Reaction of Tetrabutylammonium Tribromide with Cyclohexene. Tetrabutylammonium tribromide (4.82 g; 0.01 mol) and cyclohexene (3.0 mL; 2.43 g; 0.0296 mol) were made up to a volume of 50 mL with acetonitrile. The bromine color disappeared as soon as the solution was mixed. Analysis by VPC indicated that cyclohexane dibromide had formed in 90% yield.

Reaction of Tetrabutylammonium Succinimide with Bromine in Acetonitrile. Bromine (3.76 g; 0.0235 mol) in purified acetonitrile (6 mL) was added portionwise with shaking and cooling to a 0.942 M solution of tetrabutylammonium succinimide in acetonitrile (25 mL; 0.0236 mol). Ether (100 mL) was added, and the solution was seeded and stored in the freezer. After crystallization had advanced, more ether (200 mL) was added. The product was the SBr-Bu$_4$NBr complex; 10.67 g (90.7% yield); mp 83–85 °C dec. The infrared spectrum of this product was identical with that of an authentic sample of the complex.

Registry No. SBr, 128-08-5; $(C_4H_9)_4NBr$, 1643-19-2; $(C_2H_5)_4NBr$, 71-91-0; $C_6H_5CH_2N(C_2H_5)_3Br$, 5197-95-5; SBr·$(C_4H_9)_4NBr$, 103191-58-8; 2SBr·$(C_2H_5)_4NBr$, 103191-59-9; SBr·$(C_2H_5)_4NBr$, 103191-60-2; SBr·$C_6H_5CH_2N(C_2H_5)_3Br$, 103191-61-3; $(C_4H_9)_4N^+Br_3^-$, 38932-80-8; $H_2C{=}CHC(CH_3)_3$, 558-37-2; $(H_3C)_3CCHBrCH_2Br$, 640-21-1; S·$(C_4H_9)_4N^+$, 74830-30-1; cyclohexene, 110-83-8; cyclohexane dibromide, 5401-62-7.

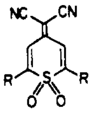
Chemistry of 1,1-Dioxothiopyrans. 2. Synthesis, Structure, and Properties of 4-Diazo-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide

John L. Fox, Chin H. Chen,* and Henry R. Luss

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received February 4, 1986

The discovery of dicyanomethylene derivatives of thiopyran 1,1-dioxides 1 (DCTD) as electron-transporting species in electrophotography[1] has stimulated much interest in the design and synthesis of many other structurally related compounds. The best method of preparing 1 is to condense malononitrile with the corresponding ketone, such as 2, in the presence of piperidine in alcohol.[2] This procedure, however, did not work well with active methylene compounds less acidic than malononitrile. In attempts to activate the carbonyl group of 2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (2), we synthesized a remarkably stable diazo derivative of 2, 4-diazo-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (3) (DATD), whose synthesis, X-ray single-crystal structure, and chemical properties are described here.



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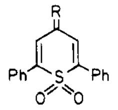
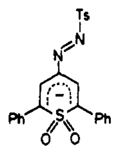


2 (R=O)
3 (R=N_2)
4 (R=N–NHTs)
5 (R=N–NH_2)
6 (R=N–N=PPh_3)
7 [R=N–NH–P(=O)$(OMe)_2$]



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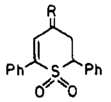
Results and Discussion

Synthesis. Most organic diazo compounds are unstable unless they are stabilized by conjugation with strong electron-withdrawing groups such as carbonyls and cyclopentadienes.[3] The only previously known diazo derivative of a heterocyclic sulfone is diazothioxanthen 1,1-dioxide, which was prepared from the corresponding 9,9-dihydro derivative and tosyl azide in the presence of EtOK in EtOH.[4] This method is not applicable to thiopyran sulfones because of the difficulty of synthesizing the corresponding 4,4-dihydro-2,6-diphenylthiopyran 1,1-dioxide.[2]

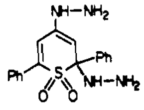
Heating 2 with 1 equiv of *p*-toluenesulfonohydrazide in ethanol produced a mixture of products. The major component isolated was not the expected tosyl hydrazone 4, but a compound (orange needles) that was free of the tosyl group. Its IR spectrum has a strong band at 2100 cm^{-1} characteristic of diazo stretching. Mass and ^{1}H NMR spectra and combustion analyses are consistent with the diazo thiopyran structure of 3. Presumably, the tosylhydrazone 4 formed in situ has an unusually acidic proton on nitrogen because of the highly stabilized anion shown in structure 8.

Deprotonation under the reaction conditions in the presence of the weakly basic *p*-toluenesulfonohydrazide followed by α elimination of toluenesulfinate led to the formation of 3. Indeed, the reaction was much cleaner when 2 was refluxed with 2 equiv of *p*-toluenesulfonohydrazide in ethanol, and the diazo compound 3 crystallized directly out of the reaction mixture on cooling. The yield of 3, after purification was 48%.

Further support of this rationale was provided by experiments in which the dihydro derivative 9 under the same reaction conditions produced only the tosylhydrazone 10. The latter, which cannot delocalize the incipient anion as can 8, cannot readily be deprotonated and α-eliminate the toluenesulfinate to give the diazo compound 11 under the reaction conditions.



9 (R=O)
10 (R=N–NHTs)
11 (R=N_2)



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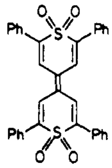

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Likewise, reaction of 2 with 1 equiv of hydrazine produced only the hydrazone 5. However, the same reaction run in the presence of 2 equiv of hydrazine gave the 2:1 adduct, which was assigned the structure 12 on the basis of elemental and ^{1}H NMR analyses. The diadduct presumably was formed from 5 by Michael addition of hydrazine at C2 followed by 1,3-prototropic shift. In Me_2SO-d_6, 12 easily reverted to 5 on addition of D_2O.

Chemical Properties. DATD (3) is a remarkably stable compound, mp 131 °C dec, which can be stored indefinitely in the solid state at ambient conditions. Structurally, diazothiopyran 3 can be considered as a sulfone analogue of *p*-diazobenzeneoxide.[5] However, 3 is far more stable than *p*-diazobenzeneoxide photochemically. For instance, when an argon-degassed 0.02 M solution of 3 in acetonitrile was irradiated with a 200-W Hg-Xe lamp for 48 h, a TLC assay showed that about 30% of 3 survived without decomposition. Thermally, DATD decomposed under toluene reflux (2 h) to at least five products, from which only a small amount of the dimer 13[2] was detected. In cyclic voltammetry, DATD displayed a single, irreversible reduction wave at −0.92 V (Pt vs. SCE).

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[1] Scozzafava, M.; Chen, C. H.; Reynolds, G. A.; Perlstein, J. H. U.S. Patent 4 514 481, 1985.

[2] Chen, C. H.; Reynolds, G. A.; Luss, H. R.; Perlstein, J. H. *J. Org. Chem.*, in press.

[3] Regitz, M. *Synthesis* **1972**, 351.

[4] Regitz, M. *Chem. Ber.* **1964**, *97*, 2742.

[5] Ried, W.; Dietrich, R. *Chem. Ber.* **1961**, *94*, 387.

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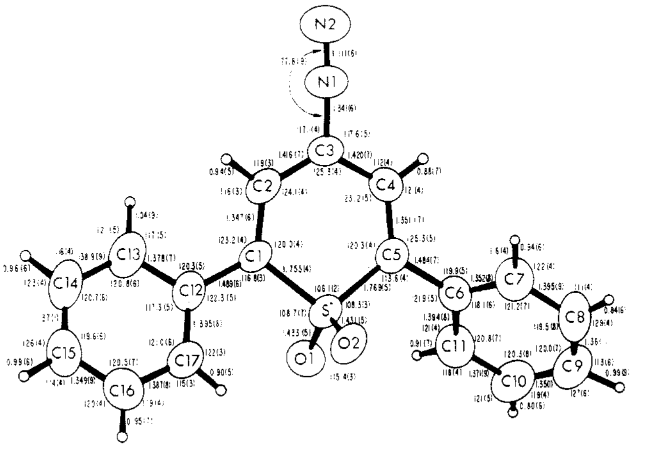
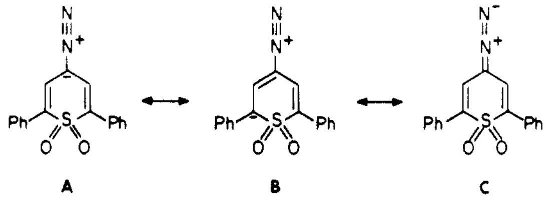


Figure 1. Plot of the DATD molecule with atomic labeling. The themal ellipsoids were drawn at the 50% probability level except for hydrogens. Labels for hydrogens were omitted for clarity but were given the same number as the parent carbon atom.

In general, **3** does not undergo nucleophilic reactions. One exception is triphenylphosphine, which adds directly to the terminal nitrogen at room temperature in acetonitrile to give the stable azaphosphorane **6**. Dimethyl phosphite added to **3** instantaneously at room temperature to give the corresponding dimethyl phosphonate **7**. Warming DATD in glacial acetic acid at ~90 °C produced **14** as the 2*H* isomer, which presumably was formed by proton rearrangement of the less stable initial 4*H* isomer. The latter is the expected product from the acid-catalyzed decomposition of DATD.[2]

Single-Crystal X-ray Analysis. Figure 1 shows the structure of DATD, with atomic labeling, bond distances, and angles. The N1–N2 bond distance (1.11 Å) is indicative of a triple bond. One can derive an expected value by considering the $C\equiv N$ bond distance (1.16 Å)[6] and subtracting the C_{sp} triple bond radius (0.60 Å),[7] giving the N_{sp} triple bond radius of 0.56 Å and a corresponding $N\equiv N$ distance of 1.12 Å.

The C3–N1 (numbering according to Figure 1) bond distance (1.34 Å) would appear to have considerable double bond character (structure C) when compared with accepted single and double bond values of 1.45 and 1.27 Å,[8] respectively. These values, however, are for C_{sp^2}–N_{sp^2} bonds, and a C_{sp^2}–N_{sp} bond would be expected to be ~0.05 Å shorter[7] (~1.40 Å), so the C3–N1 bond is probably mostly single. The nearly linear arrangement of the azo group (C–N–N angle = 177.8 Å) is also supportive of the sp hybridization state of nitrogen.



Bonds C2–C3 and C3–C4 are shorter than normal single bonds (1.48 Å), whereas C1–C2 and C4–C5 are slightly longer than a double bond (1.34 Å).[8] All these results suggest that structures A and B are much more important contributors to the overall structure than C, with A probably the most important.

Experimental Section

Melting points, obtained on a Thomas-Hoover melting point apparatus, are uncorrected. ^1H NMR spectra of $CDCl_3$ solutions were recorded on Varian EM-390 and Bruker WH-270 spectrometers, with Me_4Si as the internal standard. Electron-impact mass spectra were obtained on an AEI MS-30 mass spectrometer. Field-desorption spectra were obtained on a Varian MAT-731 spectrometer. IR spectra were obtained on a Beckman IR 4250 spectrophotometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories. The cyclic voltammogram was recorded on a Princeton Applied Research Model 173 potentiostat and a Model 175 Universal programmer in the standard three-electrode configuration. A platinum inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a fiber standard calomel electrode. The electrolyte was 0.1 M of tetrabutylammonium tetrafluoroborate in methylene chloride. UV–vis spectra were recorded on a Perkin-Elmer 3600 spectrophotometer.

4-Diazo-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide (DATD, 3). A solution of 1.48 g (5 mmol) of 2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (**2**) and 1.9 g (2 equiv) of *p*-toluenesulfonohydrazide in 35 mL of ethanol was refluxed for 30 min. The mixture was cooled (freezer, overnight), and the precipitated yellow solid was filtered and recrystallized from 150 mL of ethanol to yield 0.75 g (48%) of pure **3** as orange needles: mp 131 °C dec; UV λ_{max} (CH_2Cl_2) 328 nm (ϵ 2.24 × 10^5); field-desorption mass spectrum, *m/e* 308 (M^+); IR (KBr) 2100 cm^{-1} (N=N); ^1H NMR ($CDCl_3$) 6.9 (s, 2 H), 7.2–7.7 (m, 10 H, Ar H). Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.2; H, 3.9; N, 9.1; S, 10.4. Found: C, 66.4; H, 4.1; N, 9.0; S, 10.4.

2,6-Diphenyl-4-(tosylhydrazino)-4*H*-dihydrothiopyran 1,1-Dioxide (10). A mixture of 2.4 g (8 mmol) of 2,6-diphenyl-4*H*-dihydrothiopyran 1,1-dioxide (**9**) and 1.80 g (9.6 mmol) of *p*-toluenesulfonohydrazide in 200 mL of ethanol was refluxed for 5 h. The mixture was cooled, and the white precipitate was collected and recrystallized from 300 mL of acetonitrile to give 2.6 g (68%) of pure **10**: mp 128–129 °C; field-desorption mass spectrum, *m/e* 310 (M^+ – tosyl H); ^1H NMR (Me_2SO-d_6) δ 2.4 (s, 3 H, methyl), 3.4 (d, *J* = 9 Hz, 2 H, methylene), 5.07 (t, *J* = 9 Hz, 1 H, benzylic), 6.83 (s, 1 H, olefinic), 7.3–7.9 (m, 14 H, Ar H). Anal. Calcd for $C_{24}H_{22}N_2O_4S_2$: C, 61.8; H, 4.8; N, 6.0; S, 13.7. Found: C, 61.5; H, 4.8; N, 6.4; S, 13.0.

4-[(Dimethoxyphosphinyl)hydrazino]-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide (7). A mixture of 200 mg (0.65 mmol) of **3** and 2 mL of dimethyl phosphite was heated in an 80 °C oil bath for 2 h. The reaction mixture, after cooling, was poured into water. The solid that precipitated was collected and washed with water to give 239 mg of crude product. Trituration of the crude material with 4 mL of 1:1 toluene/hexanes gave 201 mg (74%) of pure **7**: mp 240–241 °C dec; field-desorption mass spectrum, *m/e* 418 (M^+); ^1H NMR ($CDCl_3$) δ 1.55 (br s, 1 H, NH), 3.73 (d, *J* = 27 Hz, 6 H, $POCH_3$), 6.94 (d, *J* = 3 Hz, 1 H, olefinic), 7.2–7.4 (m, 6 H, Ar H), 7.66 (d, *J* = 3 Hz, 1 H, olefinic), 7.77 (dd, 2 H, Ar H), 7.96 (dd, 2 H, Ar H). Anal. Calcd for $C_{19}H_{19}N_2O_5P$: C, 54.5; H, 4.6; N, 6.7. Found: C, 54.2; H, 4.3; N, 6.8.

4-[(Triphenylphosphoranylidene)hydrazino]-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide (6). To a solution of 0.154 g (0.5 mmol) of DATD in 3 mL of acetonitrile at room temperature was added 0.131 g (1 equiv) of triphenylphosphine. A yellow precipitate immediately formed. The mixture was refluxed for 20 min, and the solid was filtered and recrystallized from 15 mL of acetonitrile containing a small amount of chloroform to give 0.22 g (76%) of pure **6**: mp 196 °C dec; field-desorption mass spectrum, *m/e* 570 (M^+); ^1H NMR ($CDCl_3$) δ 7.0 (d, *J* = 3 Hz, 1 H, olefinic), 7.3–7.9 (m, 25 H, Ar H), 8.08 (d, *J* = 3 Hz, 1 H, olefinic). Anal. Calcd for $C_{35}H_{27}N_2O_2PS$: C, 73.7; H, 4.8; N, 4.9; P, 5.4; S, 5.6. Found: C, 73.4; H, 4.9; N, 4.9; P, 5.5; S, 5.7.

4-Acetoxy-2,6-diphenyl-2*H*-thiopyran 1,1-Dioxide (14). To 10 mL of glacial acetic acid was added 0.18 g (0.58 mmol) of DATD (**3**). The mixture was warmed at 90 °C for ~4 h, poured into ice, and allowed to stand overnight. The precipitated golden orange solid was filtered and chromatographed over silica gel in CH_2Cl_2/cyclohexane (3:1) to yield 67 mg (34%) of **14** as an oil: field-desorption mass spectrum, *m/e* 340 (M^+); ^1H NMR ($CDCl_3$)

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(6) *Tables of Interatomic Distances and Configurations in Molecules and Ions*; The Chemical Society: London, 1965; Supplement.

(7) Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147.

(8) Burke-Laing, M.; Laing, M. *Acta Crystallogr. Sect. B* **1976**, *32*, 3216.

δ 2.15 (s, 3 H, CH_3), 5.15 (d, J = 4.5 Hz, 1 H, H_A), 6.03 (dd, J = 4.5, 3 Hz, 1 H, H_B), 6.42 (d, J = 3 Hz, 1 H, H_C), 7.1–7.7 (s, 10 H, Ar H).

4-Hydrazino-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide (5). To a solution of 0.89 g (3 mmol) of **3** in 50 mL of ethanol was added 3 mL (1 equiv) of a solution of 1.0 M of hydrazine in ethanol. The reaction mixture, which turned from yellow to orange, was heated at 50 °C overnight. The solvent was removed under vacuum, and the residue was recrystallized from methanol to give 0.26 g (28%) of pure **5**: mp 162–163 °C; ^1H NMR (Me_2SO-d_6) δ 3.4 (br s, 2 H, NH_2), 6.96, 6.97 (s, s, 2 H, olefinic), 7.3–7.85 (m, 10 H, Ar H). Anal. Calcd for $C_{17}H_{14}N_2O_2S$: C, 65.8; H, 4.5; N, 9.0; S, 10.3. Found: C, 64.7; H, 4.5; N, 9.1; S, 10.6.

2,4-Dihydrazino-2,6-diphenylthiopyran 1,1-Dioxide (12). A mixture of 0.89 g (3 mmol) of **3** and 2 equiv of hydrazine in 40 mL of ethanol was heated at 50 °C for 12 h. The reaction mixture was concentrated on a rotary evaporator to ~20 mL, and 200 mL of ether was added dropwise. The precipitated white solid was collected and washed with ether to give 0.63 g (60%) of **12**: mp 158–160 °C dec (gas evolution); ^1H NMR (Me_2SO-d_6) δ 3.4 (br s, NH_x), 6.38 (s, 1 H, olefinic), 6.8 (s, 1 H, olefinic), 7.25–7.85 (m, 10 H, Ar H). On addition of D_2O, the ^1H NMR spectrum of **12** reverted quickly to that of **5**. Anal. Calcd for $C_{17}H_{18}N_4O_2S$: C, 59.6; H, 5.3; N, 16.4; S, 9.4. Found: C, 59.5; H, 5.3; N, 16.3; S, 9.7.

Crystal Structure Determination. Six-sided brownish yellow needles were grown by slow evaporation from ethanol. Data were collected on an Enraf-Nonius CAD4 diffractometer.[9] Unit cell data and other pertinent crystallographic data are given in the crystal data table as supplementary material. Choice of space group $Pn2_1a$ over $Pnma$ was confirmed by the successful structure refinement. Data were corrected for a 30% decrease in intensities over the data collection period, as determined by hourly monitoring of three standard reflections. The structure was solved by direct methods (MULTAN 11/82) and refined by the full-matrix least-squares method. Anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogens were applied in the final cycles of refinement.

Registry No. 2, 41068-60-4; 3, 103438-51-3; 5, 103438-56-8; 6, 103438-54-6; 7, 103438-53-5; 9, 66510-40-5; 10, 103438-52-4; 12, 103438-57-9; 14, 103438-55-7; *p*-toluenesulfonohydrazide, 1576-35-8.

Supplementary Material Available: Tables of crystal data and positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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[9] Programs were from the Structure Determination Package SDP-PLUS V1.1, 1983, Enraf-Nonius Corp., Delft, Holland.

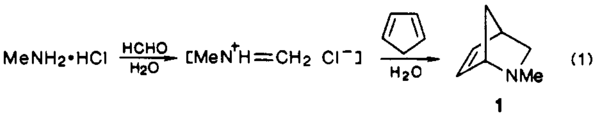
An Intramolecular Immonium Ion Variation of the Diels–Alder Reaction: Synthesis of (±)-Dihydrocannivonine

Paul A. Grieco* and Scott D. Larsen

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received May 2, 1986

During studies on the intermolecular cycloaddition of dienes with simple unactivated immonium salts in aqueous medium, we found that the reaction of cyclopentadiene with methylmethyleneammonium chloride in water at ambient temperature gives rise to an 82% yield of bicyclic amine **1** after 3 h (cf. eq 1).[1] This result is particularly striking in view of the negligible concentration of methylmethyleneammonium chloride in water. In contrast the less reactive cyclohexadiene upon reaction with either methyl- or benzylmethyleneammonium chloride gives rise after long reaction times and elevated temperatures to only modest yields of Diels–Alder adducts. For example, cyclocondensation of benzylmethyleneammonium chloride with cyclohexadiene in water required 42 h at 55 °C in order to realize a 35% yield of bicyclic amine **2** (cf. eq 2).



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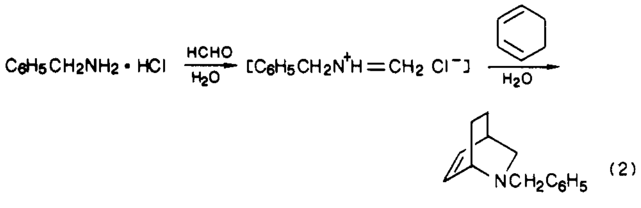

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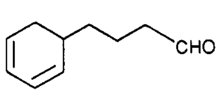
In order to further probe reactions employing cyclohexadiene we set out to examine a system wherein an aldehyde unit was directly incorporated into a cyclohexadiene system. Detailed below is the synthesis of cyclohexadiene **3** and its transformation via an intramolecular immonium ion Diels–Alder reaction into racemic dihydrocannivonine **4**.



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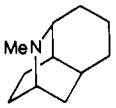

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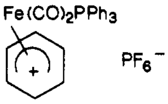
The synthesis of substituted cyclohexadiene **3** follows from methodology recently developed by Pearson.[2] Treatment of dicarbonyl(cyclohexadiene) (triphenylphosphine)iron complex **5**[3] with the Grignard reagent derived from 4-bromobutyl tetrahydropyranyl ether (**6**) gave rise to the (cyclohexadiene)iron complex **7** as the sole product in 90% isolated yield. Simultaneous demetalation of complex **7** and cleavage of the tetrahydropyranyl ether proceeded smoothly upon exposure of **7** to copper(II) chloride in ethanol[4] at room temperature, giving rise after 5 h to 4-(5-cyclohexadienyl)butanol (**8**) in 63% isolated yield. The actual decomplexation of **7** occurs immediately whereas deprotection of the alcohol requires several hours. Swern oxidation of **8** provided access to aldehyde **3** which



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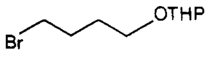

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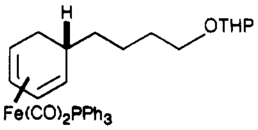

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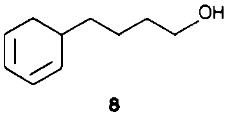

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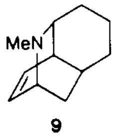

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[1] Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 1768.

[2] Pearson, A. J.; Yoon, J. *Tetrahedron Lett.* **1985**, *26*, 2399.

[3] Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 884. Birch, A. J.; Raverty, W. D.; Hsu, S.-Y.; Pearson, A. J. *J. Organomet. Chem.* **1984**, *260*, C59.

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