**Table I. Reaction of Keto Aldehydes 1 with *N*-Phenylhydroxylamine (2)**[a]

| keto aldehyde | products (% yield) | recovered 1 (%) |
|---|---|---|
| **1a** | **4a** (57) | **1a** (35) |
| **1b** | **4b** (56) | **1b** (32) |
| **1c** | **4c** (65),[b] **5** (30) | **1c** (3) |
| **1d** | **4d** (36) | **1d** (50) |
| **1e** | **4e** (47)[c] | **1e** (30) |
| **1f** | **3f** + **4f** (46), **6** (12) | **1f** (25) |

[a] A mixture of a keto aldehyde **1** (2 mmol) and **2** (2 mmol) in ethanol (20 mL) was kept with stirring at room temperature for 15 h. [b] The exo:endo ratio = 68:32. [c] The exo:endo ratio = 67:33.

**Reaction of Keto Aldehydes 1a–e with *N*-Phenylhydroxylamine (2).** An equimolar mixture of **1a** (2 mmol) and **2** (2 mmol) in ethanol (20 mL) was kept with stirring at room temperature for 15 h. The mixture was poured into water and extracted with ether. Then, the crude products were column chromatographed on silica gel. Elution with benzene–hexane (1:1 v/v) yielded the 1,4,2-dioxazolidine **4a** (57% yield): mp 147–148 °C (from ether–hexane); $^{1}$H NMR (CDCl$_3$) $\delta$ 6.26 (s, 1 H), 6.4–8.0 (m, 16 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 97.63 (1 C), 108.17 (1 C), 118.82–137.07 (21 C), 151.12 (1 C); IR 1600, 1490, 1450, 1070, 960, 780, 725, 700 cm$^{-1}$. Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.26; H, 4.95; N, 3.76.

The reactions of **1b–e** were undertaken under similar conditions. **4b**: mp 145–146 °C (from ether–hexane); $^{1}$H NMR (CDCl$_3$) $\delta$ 2.35 (s, 3 H), 6.41 (s, 1 H), 7.0–7.9 (m, 11 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.06 (1 C), 96.83 (1 C), 106.56 (1 C), 117.71–135.96 (17 C), 151.27 (1 C); IR 1595, 1485, 1310, 1090, 960, 810, 775 cm$^{-1}$. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.83; H, 5.15; N, 4.80. **4c**: a 2:1 mixture of the exo and endo isomer; mp 129–131 °C (from ether–hexane); $^{1}$H NMR (CDCl$_3$) $\delta$ 4.54 (s, exo), 4.94 (d, $J$ = 4 Hz, endo), 5.56 (d, $J$ = 4 Hz, endo), 5.62 (s, exo), 6.5–7.9 (19 H);[9] IR 1600, 1490, 1450, 985, 750, 695 cm$^{-1}$. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.77; H, 5.30; N, 3.44. **4d**: mp 197–198 °C (from methylene chloride–hexane); $^{1}$H NMR (CDCl$_3$) $\delta$ 6.67 (s, 1 H), 6.69 (s, 1 H), 7.1–8.0 (m, 13 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 100.39 (1 C), 105.48 (1 C), 116.33–136.44 (19 C), 149.92 (1 C); IR 1595, 1485, 1440, 1300, 1060, 825, 760 cm$^{-1}$. Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31. Found: C, 81.21; H, 4.61; N, 4.28. **4e**: a 2:1 mixture of the exo and endo isomer: mp 155–156 °C (from ethanol); $^{1}$H NMR (CDCl$_3$) $\delta$ 4.51 (s, 1 H), 6.18 (s, endo), 6.32 (s, exo), 7.1–8.0 (m, 19 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 55.14 (exo), 57.61 (endo), 96.49 (exo), 96.54 (endo), 109.48 (endo), 110.03 (exo), 118.07–140.19 (complex signals exo + endo), 150.59 (exo), 150.88 (endo); IR 1595, 1485, 1450 cm$^{-1}$. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 83.07; H, 5.36; N, 3.57. A vinyl ether **5**: an oil; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.21 (t, $J$ = 7 Hz, 3 H), 3.6–4.2 (m, 2 H), 6.66 (s, 1 H), 6.8–7.6 (m, 14 H).

**Reaction of a Keto Aldehyde 1f with *N*-Phenylhydroxylamine.** An equimolar mixture of **1f** (2 mmol) and **2** (2 mmol) in ethanol (20 mL) was kept with stirring at 20 °C for 15 h. After evaporation of the solvent, the $^{1}$H NMR spectra of the crude products were measured, which showed the existence of both the nitrone **3f** and the 1,4,2-dioxazolidine **4f**. Column chromatography of the crude products on silica gel (elution with benzene–hexane, 1:1, v/v) gave the vinyl ether **6**: an oil; $^{1}$H NMR (CCl$_4$) $\delta$ 1.20 (t, $J$ = 7 Hz, 3 H), 3.3–3.7 (m, 2 H), 6.66 (s, 1 H), 6.8–7.6 (m, 14 H). From the second fraction (elution with ether–benzene, 1:1, v/v) was obtained a mixture of the keto nitrone **3f** and the dioxazolidine **4f**, the **3f**:**4f** ratio in CDCl$_3$ being ca. 2:1: mp 174–178 °C (from ethanol); IR 1680, 1595, 1550, 1345, 1210, 1070, 750, 685 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 3.23 (d, $J$ = 18 Hz, **4f**), 3.50 (d, $J$ = 18 Hz, **4f**), 4.41 (s, **3f**), 6.23 (s, **4f**), 7.0–8.1 (m), 8.13 (s, **3f**), 9.18–9.33 (m); $^{13}$C NMR (CDCl$_3$) $\delta$ 40.51 (**4f**), 44.21 (**3f**), 96.12 (**4f**), 108.02 (**4f**), 118.06–138.28 (complex signals, **3f** + **4f**), 149.47 (**3f**), 150.84 (**4f**), 197.34 (**3f**). Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.08; H, 5.33; N, 4.32.

**Acknowledgment.** We appreciate the financial support from the Ministry of Education, Japan (Gr. No. 63550647) for the measuring of $^{13}$C NMR spectra, mass spectra, and FT-IR spectra with JEOL JNM-GSX-400, JEOL JMS-DX303, and JEOL JIR-AQS20M instrument, respectively.

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[9] The assignment of the stereochemistry was based on the fact that for the relevant exo-endo 1,3-diphenylindene ozonide and exo–endo 2,3-diphenylindene ozonide the same relation holds for the chemical shift and coupling constant between the exo and endo protons attached to the phenyl substituent in $^{1}$H NMR spectra: Miura, M.; Nojima, M.; Kusabayashi, S.; McCullough, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 2932.

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# Synthesis of Aryl-Substituted Sulfonium Salts by the $P_2O_5$–Methanesulfonic Acid Promoted Condensation of Sulfoxides with Aromatic Compounds

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Interest in aryl-substituted sulfonium salts in this laboratory has stemmed from the observation that such compounds are highly photosensitive and can be used as efficient photochemical sources of strong Brønsted acids.[1,2] This discovery has led to extensive use of triarylsulfonium salts as photoinitiators in cationic vinyl and ring-opening polymerizations and in the design of novel microelectronic photoresists. More recently, we have been exploring the relationship between the structure of various sulfonium salts and their photosensitivity and spectral response. These efforts have prompted a number of attempts from this and other laboratories to discover new methods for the synthesis of photoactive aryl-substituted sulfonium salts.

A considerable number of synthetic routes have been derived for the preparation of symmetric and asymmetric aryl-substituted sulfonium salts. Several excellent reviews of the subject reflect the current state of activity in this field.[3–6] Of particular note is the recent report by Julia and co-workers[7] of the facile synthesis of alkyldiarylsulfonium salts by the acid-catalyzed alkylation of diphenyl sulfide with alcohols and ethers. In previous communications from this laboratory, we described the preparation of triarylsulfonium salts in high yields by the copper-catalyzed condensation of diaryliodonium salts with diaryl sulfides[8] and with aryl thiols.[9] In general, currently available synthetic methods for the preparation of aryl-substituted sulfonium salts suffer from low yields, utilize unavailable starting materials, or involve complex multistep procedures. Because of the ready availability of diaryl sulfides and diaryl sulfoxides, most syntheses of aryl-substituted sulfonium salts rely on the use of these compounds as substrates. For example, unsymmetrical aryl-substituted sulfonium salts in moderate yields can be prepared by the condensation of diaryl sulfoxides with aryl and alkyl Grignard reagents in the presence of trialkylsilyl triflates.[10] Triarylsulfonium salts can also be synthesized by the condensation of diaryl sulfoxides with aromatic hydrocarbons in the presence of aluminum chloride or sulfuric acid.[11–14] However, the low yields and restrictions placed on substrates due to the harsh reaction conditions employed severely restrict the generality of this method.

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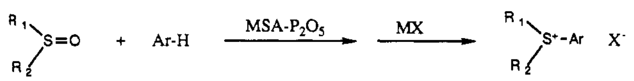
**Table I.[a] Synthesis of Triarylsulfonium Salts $(R_1)_2S^+{-}R_2X^-$**

| $R_1$ | $R_2$ | $X^-$ | yield, % | mp, °C (lit.) | $\lambda_{max}$ (ε) | | elemental analysis | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | % C | % H | % S |
| $C_6H_5$ | 4-$C_6H_4OCH_3$ | $SbF_6^-$ | 87 | 135–136 | 260 | calc: | 43.10 | 3.21 | 6.05 |
| | | | | | (16700) | fnd: | 43.02 | 3.41 | 6.02 |
| $C_6H_5$ | 4-$C_6H_4OCH_3$ | $AsF_6^-$ | 88 | 143–145 | – | calc: | 47.30 | 3.53 | 6.64 |
| | | | | | | fnd: | 47.11 | 3.59 | 7.01 |
| $C_6H_5$ | 4-$C_6H_4OC_2H_5$ | $PF_6^-$ | 76 | 102–103 | 261 | calc: | 53.10 | 4.20 | 7.08 |
| | | | | | (17100) | fnd: | 53.40 | 4.31 | 7.56 |
| $C_6H_5$ | 4-$C_6H_4OC_8H_{17}$ | $PF_6^-$ | 74 | 95–97 | 262 | calc: | 58.21 | 5.78 | 5.97 |
| | | | | | (18600) | fnd: | 58.21 | 5.80 | 6.10 |
| $C_6H_5$ | 4-$C_6H_4OC_{10}H_{21}$ | $SbF_6^-$ | 50 | 70–72 | 262 | calc: | 51.30 | 5.34 | 4.89 |
| | | | | | (17600) | fnd: | 51.27 | 5.44 | 4.66 |
| $C_6H_5$ | 4-$C_6H_4OC_{10}H_{21}$ | $PF_6^-$ | 99 | 103–105 | 262 | calc: | 59.57 | 6.21 | 5.67 |
| | | | | | (18200) | fnd: | 59.74 | 6.32 | 6.00 |
| $C_6H_5$ | 4-$C_6H_4OC_{12}H_{25}$ | $SbF_6^-$ | 76 | 79–82 | 262 | calc: | 52.71 | 5.71 | 4.69 |
| | | | | | (18100) | fnd: | 52.70 | 5.89 | 4.92 |
| $C_6H_5$ | 4-$C_6H_4OC_{18}H_{37}$ | $SbF_6^-$ | 98 | 92–95 | 262 | calc: | 56.32 | 6.65 | 4.17 |
| | | | | | (17400) | fnd: | 56.02 | 6.79 | 4.55 |
| $C_6H_5$ | 4-$C_6H_4SC_6H_5$ | $SbF_6^-$ | 90 | 118–119 | 246, 305 | calc: | 47.59 | 3.14 | 10.58 |
| | | | | (118–119)[15] | (25500, 17700) | fnd: | 47.58 | 2.95 | 10.69 |
| $C_6H_5$ | 2-$C_6H_3SC_6H_4$ | $SbF_6^-$ | 19 | 184–185 | 235, 267, 330 | calc: | 47.60 | 2.81 | 10.58 |
| | (2-dibenzothienyl) | | | | (45800, 30400, 3500) | fnd: | 47.90 | 2.81 | 10.53 |
| $C_6H_5$ | 4-$C_6H_4OC_6H_5$ | $PF_6^-$ | 76 | 110–111 | 267 | calc: | 57.60 | 3.80 | 6.40 |
| | | | | | (18700) | fnd: | 57.31 | 3.86 | 6.77 |
| $C_6H_5$ | 4-$C_6H_4C(CH_3)_3$ | $PF_6^-$ | 37 | 136–140 | 237 | calc: | 56.90 | 4.96 | 6.90 |
| | | | | (133–136)[8] | (15900) | fnd: | 56.80 | 4.86 | 7.04 |
| $C_6H_5$ | 3,5-$(CH_3)_2$-4-$HOC_6H_2$ | $PF_6^-$ | 37 | 155–165 | 268 | calc: | 53.10 | 4.20 | 7.08 |
| | | | | | (11600) | fnd: | 53.13 | 4.17 | 6.99 |
| $C_6H_5$ | 2-$C_4H_3S$ | $PF_6^-$ | 51 | 177–183 | 268 | calc: | 46.30 | 3.14 | 15.46 |
| | | | | | (10300) | fnd: | 46.80 | 3.12 | 15.75 |
| $CH_3$ | 4-$C_6H_4OCH_3$ | $PF_6^-$ | 47 | 74–90 | 244 | calc: | 34.39 | 4.14 | 10.19 |
| | | | | | (10200) | fnd: | 34.42 | 4.19 | 10.14 |
| c-$C_4H_8$ | 4-$C_6H_4OCH_3$ | $PF_6^-$ | 59 | 104–106 | 246 | calc: | 38.82 | 4.41 | 9.41 |
| | | | | | (11000) | fnd: | 38.90 | 4.49 | 9.35 |

[a] Reactions were carried out using 0.05 mol of sulfoxide and aromatic compound in 20 mL of 1:10 $P_2O_5$/MSA at 20–40 °C for 1–3 h.

Recently, Smith and Olofson[15] have investigated the condensation of diphenyl sulfoxide with aromatic compounds in the presence of phosphorus pentoxide to give triarylsulfonium salts. Again, in this case, yields are low. When the latter reaction was examined in this laboratory, it appeared that the major source of the low yields was the heterogeneity of the reaction medium due to the insolubility of the phosphorus pentoxide in the reaction mixture. Our attempts to replace $P_2O_5$ with polyphosphoric acid (PPA) met with similar results due again to the difficulty in obtaining homogeneous reaction conditions. Eaton and his co-workers[16] have recently reported that a 1:10 solution of phosphorus pentoxide in methanesulfonic acid ($P_2O_5$/MSA) is a convenient strong acid and dehydrating reagent which can be used in place of PPA in many reactions. They have pointed out that among the advantages of this reagent are the general solubility of organic compounds in this mixture, its low viscosity, and the simplicity of work up of reactions carried out using this new reagent. In addition, we have noted that sulfonation of electron-rich aromatic compounds which can occur with methanesulfonic acid in the presence of $P_2O_5$[17] are avoided by carrying out reactions in this reagent at temperatures from 25–60 °C. Presumably, $P_2O_5$ reacts on dissolution in MSA to generate mixed anhydrides which are responsible for its superior reactivity in such reactions as the intramolecular acylation of olefin acids and the Beckmann rearrangement of amides which are normally carried out in PPA.[16]

Accordingly, it was decided to attempt the condensation of dialkyl and diaryl sulfoxides with aromatic compounds in the presence of $P_2O_5$/MSA (eq 1). Table I gives the results of our investigations. All the sulfonium salts appearing in this table were thoroughly characterized by means of their $^1H$ and $^{13}C$ NMR and UV spectra and, in some cases, by secondary ion mass spectroscopy (SIMS). Their melting points were compared with those of the



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authentic compounds prepared by alternate methods, and in nearly all cases, satisfactory elemental analyses were obtained.

Typically, reaction proceeds rapidly and homogeneously under very mild conditions. Simply, mixing the dialkyl or diaryl sulfoxide with the aromatic compound at 25 °C in the presence of $P_2O_5$/MSA is accompanied by the liberation of heat and in many cases the immediate formation of red and purple solutions which are presumed to be due either to Meisenheimer or charge-transfer complexes. Colored solutions were not observed when either the sulfoxides or aromatic substrates were dissolved alone in $P_2O_5$/MSA. As the condensation proceeds, the color is usually discharged with the formation of colorless to pale green or yellow solutions. Reaction times range from 1 to 3 h at 25–65 °C depending on the nature of the aromatic substrate employed. Reactions carried out at temperatures above 65 °C showed the presence of dark byproducts due to side reactions which take place under these conditions.

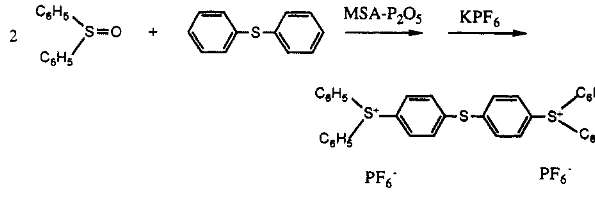
In his studies of the intermolecular acylation of lactones to give cyclopentanones, Eaton and his co-workers[15] observed that it was necessary to purify the methanesulfonic acid by distillation prior to formation of the $P_2O_5$/MSA reagent to obtain good yields. The yields of sulfonium salts from the condensation of dialkyl and diaryl sulfoxides with aromatic compounds appear to be only slightly reduced if the methanesulfonic acid was not purified by distillation prior to the reaction. However, as a routine measure, the methanesulfonic acid used in the experiments described in this communication was distilled prior to use. Optimization studies carried out using diphenyl sulfoxide and anisole as substrates showed that the best yields were obtained using equimolar amounts of the latter reagents together in a solution of a 1:10 mixture of $P_2O_5$ dissolved in MSA. Under these conditions, the reaction was complete within 1 h at 35–45 °C or 3 h at 25 °C. Typical yields of diphenyl(4-methoxyphenyl)sulfonium salts isolated after metathesis with either $NaSbF_6$, $KPF_6$, or $KAsF_6$ range from 85 to 90%. Attempts to replace $P_2O_5$ with acetic anhydride in this reaction resulted in greatly lowered yields (7–9%).

The sulfonium salts shown in Table I were isolated by pouring the reaction mixtures into water followed by adding 1 equiv of an alkali or an alkaline earth salt of the desired anion (MX in eq 1) to precipitate the water-insoluble sulfonium salt. Purification consisted of washing the solid or semisolid impure salt several times first with water and then with ethyl ether to remove the inorganic and organic starting materials. The sulfonium salts isolated at this point were in many instances analytically pure compounds. Where further purification was required, a single recrystallization, from either ethanol or 2-propanol, or trituration of a dichloromethane solution of the salt with ether was sufficient. In some cases, where dark colored products contaminated the product, purification could be accomplished by passing a dichloromethane solution of the crude reaction mixture through a column of silica gel or neutral alumina. Usually, an anion of low nucleophilic character is desired for sulfonium salts intended for use as photoinitiators for cationic polymerization since on photolysis these compounds generate the strongest acids. Thus, most commonly, salts containing the $PF_6^-$, $AsF_6^-$, or $SbF_6^-$ anions were prepared, although on occasion, the corresponding triflates, fluoroborates, and perchlorates were likewise synthesized.

Since the protonated sulfoxide is a comparatively weak electrophile, the reaction is best applied to aromatic substrates bearing activating electron-donating substituents such as phenols, alkyl aryl ethers, and alkylbenzenes. When phenols and other easily oxidized polynuclear aromatic compounds such as pyrene and triphenylene are used as substrates, electrophilic substitution is accompanied by oxidation to produce quinones and other dark colored byproducts. As the electron density of the aromatic substrate is decreased by substitution with electron-withdrawing groups, the temperature must be raised and the reaction time lengthened to obtain acceptable yields. Thus, while toluene, benzene, biphenyl, and halobenzenes give good to fair yields of triarylsulfonium salts with diphenyl sulfoxide in the presence of $P_2O_5$/MSA, only very low yields of sulfonium salt products were obtained when nitrobenzene was used as the substrate. Of particular interest in this work was the preparation of triarylsulfonium salts bearing alkyl and alkoxy substituents. Variations in the number and length of the alkyl and alkoxy groups allow one to vary both the UV absorption and the solubility characteristics. For example, diphenyl(4-octadecyloxyphenyl)sulfonium salts have their $l_{max}$ at 262 nm in the UV and are soluble in toluene while the corresponding triphenylsulfonium salts absorb at 237 nm and are insoluble in all aromatic hydrocarbons. As shown in Table I, condensation of diphenyl sulfoxide with aromatic compounds bearing electron donating substituents proceeds with considerable regioselectivity. In these cases, only the 4-isomers are isolated as the sole products of the reaction. This is presumably due to the large steric requirements of the reactive electrophile, i.e. the protonated sulfoxide. As a result of this regioselectivity, such sulfonium salts are usually highly crystalline and the isolated yields are typically high. When other substrates possessing less activating substituents or when less bulky sulfoxides are employed, considerable ortho as well as para substitution is observed by $^{13}C$ NMR spectroscopy. In such cases, the yields of the 4-substituted isomers are lowered due to difficulties encountered in the isolation and purification steps. Blocking of the 2- and 6-positions of phenol with methyl groups resulted in a good yield of the desired (3,5-dimethyl-4-hydroxyphenyl)diphenylsulfonium salt, whereas phenol itself gave a mixture of isomeric and oxidized products which could not be purified. It is interesting to note that SIMS provides a convenient method for the confirmation of structures of aryl-substituted sulfonium salts including even the higher molecular weight members of the series of alkoxy-substituted triarylsulfonium salts. For example, the 4-(octyloxy)- and 4-(octadecyloxy)-substituted triphenylsulfonium hexafluorophosphate salts show molecular ions at 391 and 531 amu, respectively, corresponding to the mass of their sulfonium cations.

When the dialkyl sulfoxides, dimethyl sulfoxide, and tetramethylene sulfoxide, were substituted for diaryl sulfoxides in the above reaction, the corresponding aryldialkylsulfonium salts were obtained in good to excellent yields. These reactions proceeded smoothly and exothermically at temperatures from 50 to 60 °C.

Condensation of a 2:1 stoichiometric ratio of diphenyl sulfoxide and diphenyl sulfide resulted in the isolation in 30% yield of the bissulfonium salt, bis[4-(diphenylsulfonio)phenyl] sulfide bishexafluorophosphate.[18]



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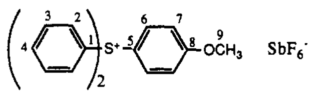
All the aryl-substituted sulfonium salts shown in Table I are photoactive and when irradiated in the presence of cationically polymerizable monomers, rapidly and exothermically initiated polymerization.

In conclusion, the use of $P_2O_5$/MSA in the condensation of dialkyl and diaryl sulfoxides with aromatic compounds substituted with electron-donating substituents provides a simple, one-pot synthesis of aryl-substituted sulfonium salts in good to excellent yields. In addition to the preparation of laboratory quantities of these salts, selected sulfonium salts have been successfully synthesized on a pilot plant scale.

## Experimental Section

**General Procedure for the Preparation of Sulfonium Salts: Diphenyl(4-methoxyphenyl)sulfonium Hexafluoroantimonate.** A mixture of 10.1 g (0.05 mol) of diphenyl sulfoxide and 5.4 g (0.05 mol) of anisole was placed in a 125-mL flask equipped with a thermometer and magnetic stirrer. To this mixture was added 20 mL of freshly prepared $P_2O_5$/MSA reagent,[18] and the reaction flask was loosely stoppered to restrict the exposure to atmospheric moisture. The color of the solution rapidly became deep purple, and the temperature rose to 55 °C. After the exotherm had subsided, the reaction mixture was stirred at 40 °C for 3 h and then poured into 200 mL of distilled water. To the slightly turbid solution there was then added 12.95 g (0.05 mol) of $NaSbF_6$, and a pale yellow oil separated which crystallized on standing. The product was isolated by filtration, washed first with water and then ether, and dried at 25 °C in vacuo to give 25.4 g (96%) or nearly pure (by $^1$H NMR) diphenyl(4-methoxyphenyl)sulfonium hexafluoroantimonate. The product was recrystallized from 2-propanol to give the pure sulfonium salt (73% yield), mp 135–136 °C.



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# Effect of a Proximate Phenyl Ring on Additions to Bridged Ketones

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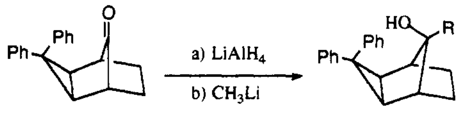
Participation by a remote phenyl group has been reported for solvolysis of *exo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane derivatives[2] and for some addition reactions of *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene.[3]

In order to further probe the effects of remote phenyl groups, we have examined several addition reactions of a series of 3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octan-6- and -8-ones. The *exo*-8-ketone **1** was prepared previously,[4a] and diimide reduction of the double bond in *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-en-*syn*-8-ol[5] followed by oxidation of the saturated alcohol afforded *endo*-8-ketone **5**.

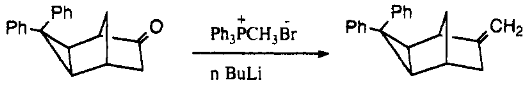
Reaction of **1** with lithium aluminum hydride gave the *syn*-alcohol **2a** exclusively and with methyllithium gave predominantly the *syn*-alcohol **2b**[4a] as shown in eq 1. In contrast, **1** did not react with toluene methyl isocyanide (TosMic),[6] with methyl Grignard,[7] or with the usual Wittig reagent.[8] On the other hand, *exo*-6-ketone **3**[9] reacted readily with the triphenylphosphonium methylide reagent to give the 6-methylene product 4 (eq 2).



1 2 (1)

a) R=H (84%)

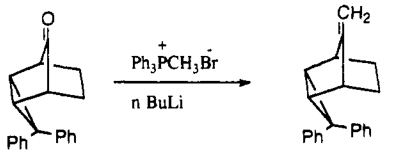
b) R=CH$_3$ (79%)



3 4 (2)

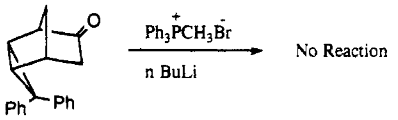
(68%)

The unhindered carbonyl in the *endo*-8-ketone **5** reacts readily with the usual ylide reagent to produce methylene derivative **6**, while the *endo*-6-ketone[4b] **7** did not react under a number of methylenation conditions[10] (eqs 3 and 4).



5 6 (3)

(57%)



7 (4)

The decreased reactivity or *exo*-8-ketone **1** and *endo*-6-ketone **7** toward Wittig, Grignard, anddTosMIC reagents is interesting. The steric bulk of the phenyl rings which, although attached to a remote carbon are spatially proximate, would restrict approach from one side. This is not, however, simply a problem of restricted approach by

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[2] Wilt, J. W.; Malloy, T. P.; Mookerjee, P. K.; Sullivan, D. R. *J. Org. Chem.* **1974**, *39*, 1327.

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[5] Wilt, J. W.; Sullivan, D. R. *J. Org. Chem.* **1975**, *40*, 1036.

[6] Bull, J. R.; Tuinman, A. *Tetrahedron* **1975**, *21*, 2151. The TosMIC reagent (Aldrich) and ketone 1 dry DME were cooled to 0 °C potassium *tert*-butoxide in DME/*tert*-butyl alcohol was added, and the solution allowed to warm to room temperature overnight.

[7] Methylmagnesium bromide (3 M in ether, Aldrich) was diluted with dry THF, ketone 1 added in a minimum volume of THF, and the solution refluxed overnight.

[8] Wittig, G.; Schoellkopf, U. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 751. A solution of ketone 1 was added to triphenylphosphorane reagent prepared from *n*-butyllithium in THF. The solution was refluxed for 8 h and then stirred for 12 h.

[9] Wilt, J. W.; Malloy, T. P. *J. Org. Chem.* **1973**, *38*, 277.

[10] The following Wittig conditions were tried at several concentrations and temperatures without success: *n*-butyllithium in ether,[8] *tert*-butyllithium recommended for hindered ketones.[11a] Silyl-substituted organometallics[11b,c] were also unreactive. Other conditions[11d] such as the Tebbe reagent[11e] were not tried.