The percentage conversion of the ruthenium starting material injected to RuO_4 was calculated by using eq 1, where $N(RuO_4^-)$

$$\% \ RuO_4 = [N(RuO_4^-)/N(Ru_{St})] \times 100 \qquad (1)$$

is the number of moles of RuO_4^- collected in the RuO_4 trap (a quantity determined spectrophotometrically) and $N(Ru_{St})$ is the number of moles of Ru starting material injected into the reaction vessel (calculated using the % Ru content of the sample). The observed value for the % RuO_4 represents a minimum, since some RuO_4 reacted with the rubber septum and the glassware (shown by blackening of both) before reacting in the hypochlorite trap.

Acknowledgment. We thank the S.E.R.C. for supporting this work. We also thank Miss Tina Lovelock and Miss Alison Green for their help with the experimental work.

Registry No. RuO_4, 20427-56-9; octan-2-ol, 123-96-6; octan-2-one, 111-13-7.

1-(1-Ethoxyethyl): An Effective Protecting Group for Imidazole Nitrogen

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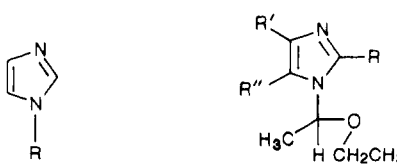
Introduction

Given the importance of substituted imidazoles in biological and pharmaceutical chemistry, it is understandable that 1-N protecting groups are continually being developed.[1-12] A large variety of these are known (**1a–g**). All allow formation of a C_2 or a C_5 anion, but each suffers from one or more disadvantage which precludes its general applicability. These may include: (1) incomplete lithiation of C_2, sometimes competitive with lithiation of the protecting group;[3,4] (2) deprotection[3-5] or protection[6,11] problems; (3) lack of reactivity of corresponding C_2 or C_5 anions with weaker electrophiles;[6-10] (4) expense.[11,12]

During the course of our work on imidazole-containing models for various enzymes,[13] we required an Im protecting group that was inexpensive, readily introduced and removed, but able to tolerate a variety of acidic and basic conditions, and allowed lithiation of C_2 or C_5 (if C_2 is blocked) with subsequent electrophilic additions proceeding in high yield. We believe the 1-ethoxyethyl[14] protecting group (EE) in **2** satisfies all these criteria.

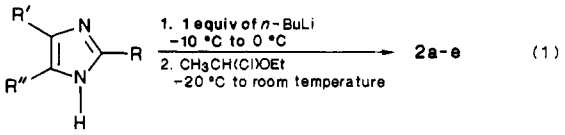


1a, R=CH_2Ph[1a,2-4]
b, R=CH_2OR[3-5]
c, R=$CH(OR)_2$[6,7]
d, R=SO_2Ar[6,8,9]
e, R=$SO_2N(CH_3)_2$[3,10]
f, R=CPh_3[6,11]
g, R=$CH_2OCH_2CH_2Si(CH_3)_3$[12]

2a, R=R′=R″=H
b, R=CH_3; R′=R″=H
c, R=Ph; R′=R″=H
d, R=$CH(OCH_3)_2$; R′=R″=H
e, R=H; R′=R″=CH_3

Results and Discussion

(a) Synthesis. The protecting group is introduced simply by dropwise addition of 1-chloro-1-ethoxyethane[15] to a THF solution of the N-anion of the parent imidazole (**3a–e**) as in eq 1. While they are not optimized, the



(1)

3a-e

isolated yields (all distilled) range from 70% to 86%. Physical data for **2a–e** are given in Table I (^1H NMR data are given as supplementary material) and a representative procedure is given in the Experimental Section.

Metalation of the ring positions (C_2 in **2a** or C_5 in **2d**) is accomplished in dry THF at −40 °C to −30 °C by treatment with *n*-butyllithium using standard syringe techniques. In the case of **2c**, C_5 metalation occurred only with *sec*-BuLi at −10 °C to 0 °C; at lower temperatures kinetic lithiation occurs both at C_5 and on the phenyl ring. The thermodynamic C_5 anion was obtained by adding first $^3/_4$ of the required 1.1 equiv of *sec*-BuLi at −10 °C to the THF solution of **2c** and stirring the resulting mixture at −5 °C for 30 min. The remaining *sec*-BuLi was then added over 15 min after which time the solution was stirred at 0 °C for 10 min. In the case of **2d** → **10** (see Table II), the initial lithiation was carried out without problems at −40 °C in THF by the addition of 1 equiv of *n*-BuLi followed by stirring for 30 min.

We have unsuccessfully attempted the formation of the dianion (C_2, C_5) of **2a** in THF by treatment with 2.1 equiv of *n*-BuLi at 0 °C. Even after prolonged stirring, a D_2O quench of the solution indicated that only the C_2 anion was formed.

A standard procedure including workup is given in the Experimental Section. Given in Table II are the isolated yields of the various products along with mp/bp data. (^1H NMR data is given as supplementary material.) While we have not attempted to optimize any case, the yields are good to excellent and the procedures are simple and

(1) (a) Shirley, D. A.; Alley, P. W. *J. Am. Chem. Soc.* **1957**, *79*, 4922. (b) Iversen, P. E.; Lund, H. *Acta Chem. Scand.* **1966**, *20*, 2649.
(2) (a) Jones, R. G. *J. Am. Chem. Soc.* **1949**, *71*, 383. (b) Roe, A. M. *J. Chem. Soc.* **1963**, 2195.
(3) Chadwick, D. J.; Ngochindo, R. I. *J. Chem. Soc., Perkin Trans 1* **1984**, 481.
(4) Tang, C. C.; Davalian, D.; Huang, P.; Breslow, R. *J. Am. Chem. Soc.* **1978**, *100*, 3918.
(5) Brown, R. S.; Huguet, J. *Can. J. Chem.* **1980**, *58*, 889.
(6) Curtis, N. J.; Brown, R. S. *J. Org. Chem.* **1980**, *45*, 4038.
(7) Brown, R. S.; Ulan, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 2382.
(8) (a) Sakakibara, S.; Fujii, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1466. (b) Fujii, T.; Sakakibara, S. *Ibid.* **1970**, *43*, 3954; **1974**, *47*, 3146.
(9) van der Eijk, J. M.; Nolte, R. J. M.; Zwikker, J. W. *J. Org. Chem.* **1980**, *45*, 547.
(10) In our hands, several attempts to react the C_2 anion of 1-(*N,N*-dimethylsulfonamido)imidazole with DMF at −20 °C or 0 °C in THF produced only starting material.
(11) (a) Kirk, K. L. *J. Org. Chem.* **1978**, *43*, 4381. (b) Kelley, J. L.; Miller, C. A.; McLean, E. W. *J. Med. Chem.* **1977**, *20*, 721. (c) Current cost of triphenylmethyl chloride (Aldrich) is $58.30 (U.S.)/500 g or $32.50/mol.
(12) (a) Whitten, J. P.; Matthews, D. P.; McCarthy, J. R. *J. Org. Chem.* **1986**, *51*, 1891. (b) Current cost of [2-(trimethylsilyl)ethoxy]methyl chloride (Aldrich) is $107.50 (U.S.)/25 g or $716.80/mol.
(13) (a) Street, J. P.; Skorey, K. I.; Brown, R. S.; Ball, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 7669. (b) Slebocka-Tilk, H.; Cocho, J. L.; Frakman, Z.; Brown, R. S. *Ibid.* **1984**, *106*, 2421. (c) Somayaji, V.; Skorey, K. I.; Brown, R. S.; Ball, R. G. *J. Org. Chem.* **1986**, *51*, 4866.

(14) Insofar as we are aware, use of the EE group has not been reported in the open literature. After completion of the experimental work, we discovered that it has been mentioned in the patent literature although its method of introduction is different (with CH_2=CHOEt; Whitney, J. G. U.S. Pat. Appl. 109923, 07 January, 1980. Adolphi, H.; et al. U.S. Pat. 3681/375, 1972. Fr. Pat. 1486817, June 30, 1967) and generalities of removal were not described.
(15) Grummitt, O.; Budewitz, E. P.; Chudd, C. C. *Organic Syntheses*; Wiley: New York, 1963, Collect. Vol. IV, p 748.

0022-3263/88/1953-1107$01.50/0

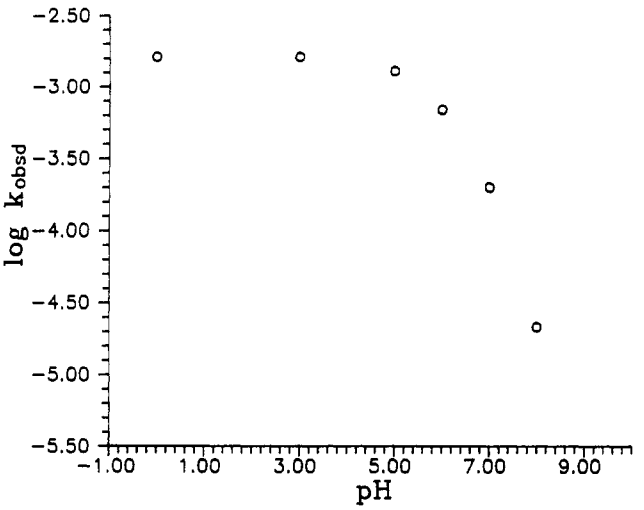


Figure 1. Plot of the log pseudo-first-order rate constant (k_{obsd}) for deprotection of **2c** vs pH: T = 72 °C, μ = 0.3 M.[16]

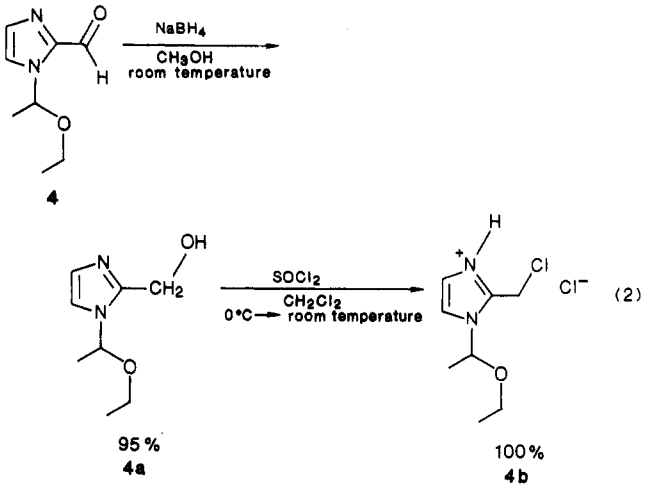
Table I. Isolated Yields and Properties of 1-(1-Ethoxyethyl)imidazoles

compd[a]	isolated yield (%)	bp (°C) (Torr)
2a	78	65–68 (1.2)
2b	76	70–74 (1.4)
2c	86	137–140 (2.2) mp 66–68
2d	70	63–65 (0.3)
2e	72	98–100 (2.6)

[a] All compounds had satisfactory elemental analyses (±0.3%, C, H, N) and gave exact mass molecular ions. (See Table 1S, supplementary material, for ^{1}H NMR data as well.)

inexpensive. Both the C_2 and C_5 anions are sufficiently reactive to attack the weak electrophile DMF and the hindered electrophile benzophenone. Hence it is reasonably expected that addition to more reactive electrophiles should proceed readily.

It is apparent that the protecting group is sufficiently robust to allow subsequent synthetic manipulations of the imidazole under acidic conditions. For example, as in eq 2, alcohol **4a** can be treated with $SOCl_2$ in CH_2Cl_2 (0 °C → room temperature, 10 h) to produce the HCl salt of the corresponding chloride in quantitative yield. Also, no detectable deprotection of **2a** was observed by ^{1}H NMR after 19 h in 20% DCl/D_2O at room temperature. However, 12% deprotection of **2c** was detected by ^{1}H NMR after 17 h under the same conditions.



(b) Deprotection. Deprotection can be accomplished by heating (50–100 °C) a mildly acidic solution of the N-EE derivative for a few hours. Given in Figure 1 is a

Table II. Preparation and Properties of 2- or 5-Substituted Imidazoles from 2a,c,d[a]

starting imidazole	electrophile	product	isolated yield (%)	mp or bp °C (Torr)	recrystallization solvent or purification method
2a	DMF	**4**, R = CHO; R′ = R″ = H	90	71–73 (2.5)	
		4a, R = CH_2OH; R′ = R″ = H	95 (from **4**)	107–109	$CHCl_3$/ether
		4b, R = CH_2Cl; R′ = R″ = H; HCl salt	100 (from **4a**)	145–147 dec	ppt from CH_2Cl_2
2a	$(C_6H_5)_2C{=}O$	**5**, R = COH $(C_6H_5)_2$; R′ = R″ = H	88	149–151	acetone–diethyl ether
2a	CH_3I	**2b**	91	see Table I	
2c	DMF	**6**, R = C_6H_5; R′ = H; R″ = CHO	61	hygroscopic solid; converted[b] directly to **7**	
		7, R = C_6H_5; R′ = H; R″ = CH_2OH	56 (from **2c**)	viscous oil	ppte from benzene–petroleum ether
2c	$(C_6H_5)_2C{=}O$	**8**, R = C_6H_5; R′ = H; R″ = $COH(C_6H_5)_2$	55	72–77 (crude)[c]	*d*
2c	CH_3I	**9**, R = C_6H_5; R′ = H; R″ = CH_3	62	oil	chromatography on neutral alumina; 10–40% $CHCl_3$ in petroleum ether
2d	DMF	**10**, R = $CH(OMe)_2$;[e] R′ = H; R″ = CHO	78 (crude)	135 (1.0) (some decomposition)	
		11, R = $CH(OCH_3)_2$;[e] R′ = H; R″ = CH_2OH	71 (from **2d**)	clear oil (chromatography)	chromatography on alumina; EtOH/$CHCl_3$ 3:10

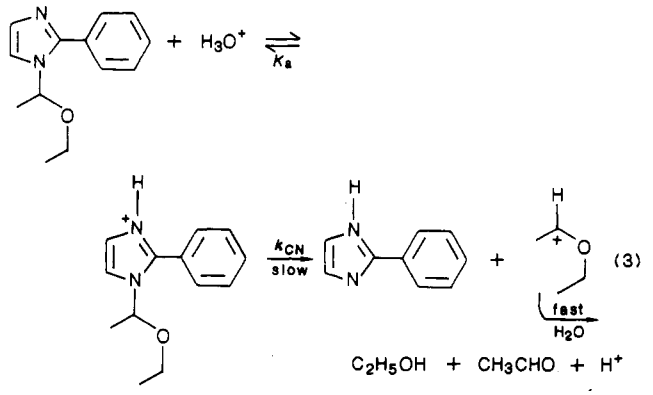
[a] All compounds gave exact mass molecular ions (given in supplementary material along with ^{1}H NMR data) and all compounds except **6** and **8** had satisfactory elemental analyses (±0.3%, C, H, N). Analysis of **4b** not attempted. [b] Reduced to **7** with $NaBH_4$ in methanol. [c] Decomposes if chromatographed on neutral alumina and attempts to crystallize this compound failed. [d] Deprotected by heating in 0.1 N HCl/CH_3OH at 55 °C for 4 h. The resultant deprotected **8** could be crystallized as its hydrochloride (**8a**) in chloroform–diethyl ether. **8a** (77% from **8**): mp 205 dec; ^{1}H NMR ($CDCl_3$–CD_3OD) δ 6.65 (s, 1 H), 7.28–7.63 (m, 13 H), 7.95–8.18 (m, 2 H). Anal. Calcd for $C_{22}H_{19}ClN_2O$: C, 72.82; H, 5.28; N, 7.72. Found: C, 72.89; H, 5.43; N, 7.61 [e] Exact mass given in Table 1S, supplementary material. These materials were carried forward to products which will be disclosed in future publications. Because **10** proved difficult to purify without decomposition, it was directly carried forward to **11**. Skorey, K. I., unpublished results.

Table III. Hydrolytic Half-Times for the Deprotection of Various Examples of 1-(1-Ethoxyethyl)imidazoles at 72 °C

compd	pK_a[c] (parent imidazole)	$t_{1/2}$ (h)	conditions, (method)[a]
2a	7.12	2.8	0.1 N HCl, (UV)
2b	7.85	15.3	1 N DCl/D_2O, (NMR)
2c	6.40	0.12	0.1 N HCl, (UV)
2e	~8.2[d]	33.9	0.1 N HCl, (UV)
4[b]		0.077	0.1 N HCO_2H, (pH 3.0), (UV)

[a] Kinetic methods described in Experimental Section. [b] Species present in solution in acid at pH ≤3 identified as aldehyde hydrate. [c] Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965. [d] Estimated from pK_a of 2-methylimidazole (7.85) and 2,4,5-trimethylimidazole (8.92) assuming the 2-methyl group enhances pK_a of imidazole by 0.7 unit.

pH vs log pseudo-first-order rate constant (k_{obsd}) profile for the deblocking of **2c** in H_2O at 72 °C. The shape of the profile indicates the mechanism to be as given in eq 3.[16] The same general mechanism also applies to the other

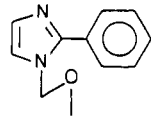


(3)

imidazoles. Operationally, this indicates that increases in $[H_3O^+]$ above that required to protonate the imidazole unit of **2** do not further enhance the rate. Hence the deprotections could be conducted at pH 5–7 if there are other acid-sensitive groups present.

Given in Table III are representative examples of the relative hydrolytic half-times for the deblocking under conditions where the imidazole units are completely protonated. Where identical comparison can be made (**2a**, **2c**, **2e**), it can be seen that the rate of C–N cleavage from the fully protonated form increases as the pK_a of the parent imidazole decreases. This trend has been noted before in the deprotection of *N*-bis(alkoxymethyl)imidazoles[7] which also hydrolyze by a mechanism analogous to that of **2**.

Finally, a crude NMR experiment was undertaken to compare the relative rates of deprotection of **2c** and its corresponding *N*-methoxymethyl derivative **12**. At 72 °C in 0.1 N HCl, the $t_{1/2}$ for **2c** is 7.2 min. At 80 °C in 1 N DCl/D_2O after 80 h, no detectable hydrolysis of **12** was observed despite the more vigorous conditions.



12

In summary, the EE group[14] appears to be a cheap, easily introduced and removed protecting group for imidazole N. It is superior to the alkoxymethyl group in terms of ease of removal. Its main advantage over the bis(alkoxymethyl) protecting group is a higher resistance to acidic conditions which allows further elaboration of the imidazole unit with the EE group intact.

(16) The k_{obsd} vs $[H_3O^+]$ data for the process in eq 3 adheres to the expression $k_{obsd} = k_{CN}[H_3O^+]/(K_a + [H_3O^+])$. Nonlinear least squares fitting of the data for **2c** to this expression yields $k_{CN} = 1.44 \times 10^{-3}$ s^{-1}; $pK_a = 6.16$.

Experimental Section

Melting and boiling points are uncorrected. ^1H NMR spectra were recorded on a Bruker WP-80 spectrometer. UV kinetic data for the imidazoles listed in Table III were determined on a Cary 210 spectrophotometer interfaced as previously described.[7] Duplicate reactions were initiated by injecting 20–40 μL of a stock solution of the imidazole (0.01 M in dry CH_3CN) into 3.0 mL of buffer in a 1-cm quartz cuvette thermostated at 72.0 ± 0.2 °C. Buffers were formulated to 0.1 M from commercially available materials; pH 1.0, 0.1 N HCl; pH 3.0, formic acid, pH 5.0, acetic acid; pH 6.0, MES (morpholinoethanesulfonic acid); pH 7.0, MOPS (morpholinopropanesulfonic acid); pH 8.0, HEPES (*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid). Ionic strength was maintained at 0.3 M (KCl) except in the case of 0.1 N HCl used for deprotection of **2a** which had $\mu = 0.1$ M. Kinetics of the rate of diminution of absorbance of **2a** were monitored at 222 nm while the increases in absorbance of **2c**, **2e**, and 1-(1-ethoxyethyl)imidazole-2-carbaldehyde were monitored at 262, 216, and 270 nm, respectively. Kinetic parameters were determined by fitting the absorbance vs time data to a standard exponential model by a nonlinear least-squares technique.[7] For **2b**, ^1H NMR was used to monitor the reaction in 1 N DCl/D_2O and the rate constant was determined from the standard ln plots of the integrated intensities of 4,5-H peaks in the starting material (δ 7.08 d, 7.18 d) and product (δ 7.00 s) as a function of time.

Syntheses. 1-chloro-1-ethoxyethane (1-chloroethyl ethyl ether) was easily prepared from paraldehyde, ethanol, and HCl gas according to a published procedure.[15] The material was found to be stable indefinitely if stored under an inert atmosphere at −78 °C: ^1H NMR ($CDCl_3$ at −5 °C) δ 1.28 (t, 3 H, J = 6 Hz), 1.80 (d, 3 H, J = 6 Hz), 3.38–4.28 (m, 2 H), 5.75 (q, 1 H, J = 6 Hz). *Caution: This material is related to methoxymethyl chloride and is therefore a cancer producing suspect. It should only be handled in a fume hood with adequate ventilation.*

General Procedure for Synthesis of 1-(1-Ethoxyethyl)-imidazoles. The desired 1*H*-imidazole (0.07 mol) was dissolved in 200 mL of dry THF and cooled to −10 °C with stirring under an atmosphere of argon. *n*-BuLi (0.077 mol) was addded via syringe at a rate which did not allow the temperature to exceed 0 °C. The solution was stirred for a further 30 min at −10 °C to 0 °C and finally cooled to −20 °C after which 0.077 mol of 1-chloroethyl ethyl ether (density 0.982 at −78 °C) was added slowly via syringe. The reaction mixture was allowed to warm to ambient temperature overnight after which time 25 mL of H_2O was added. The mixture was then extracted with 3 × 200 mL of CH_2Cl_2 and the combined organic extracts were dried over Na_2SO_4. After filtration and evaporation of the volatiles, Kügelrohr or regular vacuum distillation of the residue yielded the desired protected imidazoles (see Table I for physical data).

General Procedure for C_2 Lithiation of 1-(1-Ethoxyethyl)-1*H*-imidazole 2a and Subsequent Electrophilic Additions. The imidazole (0.03 mol of **2a**) was dissolved in 75 mL of dry THF, and the solution was cooled to −40 °C with stirring under Ar. *n*-BuLi (0.033 mol in hexane) was added via syringe at a rate which did not allow the temperature to increase above −30 °C. After addition, the mixture was stirred at −40 °C to −30 °C for 30 min. Following this, the electrophile (0.033 mol) was added (neat if liquid, in a minimum amount of THF if solid) and the mixture was then allowed to come to ambient temperature overnight. Water (20 mL) was added, and the mixture was then extracted with 3 × 120 mL of chloroform. The combined chloroform extracts were then dried (Na_2SO_4), after which the mixture was filtered and stripped of solvent to yield the crude product. This could be purified by distillation under vacuum if liquid or by recrystallization if solid. Physical data of the products, yields, and methods of purification are given in Table II.

General Procedure for Deprotection of 1-(1-Ethoxyethyl)imidazoles 8 → 8a (Table II). Freshly prepared **8** was placed in a 0.1 N HCl solution containing enough CH_3OH to

solubilize the salt of 8. The mixture was heated at 55 °C for 4 h after which time the solution was basified ($NaHCO_3$ solid) and extracted with $CHCl_3$. The volatiles were removed and the residue acidified to ~pH 2 with 0.1 N HCl. The resulting solution was again stripped of volatiles to yield a crude solid, 8a as the HCl salt. This was purified as in footnote d, Table II.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support and Ms. K. I. Skorey for the preparation of **2d**, **10**, and **11**.

Supplementary Material Available: Table of C, H, N analytical data, exact masses, and ^1H NMR data (2 pages). Ordering information is given on any current masthead page.

Synthetic Elaboration of Diosphenols. 3.† Replacement of Enolic Oxygen by Hydrogen

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Received April 29, 1987

In the course of applying the diosphenol Claisen rearrangement[1] to natural products synthesis, we desired to deoxygenate C-allylated diosphenols in the sense a → c (Figure 1). Reported sequences[2] for effecting this transformation involve a catalytic hydrogenation step incompatible with preservation of the allyl group. In our hands lithium/ammonia reduction of diosphenol methyl ethers gave predominantly α-methoxy ketones; similar reduction of diosphenol acetates gave complex mixtures. We therefore examined a different approach to activation of the enolic hydroxyl toward reductive fission.

Our previous work[3] showed that functionalization of diosphenols as dialkylthiocarbamates b activates the system toward reaction with bromide or chloride ion. The products of this reaction depend on the substitution pattern of the ring: when R = H, α-halo-α,β-unsaturated ketones are obtained cleanly;[3a] when R = alkyl, a variety of products is obtained.[3b] We now report that, *irrespective of substitution pattern*, diosphenol dialkylthiocarbamates are converted in high yield to c when treated with iodide ion in hot acetic acid. Figure 2 shows 13 enones prepared by this method (yields in parentheses) from the corresponding diosphenol dimethylthiocarbamates.

Since diosphenols may be C-alkylated via their dianions[4] (or, where allylic groups are concerned, via O-alkylation and Claisen rearrangement[1]), our reaction sequence allows the preparation of 3-alkyl-2-cycloalkenones from 1,2-diketones, *introducing the alkyl group as an electrophile.* This protocol complements other methods proceding from 1,3-diketones[5] or 3-unsubstituted enones[6] where the alkyl group is introduced as a nucleophile.

The replacement of enolic oxyygen by hydrogen may be rationalized by extension of our previous mechanistic postulates:[3] fused-cyclization followed by attack of iodide ion at the α-carbon leads to e which, via reductive elimination, gives c (Figure 3).

The insensitivity of the reduction process with iodide ion to the substitution pattern of the ring (cf. chloride ion, ref 3b) is probably the consequence of the greater nucleophilicity of iodide (reversion of d to b is not significant);

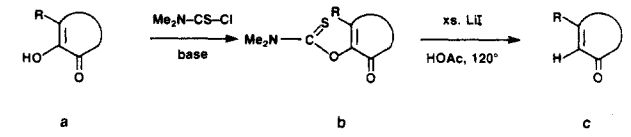

Figure 1.

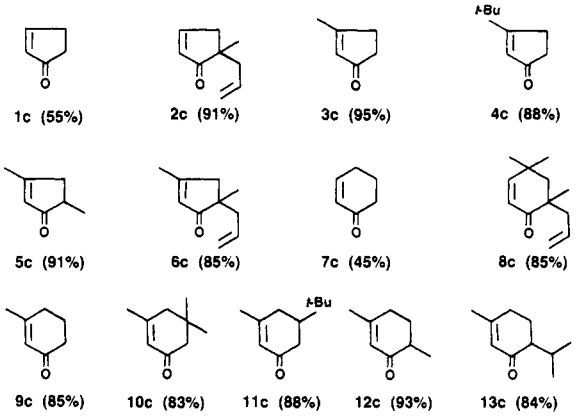

Figure 2.

the existence of other reduction mechanisms is also under present consideration. Diosphenol **2a** and its derived dimethylcarbamate or brosylate are *not* reduced by iodide ion under the standard conditions (1 h). If the brosylate is subjected to these conditions for 24 h some **2c** can be detected in the reaction mixture among several other products including starting material. We are continuing to explore the mechanism(s) and utility of these reactions.

Experimental Section

General Methods: see ref 3b.

Preparation of Diosphenol Dimethylthiocarbamates and Related Substances. General Procedure A. 6-Allyl-3,3,6-trimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (8b). A solution of 11.29 g (58 mmol) of 3-allyl-3,5,5-trimethyl-1,2-cyclohexanedione[1a] in 20 mL of THF was added dropwise at 0 °C, under nitrogen, to a magnetically stirred suspension of 3.34 g (70 mmol) of sodium hydride (50% dispersion in mineral oil) in 20 mL of THF. A solution of 8.36 g (70 mmol) of dimethylthiocarbamoyl chloride in 15 mL of THF was added and the reaction mixture was stirred overnight and then diluted with 180 mL of ether and washed successively with 180 mL of water, 180 mL of 1 M aqueous sodium hydroxide solution, and 180 mL of brine. The organic phase was dried over anhydrous magnesium sulfate and evaporated, giving 11.7 g of a solid whose NMR spectrum indicated that it was mainly the desired product. The crude product was chromatographed on 300 g of silica gel packed in a mixture of cyclohexane/ethyl acetate (3:1), giving 8.234 g (51%) of a white solid. Crystallization from pentane gave white crystals: mp 51–53 °C; IR 1677, 1645, 1633, 1525 cm^{-1}; ^1H NMR δ 1.22 (s, 3 H), 1.28 (s, 6 H), 1.82 (m, 2 H), 2.40 (d, J = 7 Hz, 2 H), 3.26 (s, 3 H), 3.38 (s, 3 H), 4.8–5.1 (dd, J = 3, 7 Hz, 1 H), 5.17 (br s, 1 H), 5.3–6.1 (m, 1 H), 6.18 (s, 1 H). Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.03; H, 8.23. Found: C, 64.17; H, 8.32.

General Procedure B. 5-*tert*-Butyl-3-methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (11b). A 2-mL portion of 10 M aqueous sodium hydroxide solution was added

† Part 2: see ref 3b.

(1) (a) Ponaras, A. A. *Tetrahedron Lett.* **1980**, *21*, 4803. (b) Ponaras, A. A. *Tetrahedron Lett.* **1983**, *24*, 3.
(2) Inter alia: (a) Cavill, G. W. K.; Goodrich, B. S.; Laing, D. G. *Aust. J. Chem.* **1970**, *23*, 83. (b) Ruzicka, L.; Plattner, P. A.; Furrer, M. *Helv. Chim. Acta* **1944**, *27*, 524.
(3) (a) Ponaras, A. A.; Zaim, Ö. *J. Org. Chem.* **1986**, *51*, 4741. (b) Ponaras, A. A.; Zaim, Ö. *J. Org. Chem.* **1987**, *52*, 5630.
(4) Kende, A. S.; Eilerman, R. G. *Tetrahedron Lett.* **1973**, 697.
(5) (a) Woods, G. F; Griswold, P. H., Jr.; Armbrecht, B. H.; Blumenthal, D. I.; Plapinger, R. *J. Am. Chem. Soc.* **1949**, *71*, 2028. (b) Piers, E.; Cheng, K. F.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 1256.
(6) (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (b) Stotter, P. L.; Hill, K. A. *J. Org. Chem.* **1973**, *38*, 2576.

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