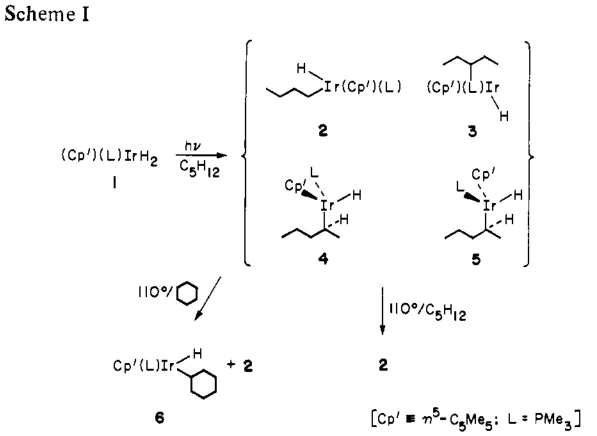
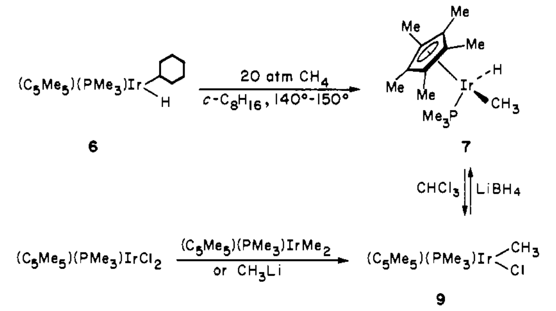
Scheme I



corresponds to $\Delta G°_{\text{reaction}} = -2.0$ kcal/mol at 140 °C. Making the reasonable assumption that $\Delta S°$ for reaction 1 is close to 0 and using 94.5 kcal/mol for the secondary C–H bond energy in cyclohexane and 98 kcal/mol for the primary C–H bond energy in *n*-pentane,[5] we calculate[6] from this $\Delta G°$ that the metal–carbon bond energy in primary complex **2** is 5.5 kcal/mol stronger than the secondary metal–carbon bond in **6**.

Attempted photolysis of dihydride **1** in perfluoroalkane solvents under 4 atm of CH_4 gave no detectable methane activation (in contrast to Graham's observations[2e] on the methane-activating photolysis of $(C_5Me_5)Ir(CO)_2$), perhaps because of the very low solubility of **1** in these solvents. Photolysis in cyclooctane, a "slow" substrate for C–H insertion of the presumed intermediate $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$, under CH_4 gave only the previously observed[1] hydridocyclooctyl complex (**8**). However, we were able to achieve methane activation thermally and in high yield under reversible conditions by taking advantage of the presumption that the hydridomethyl complex **7** would be thermodynamically more stable even than primary alkyl complexes such as **2**. Thus, as shown in Scheme II, heating hydridocyclohexyl complex **6** in cyclooctane solvent in a sealed Pyrex vessel under 20 atm of CH_4 at temperatures between 140 and 150 °C for 14 h led to a 58% yield (NMR)[7] of hydridomethyl complex **7** (^{1}H NMR δ 1.87 (dd, J = 2.0, 0.7 Hz, C_5Me_5), 1.22 (d, J = 9.8 Hz, PMe_3), 0.71 (d, J = 5.8 Hz, IrMe), −17.22 (d, J = 35.9 Hz, IrH)) along with 8% of dihydride **1**. Attempted isolation of the hydridomethyl complex by crystallization or chromatography proved difficult, as it has in other cases,[1] and so the material was treated with $CHCl_3$, converting it to the corresponding chloromethyl complex **9**, which could be purified and characterized by conventional means.[8] The isolated yield of **9** from starting hydridocyclohexyl complex **6** was

Scheme II



50%. Confirmation of these structural assignments was obtained by independent synthesis: chloromethyl complex **9** was prepared by either ligand interchange between the corresponding dichloro and dimethyl complexes (82% yield) or treatment of the dichloro complex with methyllithium (80% yield) (Scheme II); it was converted to hydridomethyl complex **7** in >90% yield by treatment with excess $LiBH_4$ in THF.

In the methane experiment, we assume that the hydridocyclohexyl complex **6** and hydridocyclooctyl complex **8** are formed reversibly but do not build up due to their thermodynamic instability relative to the hydridomethyl complex **7**; i.e., **7** is the "thermodynamic sink" for the system. The ability to functionalize methane thermally and convert it quantitatively to a metalated species is an essential step in the development of possible catalytic functionalization schemes for this molecule; work along these lines is continuing. Efforts are also under way aimed at applying our method for determining relative metal–carbon bond energies to additional pairs of alkyliridium complexes.

Acknowledgment. We are grateful to Dr. P. L. Watson and Prof. W. A. G. Graham for disclosing their results on methane activation prior to publication and to Prof. W. D. Jones for helpful discussions. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. J.M.S. acknowledges an NIH National Research Service Award (Grant No. F32-GM09289), and R.G.B. is grateful for an unrestricted grant from the Chevron Research Co.

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[5] Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976.

[6] As pointed out by a referee, this calculation also assumes, since bond dissociation energies are defined for the gas phase, that the heats of solution and vaporization of the compounds in eq 1 do not perturb the equilibrium constant significantly. Data appropriate to resolve this question fully are not available. Although it has often been assumed that heats of sublimation of structurally related organometallic complexes are identical, other data indicate that heats of sublimation of organometallic complexes vary with relatively subtle changes in structure.[6a,b] Given this situation, and the presently crude level of our data, we would prefer to make the assumption (as we did for contributions to the entropy change for the system) that contributions to heats of sublimation are approximately additive—that is, that the difference in heats of vaporization between *n*-pentane and cyclohexane (about 1.0 kcal/mol) is approximately balanced by the estimated difference in heats of sublimation of complexes **6** and **2**. (a) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

[7] The yield was obtained by NMR integration vs. a known amount of hexamethyldisiloxane added as internal standard. Control experiments demonstrated that no hydridomethyl complex is formed in the absence of CH_4.

[8] Data on chloromethyliridium complex **8**: ^{1}H NMR (200 MHz; C_6D_6) δ 1.47 (d, J = 1.9 Hz, C_5Me_5), 1.17 (d, J = 10.3 Hz, PMe_3), 1.08 (d, J = 7.0 Hz, IrMe); ^{13}C NMR (C_6D_6) δ 90.86 (d, J = 3.8 Hz, C_5Me_5), 13.88 (d, J = 37.2 Hz, PMe_3), 8.87 (s, C_5Me_5), −18.09 (d, J = 10.9 Hz, Ir-*Me*). Exact mass: three resolvable isotopomers for $C_{14}H_{27}ClPIr$ M^+: calcd 456.1139, 454.1160 (weighted average of two peaks), 452.1145; found 456.1148, 454.1133, 452.1123.

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anti-6-Tetracyclo[4.4.0.$1^{1,4}$.$1^{7,10}$]dodecyl Cation Cascade. Sequencing of Rearrangement Routes in a Norbornyl-Fused Norbornyl System

Leo A. Paquette,*[1a] George DeLucca,[1a] James D. Korp,[1b]
Ivan Bernal,[1b] John K. Swartzendruber,[1c] and
Noel D. Jones[1c]

Departments of Chemistry, The Ohio State University
Columbus, Ohio 43210
University of Houston, Houston, Texas 77004
The Lilly Research Laboratories, Eli Lilly and Company
Indianapolis, Indiana 46285

Received November 25, 1983

Intense current interest is focused on understanding the electronic origins and consequences of π bond deformation in norbornenes and methylenenorbornanes. Crystallographic data[2] and supporting theoretical calculations[3] reveal that internally positioned

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[1] (a) The Ohio State University. (b) University of Houston. Inquiries concerning the X-ray crystal structure of **5**-OPBB should be directed to I.B. (c) The Lilly Research Laboratories. Inquiries concerning the X-ray crystal structure of **4**-OPBB should be directed to N.D.J.

[2] (a) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642. (b) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *Ibid.* **1981**, *103*, 2022. (c) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H.; Carrupt, P.-A.; Vogel, P. *Ibid.* **1981**, *103*, 2095. (d) Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943. (e) Mackenzie, K.; Miller, A. S.; Muir, K. W.; Manojlovic-Muir, Lj. *Tetrahedron Lett.* **1983**, 4747 and additional references cited in these papers.

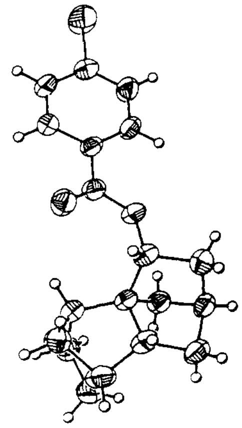


Figure 1. X-ray stereoview of **4**-OPBB.

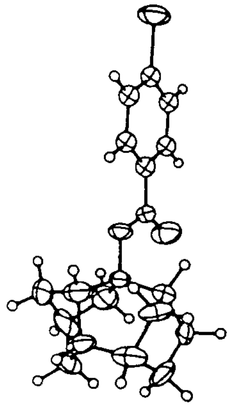
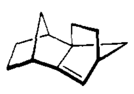


Figure 2. X-ray stereoview of **5**-OPBB.

double bonds of this type experience an often pronounced downward tilt, while substituents attached to an exocyclic methylene group are pyramidalized in the opposite (exo) direction.[4] These considerations cause the recently synthesized hydrocarbon **1**[5] to hold particular fascination because both structural fragments are contained therein. To ascertain the manner in which **1** responds to electrophilic attack, we have carried out controlled protonation studies and herein describe the unusual cascade of carbocation rearrangements characteristic of this double norbornyl network.



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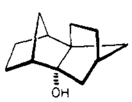

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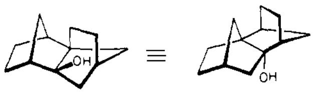

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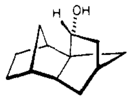

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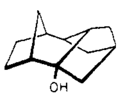

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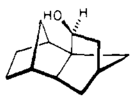

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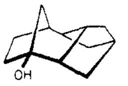
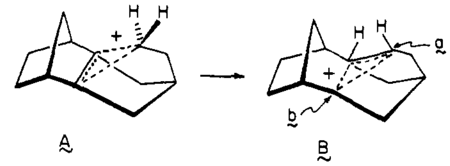
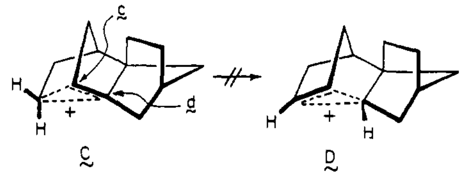


7

Treatment of **1** in dioxane–water (3:2) with several drops of perchloric acid (20 °C, 2 h) afforded a mixture of four products, which were separated by MPLC on silica gel (**2**, 50%; **3**, 4%; **4**, 2%; **5**, 4%). Minor alcohols **4** and **5** were identified by X-ray crystal structure analysis of their *p*-bromobenzoates (Figures 1 and 2). The epimeric nature of **2** and **3** follows from the similarity of their 300-MHz ^{1}H NMR spectra. Rigorous chemical proof of hydroxyl stereochemistry in **2** derives from its isomerization to a mixture of **4** (69%) and **5** (31%) when exposed to $HClO_4$ in CH_3COOH followed by $LiAlH_4$ reduction. Two mechanistic considerations are central to these interesting transformations. First, neighboring group participation by the trans-disposed ethano bridge occurs to deliver carbocation A. Next, A is subject to 1,2-hydride migration to arrive at ion B. Subsequent solvent capture at a and b delivers **4**-OAc and **5**-OAc, respectively.[6] Alcohol **3** is transformed cleanly into **3**-OAc when treated in the same manner. Should ion C be involved in this case, pathway d (to return **3**) is kinetically dominant due to the large steric demands imposed upon nucleophile entry from inside the "cage" along pathway c. No hydride shift to generate D was in evidence.





An important consequence of exposing **1** to this more acidic medium was an increase in the proportion of **4** (35%) and **5** (15%) at the expense of **2**, which was not found.[7] Although the formation of **3** persisted, the amount remained at a low level (3.3%). Still more stringent conditions (CF_3COOH, 0 °C, 1 min; $LiAlH_4$) led to isolation only of **4** (8%) and **5** (22%).[7] A heightened preference for formation of the tertiary alcohol is clearly apparent.

The stage was now set for examination of the relationship between hydroxyl group stereochemistry in **4** and the ability of the system to enter the A → B manifold. Prepared by sequential Jones oxidation and $LiAlH_4$ reduction of **4**, **6** was cleanly transformed to unrearranged **6**-OAc under conditions ($HClO_4$/CH_3COOH) that cause **4** to equilibrate readily with **5**.

In a significant experiment, **5** was found to undergo a remarkable bridgehead → bridgehead cationic rearrangement when exposed to still more acidic conditions (CF_3SO_3H in CH_2Cl_2, 0 °C, 10 min). Since alcohol **7** (85% isolated) shows no penchant for additional chemical change, it likely represents the end point of the cascade.

Table I summarizes the kinetic behavior of four relevant *p*-nitrobenzoates in 80% aqueous acetone. One of the more inter-

Table I. Rates of Solvolysis of Selected *p*-Nitrobenzoates in 80% Aqueous Acetone

compd	T, °C	k, s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
2-OPNB	55.10	7.24×10^{-6}		
	65.10	2.41×10^{-5}		
	80.00	1.36×10^{-4}	26.5	−1.62
5-OPNB	65.20	3.18×10^{-6}		
	79.70	1.81×10^{-5}		
	95.00	7.94×10^{-5}	26.0	−8.74
4-OPNB	79.70	5.89×10^{-6}		
	95.00	2.72×10^{-5}		
	110.00	1.06×10^{-4}	24.9	−12.2
6-OPNB	130.0	$<1.0 \times 10^{-7}$		

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[3] (a) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *927*, 2435. (c) Wipff, G.; Morokuma, K. *Ibid.* **1980**, 4446 and additional references cited in these reports.

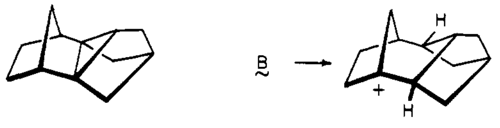
[4] Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

[5] Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.

[6] As expected from these considerations, analogous individual processing of **4** and **5** leads only to 69:31 mixtures of the same two alcohols.

[7] A quantity of nonpolar material was also produced under these conditions, in particularly notable amounts in CF_3COOH solution. The characterization of these mixtures of compounds was not pursued.

esting facets of these data is the near comparable solvolytic reactivity of secondary derivative **4**-OPNB and tertiary systems **2**-OPNB and **5**-OPNB.[8] The contrasting high propensity of **4**-ODNB for ionization and unreactivity of **6**-ODNB is notable. *This exo/endo rate ratio may well represent the largest yet determined experimentally.*[9] Product studies, conducted under $CaCO_3$-buffered conditions, reveal that **2**-OPNB (at 80 °C) leads to **1** (25%) and **2** (75%). In contrast, **4**-OPNB (95 °C) and **5**-OPNB (110 °C) solvolyze to identical mixtures of **4** (18%), **5** (70%), and hydrocarbon **8** (12%).



8 **E**

The global collection of data reported herein implicate preferential conversion of **1** to carbocation A rather than C and the existence of a significant barrier to that 1,2-hydride shift that leads from A to B. An increase in the acidity of the reaction medium facilitates this migration. Lastly, the ultimate conversion of **5** to 7, made possible by good stereoalignment, may be driven by bridgehead strain energy considerations related to those found in manxanes and related medium-ring bicyclic compounds.[10]

Acknowledgment. This work was supported at The Ohio State University by the National Science Foundation (Grant CHE-7900333) and at Houston by the Robert A. Welch Foundation (Grant E-594).

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(8) The rates for these tertiary systems are in line with those of structurally less encumbered tertiary norbonyl derivatives [compare: Brown, H. C.; Chloupek, F. J.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 1248. Brown, H. C.; Rei, M.-H. *Ibid.* **1964**, *86*, 5004].

(9) See: Berson, J. A. In "Molecular Rearrangements"; de Mayo, P.; Ed.; Interscience: New York, 1963; p 182.

(10) (a) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121. (b) Olah, G. A.; Liang, G.; Schleyer, P. V. R.; Parker, W.; Watt, C. I. F. *Ibid.* **1977**, *99*, 966. (c) Murray-Rust, P.; Murray-Rust, J.; Watt, C. I. F. *Tetrahedron* **1980**, *36*, 2799.

Viologens Used in "Electron Phase Transfer". Catalytic Debromination of *vic*-Dibromides under Heterophase Condition Using Viologens

Takeshi Endo,* Yashushi Saotome, and Makoto Okawara

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

Received September 19, 1983

Viologens (1,1′-dialkyl-4,4′-bipyridinium, V^{2+}) are known to undergo one-electron reduction to produce the cation radicals ($V^{+}\cdot$), which is easily reoxidized to V^{2+}. Recently, viologens have received much attention as an electron-transfer catalyst (ETC) in oxidation–reduction systems,[1] especially in hydrogen production by photoreduction of proton. We, on the other hand, have been interested in the reaction using V^{2+} as ETC for the reduction of organic compounds. For instance, it was found that aromatic aldehydes and ketones,[2] α-keto esters,[3] and azobenzene[4] could be reduced smoothly in the presence of V^{2+} as ETC.

Table I. Debromination of *meso*-1,2-Dibromo-1,2-diphenylethane[a]

run	catalyst[b]	solvent	PhC=CPh, %
1a		H_2O	0
b	MV^{2+}		4
c	PrV^{2+}		2
2a		H_2O-CH_3OH (1:1)	0
b	MV^{2+}		4
c	PrV^{2+}		5
3a		CH_2Cl_2	0
b	MV^{2+}		0
c	PrV^{2+}		0
4a		H_2O-CH_2Cl_2 (1:3)	0
b	MV^{2+}		1
c	EV^{2+}		54
d	PrV^{2+}		97
e	HpV^{2+}		95
f	DdV^{2+}		95
5	Bu_4N^+		0
6	PrV^{2+}	DMF-H_2O (1:1)	35

[a] The experiment was performed with 1.4 mmol of $Na_2S_2O_4$, 1.5 mmol of K_2CO_3, 0.2 mmol of the catalyst, and 1.0 mmol of *meso*-1,2-dibromo-1,2-diphenylethane in 20 mL of the solvent at room temperature for 40 min. [b] MV^{2+} = methylviologen, PrV^{2+} = propylviologen, EV^{2+} = ethylviologen, HpV^{2+} = heptylviologen, DdV^{2+} = dodecylviologen.

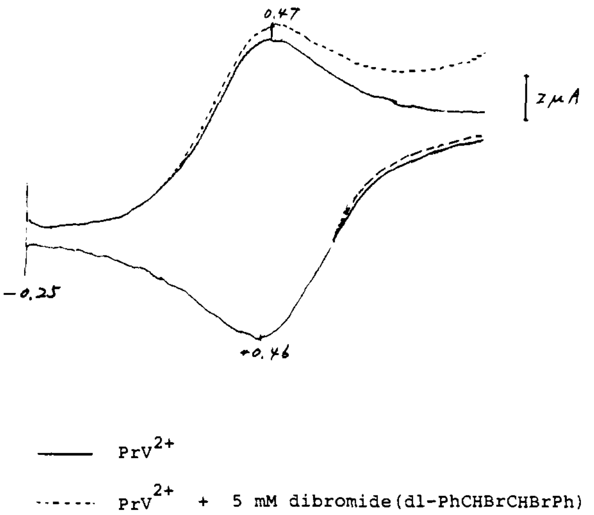

Figure 1. Cyclic voltammograms of a 1 mM PrV^{2+} solution in 0.1 M LiCl EtOH at Pt electrode, scan rate 0.1 V/s.

The technique using the phase-transfer catalyst (PTC) has been widely used in the field of the organic synthesis.[5]

We report here a study of the viologen-catalyzed debromination of *vic*-dibromides in heterophase to demonstrate "electron phase transfer" (EPT).

Many reagents[6,7] including metals, metal ions, and some nucleophilic reagents have been employed for debromination. However, sodium dithionite, which is a cheap and available reducing agent, has never been applied for debromination. Firstly, the debromination of 1,2-dibromo-1,2-diphenylethane was performed by sodium dithionite with or without various kinds of viologens, as shown in Table I. In water (runs 1a–1c) or water–methanol mixture (runs 2a–2c), debromination scarcely proceeded because of the insolubility of 1,2-dibromo-1,2-diphenylethane. However, debromination proceeded in a *N,N*-dimethylformamide (DMF)–H_2O mixture (run 6). In dichloro-

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(1) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta.* **1998**, *61*, 2720. Okura, I.; Kim-Thuan, N. N. *J. Mol. Catal.* **1979**, *5*, 311. Kawai, T.; Tanimura, K.; Sakata, T. *Chem. Lett.* **1979**, 137. Ageishi, K.; Endo, T.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1085.

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(3) Okawara, M.; Hirose, T.; Kamiya, N. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 927.

(4) Saotome, Y.; Endo, T.; Okawara, M. *Macromolecules* **1983**, *16*, 881.

(5) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978.

(6) Young, D. W. In "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum: London, 1973; p 309 and references cited therein.

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