-7; **2c**, 81423-91-8; **2d**, 70445-87-3; **3b**, 81423-92-9; **3d**, 81423-93-0; (*E*)-**4**, 81423-94-1; **5b**, 55118-77-9; **5d**, 27183-55-7; **6**, 201-69-4; **7**, 1055-26-1; (*p*-methoxyphenyl)propiolic acid, 2227-57-8; SbF_5, 7783-70-2; SO_2, 7446-09-5.

Notes

Stereoselective Ketone Reductions: Reduction of 4-*tert*-Butylcyclohexanone by Alkylsilanes in the Presence of Rhodium(I) and Ruthenium(II) Catalysts

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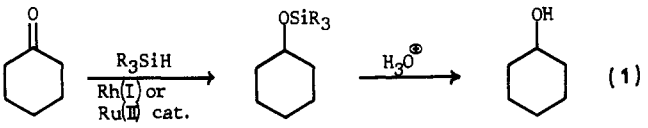
A number of years ago, it was established that ketones undergo facile reduction by alkylsilanes to afford silyl ethers in the presence of homogeneous rhodium(I) or ruthenium(II) catalysts (eq 1).[1-4] The reaction allowed, after



(1)

hydrolysis, the overall transformation of ketones to alcohols which could not be accomplished under mild conditions with molecular hydrogen and similar soluble catalysts.[5,6] In particular, commerically available tris(triphenylphosphine)rhodium(I) chloride and to a lesser extent tris(triphenylphosphine)ruthenium(II) dichloride were reported to be efficient catalysts, providing silyl ethers in high yields and under mild, neutral conditions. These attractive features notwithstanding, the reaction has rarely been used for the reduction of ketones and aldehydes.

A brief study of menthone and camphor showed remarkable stereochemical control.[1d] Bulky trialkylsilanes gave predominantly the more stable reduction product, and the mono- or dialkylsilanes gave predominantly the less stable reduction product. This limited set of data was suggestive of a powerful method for stereoselective reductions, where the product configuration could be varied by choosing the appropriate silane, but it has not been pursued.[7] Here we report an examination of the reduction of a standard test case, 4-*tert*-butylcyclohexanone, using di- and trialkylsilanes in an effort to define the optimum conditions for high stereoselectivity and the variables which influence selectivity.

Table I. Rh(I)-Catalyzed Hydrosilylation of 4-*tert*-Butylcyclohexanone[a]

entry	silane	temp, °C	time, h	Ax/Eq ratio[b]
1	Et_3SiH	25	144	33:67
2	Et_3SiH	45	20	23:77
3	Et_3SiH	80	3	11:89
4	Et_3SiH	110	1.5	12:88[c]
5	Ph_3SiH	25	64	19:81[e]
6	Ph_3SiH	80	24	12:88
7	$PhMe_2SiH$	80	12	29:71
8	$(EtO)_3SiH$	80	20	29:71[d]
9	Cl_3SiH	80	18	37:63[e]
10	Et_2SiH_2	25	0.25	46:54
11	Ph_2SiH_2	25	0.25	57:43

[a] Reactions were performed by using 2 mol % of tris(triphenylphosphine)rhodium(I) chloride, 1.5 equiv of the alkylsilane, and 1 equiv of 4-*tert*-butylcyclohexanone in benzene solution. [b] Ratios determined by GLC analysis of the derived alcohols after hydrolysis (catalyst *p*-TsOH·H_2O/aqueous MeOH/25 °C/1 h) of the crude silyl ethers. [c] Toluene solvent. [d] A major side reaction was the formation of the silyl enol ether. [e] Reaction was <20% complete.

Results and Discussion

(A) Tris(triphenylphosphine)rhodium(I) Chloride Catalyst. The results obtained from the reduction of 4-*tert*-butylcyclohexanone by various di- and trialkylsilanes in the presence of tris(triphenylphosphine)rhodium(I) chloride are shown in Table I. The reactions were conducted in benzene solution[8] by using 1.5 molar equiv of the alkylsilane and 2 mol % of the rhodium catalyst. In general, the reductions with trialkylsilanes (entries 1–7) required heating at 80 °C to obtain reasonable reaction rates. In most cases these reactions were incomplete (60–90% conversion), using only 2 mol % of the catalyst. Increasing the amount of catalyst to 5 mol % gave essentially complete consumption of starting ketone in the case of triethylsilane and dimethylphenylsilane. The addition

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(2) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* **1973**, 38.

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(5) Review: Birch, A. J.; Williamson, D. H. *Org. React.* **1976**, *24*, 1.

(6) For hydrosilylations of ketones with platinum catalysts see: (a) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1972**, *46*, C65. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *Ibid.*, **1976**, *112*, 253.

(7) An isolated report of the hydrosilylation of 4-*tert*-butylcyclohexanone by a rhodium catalyst has appeared although the stereochemistry of the product is not clear; see: Bottrill, M.; Green, M. *J. Organomet. Chem.* **1976**, *111*, C6.

(8) Ojima's work generally was performed without solvent.

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