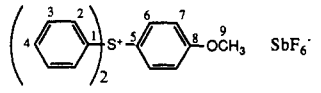
All the aryl-substituted sulfonium salts shown in Table I are photoactive and when irradiated in the presence of cationically polymerizable monomers, rapidly and exothermically initiated polymerization.

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,[16] 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 ^1H 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

Mehboob Peeran,[1a] James W. Wilt,[1b] Michael D. Tufano, Ramakrishnan Subramanian, and David S. Crumrine*

Department of Chemistry, Loyola University of Chicago, 6525 North Sheridan Road, Chicago, Illinois 60626

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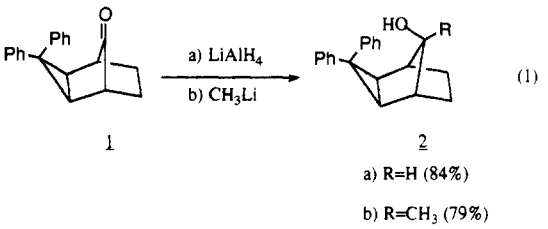
Participation by a remote phenyl group has been reported for solvolysis of *exo*-3,3-diphenyltricyclo-[3.2.1.$0^{2,4}$]octane derivatives[2] and for some addition reactions of *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene.[3]

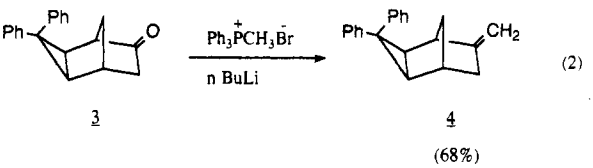
In order to further probe the effects of remote phenyl groups, we have examined several addition reactions of a series of 3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octan-6- and -8-ones. The *exo*-8-ketone **1** was prepared previously,[4a] and diimide reduction of the double bond in *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-en-*syn*-8-ol[5]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



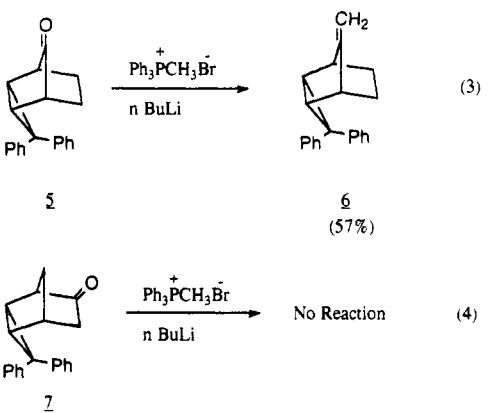
(1)

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).



(2)

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).



(3)

(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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(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.

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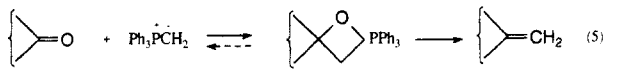
(10) The following Wittig conditions were tried at several concentrations and temperatures without success: *n*-butyllithium in ether,[8] *tert*-butyllithium recommended for hindered ketones.[11a] Silyl-substituted organometallics[11b,c] were also unreactive. Other conditions[11d] such as the Tebbe reagent[11e]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

reagents, but of steric hindrance to rehybridization. If the rate-determining transition states occur after the sp^2-hybridized ketones have begun to rehybridize toward sterically more demanding sp^3 intermediates, the energy of the transition states could be quite high.

Inspection of models suggests that the phenyl rings are very close to the carbonyls and would restrict movement of the oxygen atom during rehybridization. Formation of the *syn*-alcohols from the *exo*-8-ketone 1, for example, would require increased distance between the C-8 bridge and the *syn*-phenyl, and thus molecular reorganization must occur. The potentially reversible additions of phosphorus ylides[11d] would be sensitive to such constraints (eq 5). The decreased reactivity of these ketones constrasts with that of ditriptycyl ketone where low reactivity[12] is caused by hindrance to reagent approach not rehybridization.



The lower IR absorption of the carbonyl group in the diphenyl-*exo*-8-ketone 1 (1750 cm^{-1}) in comparison to the unsubstituted *exo*-8-ketone (1794 cm^{-1})[13] suggests that π overlap with the proximate phenyl ring has diminished the electrophilic nature of the carbonyl group, thus rendering it less reactive to less nucleophilic reagents.

The reactions of the *exo*-8-ketone 1 with lithium aluminum hydride and methyllithium must involve earlier transition states that are less affected by steric problems of rehybridization. These bridged ketones with proximate phenyls appear to be good probes of transition-state timing in carbonyl additions.

Experimental[14] Section

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-*syn*-8-ol.** To *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-en-*syn*-8-ol[5] (516 mg, 2.0 mmol) in 20 mL of methanol, under nitrogen, in a three-necked flask fitted with a condenser and a barium hydroxide trap, was added freshly prepared potassium azodicarboxylate[15] (0.75 g, 3.9 mmol) with stirring. A solution of glacial acetic acid (0.4 mL in 5 mL of methanol) was then added dropwise over a period of 30 min, and stirring was continued for 1 h. Then, 100 mL of cold water was added and the mixture was repeatedly extracted with hexane. The hexane solution was dried ($MgSO_4$). Concentration afforded the desired *endo-syn*-8-alcohol as a white solid: 480 mg (87%); mp 204-205 °C; ^1H NMR δ 7.03-7.90 (10 H, m, ArH), 4.30 (1 H, br s, H_8), 2.38 (2 H, br s, $H_{1,5}$), 2.13-2.33 (3 H, m, $H_{2,4}$ and OH), 1.23 (4 H, br s, $H_{6,7}$); IR 3500-3380, 2980, 1600, 1500, 1450, 1410 cm^{-1}; ^{13}C NMR δ 141.9 (Ar ipso), 125.96, 126.51, 127.39, 127.60, 128.41, 130.80 (Ar), 96.03 (C_8), 58.75 (C_3), 43.20 ($C_{1,5}$), 32.22 ($C_{2,4}$), 22.46 ($C_{6,7}$). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.89; H, 7.26.

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-8-one (5).** Pyridinium chlorochromate oxidation[16] of 138 mg (0.5 mmol) of the *endo-syn*-8-alcohol produced 113 mg (83%) of ketone 5: mp 173.5-174.5 °C; ^1H NMR δ 7.03-7.87 (10 H, m, ArH), 2.63 (2 H, br s, $H_{1,5}$), 1.93 (2 H, t, J = 3 Hz, $H_{2,4}$), 1.4 (4 H, s, $H_{6,7}$); IR 3000, 1770, 1600, 1500, 1450 cm^{-1}; ^{13}C NMR δ 199.69 (C=O), 148.79, 140.61 (Ar ipso), 126.42, 126.94, 127.61, 127.81, 128.59, 130.48 (Ar), 46.47 (C_3), 41.12 ($C_{1,5}$), 20.45 ($C_{2,4}$), 19.64 ($C_{6,7}$). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.57; H, 6.65.

8-Methylene-*endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane (6). In a flame-dried, three-necked flask, equipped with a magnetic stirrer and a reflux condenser, under nitrogen was placed triphenylmethylphosphonium bromide (680 g, 1.95 mmol) along with 30 mL of anhydrous ether. Standardized *n*-butyllithium[17] (1.8 mL, 1.95 mmol) was introduced by syringe through a septum while the flask was kept at 0 °C and the mixture was stirred for 1.5 h. To the yellow suspension of the ylide was added a solution of 5 (180 mg, 0.65 mmol) in 5 mL of anhydrous ether. After overnight reflux, 20 mL of cold water was carefully added until the precipitate completely dissolved, and the resulting solution was extracted with ether. The ether solution was dried ($MgSO_4$), concentrated, and subjected to rotational TLC with hexane-ether eluent. The alkene 6 (100 mg, 57%) was obtained as white crystals: mp 152-153.5 °C; ^1H NMR δ 6.97-7.83 (10 H, m, ArH), 4.23 (2 H, s, H_9), 2.77 (2 H, br s, $H_{1,5}$), 1.97 (2 H, t, J = 3 Hz, $H_{2,4}$), 1.27 (4 H, br s, $H_{6,7}$); IR 3020, 2980, 1685, 1600, 1500, 1450 cm^{-1}; ^{13}C δ NMR 140.76, 150.23 (Ar ipso), 125.78, 126.46, 127.33, 127.57, 128.26, 130.94 (Ar), 167.28 (C_8), 89.50 (C_9), 55.12 (C_3), 42.23 ($C_{1,5}$), 31.24 ($C_{2,4}$), 24.32 ($C_{6,7}$). Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.25; H, 7.58.

6-Methylene-*exo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octane (4). The procedure used to prepare 6 was applied to *exo*-6-ketone 3 to afford white crystals (120 mg, 68%) of alkene 4: mp 81.5-83.5 °C; ^1H NMR δ 7.35 (5 H, pseudo s, ArH), 7.23 (5 H, pseudo s ArH), 4.90 (1 H, s, H_{9a}), 4.60 (1 H, s, H_{9b}), 2.95 (1 H, s, H_5), 2.60 (1 H, s, H_1), 2.10 (1 H, s, H_7), 1.60 (2 H, s, $H_{2,4}$), 0.65 (2 H, s, H_8); IR 3000, 2950, 1680, 1600, 1500, 1450 cm^{-1}. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.57; H, 7.43.

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(14) Chemicals used were from Aldrich Chemical Co. except where mentioned. All solvents were purchased from Fisher Scientific except where mentioned. All melting points were determined on a calibrated Fisher-Johns apparatus. Thin-layer chromatography was performed with use of plastic-backed silica gel coated plates (EM Science and Eastman and Kodak Co.). Chromatographic separations were performed by rotational TLC using a Chromatotron (Harrison Reseach Model 7294) with 1-, 2-, and 4-mm plates coated with silica gel 60 PF_{254} containing calcium sulfate binder (EM Science). ^1H NMR spectra were recorded at 60 or 80 MHz, in $CDCl_3$ solution. ^{13}C NMR spectra were similarly recorded at 20 MHz. Solution IR spectra were recorded with 0.1-mm sodium chloride cells.

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Regioselectivity in the Alkylation of Ambident Anions of 1-Acyl-1,2-dihydroquinaldonitriles (Quinoline Reissert Compounds)

Harry W. Gibson* and Bardia Guilani

Department of Chemistry and NSF Science & Technology Center for High Performance Polymeric Adhesives & Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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Introduction

Structure 1 is a 1-acyl-1,2-dihydroquinaldonitrile or quinoline Reissert compound. By virtue of the acidity of the proton α to the cyano group this class of compounds can be elaborated with a number of electrophiles such as alkyl halides. Such reactions make Reissert compounds valuable synthetic intermediates.[1]

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