Reactions of 2,8-Dihalo-8-thiatricyclo[3.2.1.0^{3,6}]octane

STEPHEN D. ZIMAN AND BARRY M. TROST*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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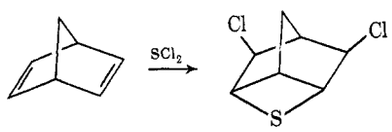
Carbonium ion, radical, or carbanion reactions of the halides of 2,8-dichloro- (1) or 2,8-dibromo-8-thiatricyclo[3.2.1.0^{3,6}]octane (3) involve participation by sulfur. Thus, treatment of the dichloro compound 1 with boron tribromide generates the dibromide 3 and with acetic acid the corresponding *exo,exo*-diacetate, whereas alane or cyanide ion produced *endo*-2,3-epithio-5-norbornene. Radical reactions initiated by tri-*n*-butyltin hydride or chromous acetate led only to a rearrangement product, nortricyclyl mercaptan. Finally, lithium dimethylcuprate produced *endo*-2-methylthio-*exo*-3-bromo-5-norbornene.

The addition of sulfur dichloride to norbornadiene proceeds exclusively and in high yield to produce 2,8-dichloro-4-thiatricyclo[3.2.1.0^{3,6}]octane (1).[1] This unusual reaction, whose high selectivity suggested the possibility of an episulfonium salt 2 as an intermediate,



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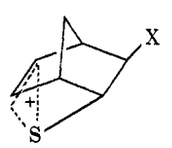
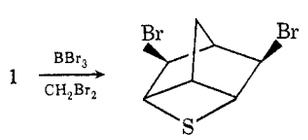


2

encouraged us to examine some of the chemistry of the adduct as a source of fascinating new reactions emanating from the flexible chemical reactivity of sulfur. Indeed, all reactions of the halides (carbonium ion, radical, carbanion) involve participation by sulfur.

If 2 is an intermediate in the addition reaction, ionization of 1 back to 2 in principle also should be possible. Although treatment with alane (AlH_3) failed to provide any support for such an ionization, boron tribromide[2] quantitatively replaced both chlorines with bromines. The assignment of the structure of the dibromide as 3 rather than as an alternative such as 4 was clearly



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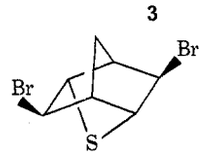

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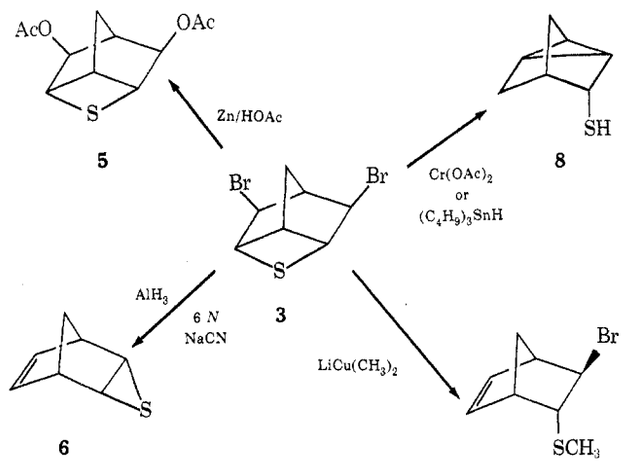
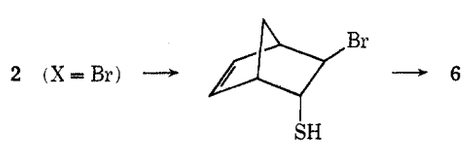
indicated by the nmr spectrum (see Experimental Section). The dibromide also ionizes readily to 2 (X = Br). Thus, attempted reduction of 3 with zinc in acetic acid only led to solvolysis and formation of diacetate 5 in 84% yield (see Scheme I). In contrast to the trapping of 2 (X = Br or Cl) at carbon with

SCHEME I

REACTIONS OF 2,8-DIBROMO-4-THIATRICYCLO[3.2.1.0^{3,6}]OCTANE



acetate or bromide as nucleophiles, hydride captures 2 (X = Br) at sulfur to give 7. Thus, the product of



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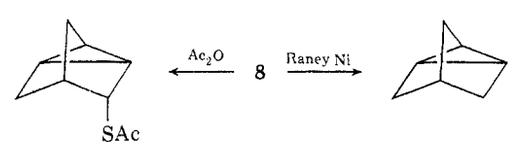
alane reduction, *endo*-2,3-epithio-5-norbornene (6), results upon subsequent cleavage of hydrogen bromide from this intermediate. Support for this interpretation arises from the inertness of dibromide 3 to refluxing lithium aluminum hydride, ruling out initiation of reaction by hydride attack on bromine. On the other hand, cyanide ion induces reduction of 3 to 6 in 84% yield, a process almost certainly involving initial reaction of cyanide at bromide.[3]

Attempts to replace bromine with hydrogen or alkyl groups led only to rearrangement products. Radical debrominations led to 2-nortricyclyl mercaptan (8).



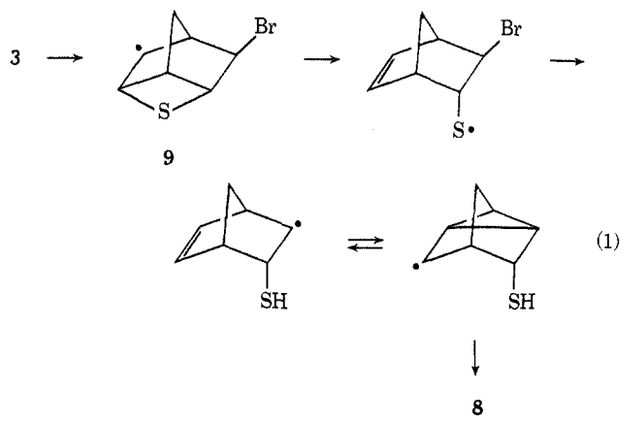
The structure of 8 was demonstrated by Raney nickel desulfurization to nortricyclene and acetylation to the

(1) (a) F. Lautenschlaeger, *J. Org. Chem.*, **31**, 1669 (1966); (b) *ibid.*, **34**, 3998 (1969).

(2) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **88**, 2481 (1966).

(3) The similar reaction with dichloride 1 proceeded in 31% yield; see ref 1b.

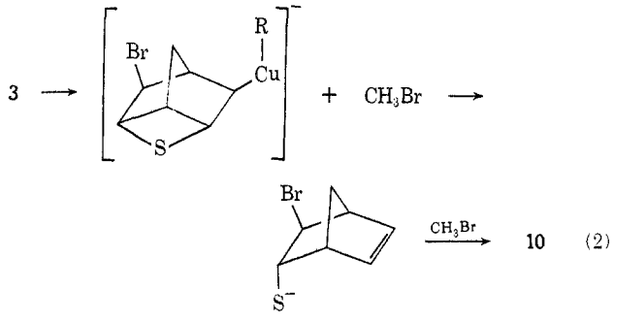
known thioacetate[4] as well as by spectral means. Equation 1 illustrates the probable pathway. In these



(1)

events, radical **9** undergoes elimination much faster than either hydrogen atom transfer in the tin hydride reduction or electron capture and protonation in the chromous ion reduction.[5,6] Identical behavior was observed with the dichloride **1** under these conditions.

Most surprising was the reaction of dibromide **3** with lithium dimethylcuprate. No products of C-alkylation were observed. The only product, isolated in 80% yield, was *exo*-2-bromo-*endo*-3-methylthio-5-norbornene. Equation 2 rationalizes its formation. Metal–



(2)

halogen exchange has been found in a few other cases of attempted alkylation with cuprates but usually when the alkyl group on copper is larger than methyl.[7]

Experimental Section[8]

Preparation of *exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.0^{3,6}]-octane (3).—*exo,exo*-2,8-Dichloro-4-thiatricyclo[3.2.1.0^{3,6}]octane (19.4 g, 0.10 mol) was dissolved in 100 ml of methylene bromide. The solution was cooled to −5° and 55.0 g (0.22 mol) of boron tribromide was added by syringe over a 15-min period. The reaction started immediately and was very exothermic. After addition, the reaction was stirred for 1 hr at 0° and then heated at 70° for 20 min. The mixture was then slowly added to 1 l. of water and 800 ml of carbon tetrachloride. After 3 × 500 ml water washes, the carbon tetrachloride layer was dried and evaporated to give 28.0 g of crude product. The product was recrystallized from hexane to give 26.5 g (94%) of gray-white crystals: mp 81–83°; nmr (CCl_4) τ 5.31 (s, 2 H), 6.0 (m, 1 H), 6.55 (d, J = 1 Hz, 1 H), 6.65 (s, 2 H), 7.72 (bs, 2 H); ir (CCl_4) 15.95 μ; mass spectrum m/e (rel intensity) 286 (9), 284 (18), 282 (9), 206 (60), 204 (60), 160 (18), 124 (41), 124 (37), 98 (30), 93 (45), 92 (100).

Anal. Calcd for $C_7H_8Br_2S$: C, 29.57; H, 2.82; Br, 56.33; S, 11.27. Found: C, 29.67; H, 2.85; Br, 56.37; S, 11.20.

Preparation of *exo,exo*-2,8-Diacetoxy-4-thiatricyclo[3.2.1.0^{3,6}]-octane (5).—A solution of 1.42 g (5.0 mmol) of *exo,exo*-2,8-dibromo-4-thiatricyclo[3.2.1.0^{3,6}]octane in 10 ml of glacial acetic acid was treated with 0.65 g (10 g-atom) of zinc dust. The mixture was heated to 80° and stirred for 24 hr. After the mixture was cooled, 25 ml of chloroform was added and the resultant slurry was filtered and washed with 2 × 50 ml of water. The chloroform layer was dried and the solvent was removed by evaporation. The crude product (1.01 g, 84% yield) was distilled to give 0.40 g (33%) of a colorless liquid, bp 113° (6.7 mm), which solidified upon standing: mp 46–48°; nmr (CCl_4) τ 4.68 (s, 2 H), 6.10 (m, 1 H), 6.98 (d, J = 4.0 Hz, 2 H), 7.05 (m, 1 H), 8.00 (s, 6 H), 8.17 (bs, 2 H); ir (CCl_4) 5.72 μ; mass spectrum m/e (rel intensity) 242 (14), 140 (15), 139 (7), 125 (5), 124 (7), 123 (5), 122 (7), 111 (11), 107 (7), 82 (13), 79 (14), 67 (10), 66 (12), 43 (100).

Anal. Calcd for $C_{11}H_{14}O_4S$: mol wt, 242.0612. Found: mol wt, 242.0579.

Reaction of *exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.0^{3,6}]octane (3) with Lithium Aluminum Hydride and Aluminum Chloride.—Lithium aluminum hydride (0.114 g, 3.0 mmol) and aluminum chloride (0.133 g, 1.0 mmol) were added to 10 ml of dry tetrahydrofuran. The suspension was stirred for 20 min and then 0.50 g (1.7 mmol) of *exo,exo*-2,8-dibromo-4-thiatricyclo[3.2.1.0^{3,6}]octane was added. The resultant slurry was refluxed for 24 hr. The solution was slowly hydrolyzed with a dilute sodium hydroxide solution. The aqueous layer was extracted with 2 × 50 ml of carbon tetrachloride. The combined carbon tetrachloride layers were dried and evaporated to give a viscous liquid. Flask distillation of this liquid in a Hickman still at 0.1 mm gave 0.036 g (17% yield) of a foul-smelling solid. The nmr and ir were identical with those of *endo*-2,3-epithio-5-norbornene:[1b] nmr (CCl_4) τ 4.35 (bs, 2 H), 6.84 (bs, 2 H), 7.02 (bs, 2 H), 7.98 (s, 2 H); ir (CCl_4) 6.10 μ; mass spectrum m/e (rel intensity) 126 (1), 125 (5), 124 (14), 123 (43), 98 (39), 92 (27), 91 (100), 79 (35).

Reaction of *exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.0^{3,6}]octane (3) with Sodium Cyanide.—*exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.0^{3,6}]octane (10.0 g, 0.035 mol) and 5.80 g (0.118 mol) of sodium cyanide were added to 105 ml of 85% ethanol. The reaction mixture was heated at 70° for 1 hr and then 100 ml of water was added to it. The aqueous phase was extracted with 2 × 50 ml of chloroform. The combined chloroform layers were dried ($MgSO_4$) and evaporated to give a yellow liquid. Distillation of the liquid gave 3.40 g (80% yield) of *endo*-2,3-epithio-5-norbornene, bp 68° (13 mm). The colorless liquid solidified to give a white, crystalline solid, mp 46–47° (lit.[1b] mp 45–47°).

Reaction of *exo,exo*-2,8-Dichloro-4-thiatricyclo[3.2.1.0^{3,6}]octane (1) with Chromous Acetate.[9]—To a solution of 175 ml of dimethylformamide, 26 ml of water, and 40 ml of ethylenediamine which was deoxygenated was added 36 g (0.192 mol) of chromous acetate monohydrate. The resultant solution was a dark purple-blue, indicating that the chromous ion–ethylenediamine complex had formed. The complex was cooled to 0° and stirred for 15 min. *exo,exo*-2,8-Dichloro-4-thiatricyclo-[3.2.1.0^{3,6}]octane (4.65 g, 0.024 mol) was dissolved in 10 ml of deoxygenated dimethylformamide and it was added all at once by syringe to the chromous solution. An immediate color change took place as the solution became reddish-purple. It was stirred at 0° for 10 min and then poured into 500 ml of water.

(4) T. V. van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968).

(5) J. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

(6) For the norbornenyl–nortricyclyl radical problem see S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 1762 (1969); D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Commun.*, 725 (1966); C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

(7) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

(8) Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A, HA-100, or XL-100 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform, magnesium sulfate was employed as a drying agent, and all reactions were run under nitrogen. Vpc analyses were performed on an Aerograph Model 90P instrument.

(9) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

The water layer was extracted with 3 × 100 ml of pentane. The combined pentane extracts were dried ($MgSO_4$) and evaporated to give a foul-smelling, viscous, colorless oil. Bulb-to-bulb distillation at 1 mm gave 0.486 g (16% yield) of a colorless liquid which was identified as tricyclo[2.2.1.$0^{2,6}$]-3-heptylthiol: nmr τ 7.25 (d, J = 7 Hz, 1 H), 8.17 (d, J = 7 Hz, 1 H), overlapping with 8.25 (b s, 1 H), 8.70 (b s, 3 H), 8.87 (m, 4 H); ir 3.25, 3.88 μ; mass spectrum m/e (rel intensity) 128 (5), 127 (5), 126 (60), 97 (19), 83 (95), 81 (100), 79 (25), 78 (15), 77 (65).

Anal. Calcd for $C_7H_{10}S$: C, 66.73; H, 8.06; S, 25.30. Found: C, 66.66; H, 7.94; S, 25.39.

Reaction of *exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (3) with Tri-*n*-butyltin Hydride.—A dry 25-ml one-neck flask was equipped with a short path distillation head and receiver flask immersed in a −78° bath. In the flask was placed 1.42 g (5.0 mmol) of *exo,exo*-2,8-dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane and 8.73 g (0.03 mol) of freshly distilled tri-*n*-butyltin hydride. A trace of AIBN was added and the reaction was heated to 100° at a pressure of 15 mm. The reaction was kept at 100° for 2 hr. A distillate was collected and was identified by vpc, ir, and nmr as pure tricyclo[2.2.1.$0^{2,6}$]heptylthiol. The yield was 100 mg (31%).

Reaction of Tricyclo[2.2.1.$0^{2,6}$]heptyl-3-thiol (8) with Acetic Anhydride.—Tricyclo[2.2.1.$0^{2,6}$]heptylthiol (0.10 g, 0.79 mmol) and 0.0829 g (0.80 mmol) of acetic anhydride were dissolved in 2 ml of dry pyridine. The mixture was heated at 90° for 1 hr and then poured into 20 ml of water. The water was extracted with 2 × 5 ml of ether. The combined ether layers were dried ($MgSO_4$) and the ether was removed by evaporation. A clear liquid (0.140 g, 100% yield) was recovered and identified as 3-thiolacetoxytricyclo[2.2.1.$0^{2,6}$]heptane[10] by mixed injection with authentic material on vpc (8 ft × 0.25 in. column of 20% Dow 710 on Chromosorb P at 138°, retention time, 64 min) and by nmr analysis: nmr (CCl_4) τ 6.62 (s, 1 H), 7.78 (s, 3 H), 8.00 (bs, 1 H), 8.32–9.00 (m, 7 H); ir 3.22, 5.90 μ; mass spectrum m/e (rel intensity) 170 (1), 169 (2), 168 (34), 140 (8), 127 (4), 126 (15), 125 (50), 110 (18), 93 (100), 92 (32), 91 (80), 79 (17), 77 (50), 66 (44), 65 (20).

(10) T. van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968).

Reaction of 2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (8) with Lithium Dimethylcuprate. A.—Tetrakis[iodo(tri-*n*-butylphosphene)copper(I)], 7.84 g (0.20 mol), was dissolved in 100 ml of dry ether. The mixture was stirred and cooled to −78°. Methyllithium (1.42 *M*, 0.05 mol, 28 ml) in ether was added by syringe to the cold solution over a 2-min period to generate the lithium dimethylcuprate. The colorless solution was then stirred for 10 min.

2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (2.84 g, 0.01 mol) was dissolved in 50 ml of dry ether and this solution was added all at once *via* syringe to the −78° lithium dimethylcurprate solution. The solution remained colorless. After the solution was stirred at −78° for 1 hr, 1.23 g (0.01 mol) of dry nitrobenzene was added all at once by syringe and the solution turned to a deep green color. The Dry Ice bath was removed and the solution was allowed to warm to 0°. The solution was then added to 250 ml of water and the water–ether mixture was filtered through Celite to remove insoluble copper salts. The ether layer was separated and washed with 3 × 100 ml of water, dried ($MgSO_4$), and evaporated. The resultant orange liquid was distilled to give 1.75 g (80% yield) of an orange liquid, bp 52° (0.1 mm). The product was identified as a new compound, *endo*-2-methylthio-*exo*-3-bromo-5-norbornene: nmr (CCl_4) τ 3.85 (m, 2 H), 6.48 (t, J = 2 Hz, 1 H), 6.68 (t, J = 2 Hz, 1 H), 6.94 (bs, 2 H), 7.81 (s, 3 H), 8.10 (m, 2 H); ir (CCl_4) 6.10, 14.50 μ; mass spectrum m/e (rel intensity) 220 (3), 218 (3), 154 (79), 152 (79), 141 (5), 140 (10), 139 (100), 124 (5), 123 (7), 92 (22), 91 (99), 73 (14).

Anal. Calcd for $C_8H_{11}BrS$: mol wt, 219.9745. Found: mol wt, 219.9710.

Registry No.—**1**, 6557-78-4; **3**, 37406-72-7; **5**, 37406-73-8; **6**, 22061-73-0; **8**, 37163-84-1; **10**, 37163-85-2; 3-thiolacetoxytricyclo[2.2.1.$0^{2,6}$]heptane, 37163-86-3.

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Aziridines. XXVI. Reactions of 1,3-Diazabicyclo[3.1.0]hex-3-enes

HAROLD W. HEINE,* THOMAS A. NEWTON, GREGORY J. BLOSICK, KAREN C. IRVING, CAROL MEYER, AND GEORGE B. CORCORAN III

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

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The selective methylation and oxidation of 4-phenyl-6-*p*-nitrophenyl-3-diazabicyclo[3.1.0]hex-3-ene (**1a**) by trimethyloxonium tetrafluoroborate and *m*-chloroperbenzoic acid to form 2,2,3-trimethyl-4-phenyl-6-*p*-nitrophenyl-1-aza-3-azoniabicyclo[3.1.0]hex-3-ene tetrafluoroborate (**3**) and 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene 3-oxide (**11**), respectively, have been achieved. The addition of nucleophiles such as potassium cyanide and sodium borohydride to **3** as well as the reaction of **3** with diazomethane were studied. The cycloadditions of **11** to *N*-phenylmaleimide and diethyl azodicarboxylate were also investigated.

Three earlier papers in this series described the synthesis of the fused aziridines 1,3-diazabicyclo[3.1.0]hex-3-enes (**1**) and 1,4-diazabicyclo[4.1.0]hept-4-enes (**2**) and their thermal cycloadditions to alkenes, alkynes, and diethyl azodicarboxylate.[1–4] These thermal reactions of **1** and **2** were readily accounted for by carbon–carbon fission of the aziridine rings of **1** and **2** to form 1,3-dipolar intermediates (azomethine ylides) which subsequently added to the unsaturated substrates (Scheme I).

Recently the photolysis of **1** has been reported in detail[5–7] and the colored species produced have been identified also as 1,3 dipoles[7] which can be trapped with suitable 1,3 dipolarphiles.

The present paper describes the methylation and oxidation of **1** by trimethyloxonium tetrafluoroborate and *m*-chloroperbenzoic acid, respectively, and the chemical reactions of the resulting methylated and oxidized derivatives of **1**.

Treatment of a methylene chloride solution of 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo-

(1) H. W. Heine, R. W. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967).
(2) H. W. Heine, A. B. Smith III, and J. D. Bower, *ibid.*, **33**, 1097 (1968).
(3) H. W. Heine and R. P. Henzel, *ibid.*, **34**, 171 (1969).
(4) See also H. W. Heine, R. H. Weese, and R. A. Cooper, U. S. Patent 3,609,165 (Sept 28, 1971).
(5) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970).
(6) T. DoMinh and A. M. Trozzolo, *ibid.*, **92**, 6997 (1970).
(7) T. DoMinh and A. M. Trozzolo, *ibid.*, **94**, 4046 (1972).