9.51 (d, 1 H, J = 5.25 Hz, exchanged with D_2O, N5-H), 8.87 (s, 1 H, exchanged with D_2O, C4-NH_aH_b), 8.21 (s, 1 H, exchanged with D_2O, C4-NH_aH_b), 6.39 (br s, 1 H, exchanged with D_2O, OH), 5.17 (v br s, 1 H, exchanged with D_2O, OH), 3.43 (d, 1 H, J = 13.3 Hz, C6-H_aH_b), 3.15 (dd, 1 H, J = 13.3 Hz and 5.25 Hz, C6-H_aH_b, collapsed to d with J = 13.3 Hz on D_2O exchange of N5-H), 2.30, 2.28, 2.27 and 2.25 (dd, 1 H), 2.10-2.01 (m, 2 H), 1.98-1.87 (m, 4 H), 1.73-1.60 (m, 3 H), 1.52-1.45 (m, 2 H); ^{13}C NMR [$(CD_3)_2SO$] δ 174.4 (C), 72.4 (C), 70.8 (C), 56.5 (CH_2), 41.3 (CH), 40.0 (CH), 35.8 (CH_2), 34.8 (CH_2), 29.9 (CH_2), 26.6 (CH_2), 20.2 (CH_2). Anal. Calcd for $C_{11}H_{19}N_2O_2Cl$: C, 53.55; H, 7.76; N, 11.35. Found: C, 53.28; H, 7.97; N, 11.11.

(B) The amidine **5b** hemihydrate (0.40 g, 1.37 mmol) was dissolved in methanol (10 mL) and 15% aqueous sodium hydroxide (1.5 mL) added. After being stirred overnight at room temperature, the mixture was extracted several times with chloroform and the combined extracts were dried (Na_2SO_4). The material was then worked up as above to give the amidinium chloride **6** (0.27 g, 80%), which was identical with that obtained previously by procedure A.

Solution and Refinement of Structure 6. Numerical details pertaining to the collection and reduction of data are included in the supplementary material, and procedures have been described elsewhere.[24]

Acknowledgment. We thank D. Nelson and Dr. J. J. Brophy (mass spectra) and H. Stender (NMR spectra) for their skillful assistance. Financial support is gratefully acknowledged from the Australian Research Council.

Registry No. 1, 21173-67-1; 4, 123903-98-0; 5, 123904-01-8; 5b, 123903-99-1; 5d, 123904-02-9; 6, 123904-00-7.

Supplementary Material Available: Details of the solution and refinement of structure 6, crystal data, tables of atomic parameters and standard deviations, bond lengths and angles, hydrogen bonding parameters, and torsion angles with standard deviations, and Figure II showing the crystal packing arrangement of 6 (8 pages). Ordering information is given on any current masthead page.

(24) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

$VO(OR)Cl_2$-Induced Oxidative Aromatization of α,β-Unsaturated Cyclohexenones

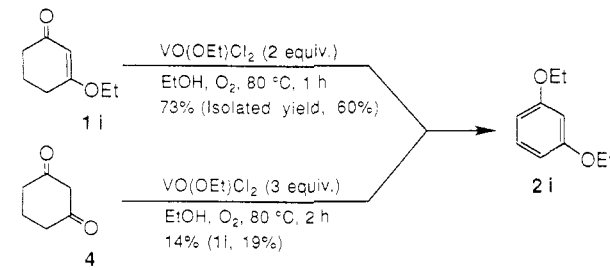
Toshikazu Hirao,* Makoto Mori, and Yoshiki Ohshiro*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

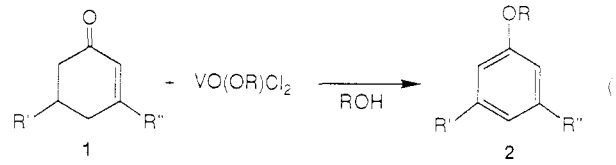
Received April 13, 1989

Vanadium compounds in a high oxidation state are considered to be versatile in oxidative transformations via one-electron transfer, but their synthetic utilization has been limited.[1] Our previous paper demonstrated that $VO(OEt)Cl_2$ catalyzes the ring-opening oxygenation of cyclic ketones in an alcohol under oxygen.[2] $VO(OR)Cl_2$ appears to be a Lewis acid with oxidation capability. We here report that oxidative aromatization[3] of α,β-unsaturated cyclohexenones to aryl ethers is achieved with $VO(OR)Cl_2$.

Scheme I



Treatment of 2-cyclohexen-1-ones (1) with $VO(OR)Cl_2$ in an alkanol led to the formation of the corresponding alkyl aryl ethers **2** in high yields (eq 1). The results are



(1)

listed in Table I. This oxidative transformation is characteristic of $VO(OR)Cl_2$; other oxovanadium compounds such as $VO(OEt)_3$, $VO(acac)_2$, and $VO(OSiPh_3)_3$ did not induce the aromatization of 2-cyclohexen-1-one (**1a**) in ethanol, giving only small amounts of the 1,4-addition product 3-ethoxycyclohexanone (**3a**).

It was found that 2 equiv of $VO(OEt)Cl_2$ was required to complete the dehydrogenative transformation. The reaction proceeded a little faster under oxygen than nitrogen. The conversion to ethyl phenyl ether (**2a**) with $VO(OEt)Cl_2$ was also observed in toluene although in low yield, suggesting that oxovanadium alkoxide plays an important role in the formation of the ether linkage. Use of 2-propanol as solvent gave predominantly the corresponding isopropyl ether **2c** even on treatment with $VO(OEt)Cl_2$. This may be due to a facile exchange within the oxovanadium alkoxide, which was independently confirmed by ^1H NMR. $VO(OEt)Cl_2$ in $CDCl_3$ was partially converted to $VO(OPr\text{-}i)Cl_2$ on addition of 2-propanol at room temperature. The ether **2c** was of course produced exclusively with $VO(OPr\text{-}i)Cl_2$ in 2-propanol. Methyl and cyclohexyl phenyl ethers (**2b** and **2d**) were similarly prepared. When allyl alcohol was employed, competitive oxidation to the acetal derivative 1,1,3-triallyloxypropane might account for the low yield of allyl ether **2e**. Running the reaction in 2-methyl-2-propanol did not give the *tert*-butyl ether.

Starting from the substituted 2-cyclohexen-1-ones **1f-g**, the expected ethers were obtained regioselectively, indicating that the alkoxyl group is introduced at the carbonyl carbon.

In the case of carvone (**1h**), the aromatization reaction was accompanied by oxidative bond cleavage between the carbon-carbon double bond of the 2-propenyl group, giving 4-acetyl-2-ethoxytoluene (**2h**) as the main product. This transformation probably is the result of oxidative cleavage after aromatization since it was also shown that α-methylstyrene was oxidized to acetophenone in 35% yield with $VO(OEt)Cl_2$ under oxygen at 80 °C for 5 h.

The present method was also applicable to oxidative aromatization of 3-ethoxy-2-cyclohexen-1-one (**1i**) into the resorcinol derivative **2i** (Scheme I). Treatment of 1,3-cyclohexanedione (**4**) with $VO(OEt)Cl_2$ in ethanol led to the same product **2i**, although in low yield. The latter transformation is assumed to proceed via **1i**, which was

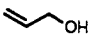
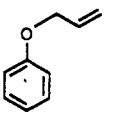
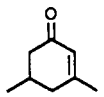
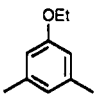
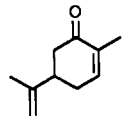
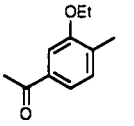
(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. Mijs, W. J.; de Jonge, C. R. H. I. *Organic Syntheses by Oxidation with Metal Compounds*; Plenum Press: New York, 1986.

(2) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399.

(3) Copper-induced aromatization to phenols has been reported: Bondon, D.; Pietrasanta, Y.; Pucci, B. *Tetrahedron Lett.* **1977**, 821.

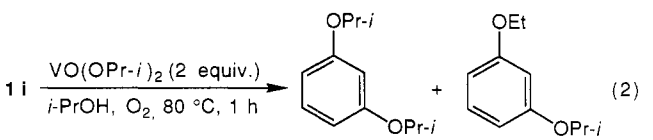
0022-3263/90/1955-0358$02.50/0

Table I. Oxidative Aromatization of 2-Cyclohexen-1-ones

1	V compd	equiv	solvt	atmosphere	time,[a] h	2	yield,[b] %
 **1a**	$VO(OEt)Cl_2$	1	EtOH	O_2	18	 **2a**	46 (tr)
1a	$VO(OEt)Cl_2$	1.5	EtOH	O_2	0.5	**2a**	57 (tr)
1a	$VO(OEt)Cl_2$	2	EtOH	O_2	0.5	**2a**	97, 93[c] (tr)
1a	$VO(OEt)Cl_2$	2	PhMe	O_2	0.5	**2a**	31 (tr)
1a	$VO(OEt)Cl_2$	2	EtOH	N_2	0.5	**2a**	87 (tr)
1a	$VO(OEt)_3$	2	EtOH	O_2	5	**2a**	tr (13)
1a	$VO(acac)_2$	2	EtOH	O_2	5	**2a**	tr (10)
1a	$VO(OSiPh_3)_3$	2	EtOH	O_2	5	**2a**	tr (6)
1a	$VO(OEt)Cl_2$	2	MeOH	O_2	0.5	 **2b**	35
1a	$VO(OEt)Cl_2$	2	*i*-PrOH	O_2	0.5	 **2c**	70[d]
1a	$VO(OPr\text{-}i)Cl_2$	2	*i*-PrOH	O_2	0.5	**2c**	92
1a	$VO(OEt)Cl_2$	2	c-$C_6H_{11}OH$	O_2	1	 **2d**	54[c,e]
1a	$VO(OEt)Cl_2$	2	*t*-BuOH	O_2	1	**2a**	16[f]
1a	$VO(OEt)Cl_2$	2		O_2	8	 **2e**	22[g]
 **1f**	$VO(OEt)Cl_2$	2	EtOH	O_2	0.5	 **2f**	90
 **1g**	$VO(OEt)Cl_2$	2	EtOH	O_2	2	 **2g**	91
 **1h**	$VO(OEt)Cl_2$	4	EtOH	O_2	3	 **2h**	32

[a] Oven oil temperature, 80 °C. [b] Yields were determined by GLC based on 1. The numbers in parentheses represent the yields of **3a**; tr = trace. [c] Isolated yield. [d] **2a**, 18%. [e] **2a**, 10%. [f] The formation of *tert*-butyl phenyl ether was not detected by GLC. [g] **2a**, 7%.

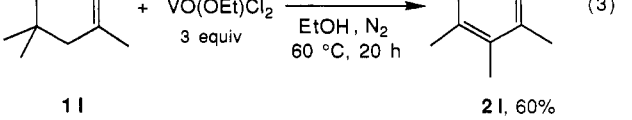
detected in a small amount in the reaction mixture. The reaction of **1i** with $VO(OPr\text{-}i)Cl_2$ in 2-propanol resulted in the predominant formation of 1,3-diisopropoxybenzene (**2j**) together with 1-ethoxy-3-isopropoxybenzene (**2k**) in consequence of the facile exchange of alkoxyl group (eq 2).



(2)

2j, 30% **2k**, 11%

The oxidative rearrangement reaction was observed with isophorone (**11**). 1,2-Migration of the 5-methyl group resulted in the formation of 5-ethoxy-1,2,3-trimethylbenzene (**21**, eq 3).[4] 4,4-Dimethyl-2-cyclohexen-1-one (**1m**), without

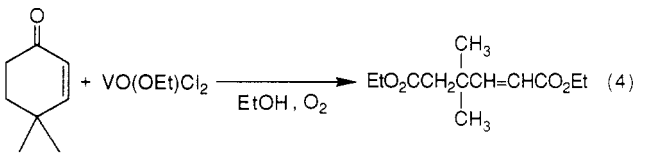


(3)

1l **2l**, 60%

(4) H_2SO_4–Ac_2O-induced aromatization: Kablaoui, M. S. *J. Org. Chem.* **1974**, *39*, 3696, and references therein. The base-induced rearrangement of 4-bromoisophorone has been reported to give 3,4,5- and 2,3,5-trimethylphenols: Mark, J. N.; Carnrick, A. W.; Cox, J. H. *Ibid.* **1972**, *37*, 2308.

a 4-proton, was not aromatized under the same conditions. The reaction under oxygen gave the ring-opened oxygenation product diethyl 4,4-dimethyl-2-hexene-1,6-dioate (**5m**), resulting from bond cleavage between C_1 and C_6 (eq 4).



1m 5m, 35% (4)

A one-electron-transfer mechanism seems to be operative in the oxovanadium-induced oxidations.[1] One plausible reaction course would involve the intermediacy of the dienolate followed by dehydrogenative elimination. $VO(OR)Cl_2$ can be considered to be a Lewis acid that induces further oxidative transformations of carbonyl compounds.

Experimental Section

IR spectra were measured with a Hitachi 270-30 spectrometer. ^1H NMR spectra were measured on JEOL JNM-FX90Q or JNM-GSX270 spectrometers. Mass spectra were determined by the electron impact method on a JEOL JMS-DX303 (Faculty of Engineering, Osaka University).

$VO(OR)Cl_2$ was prepared by dropwise addition of an alcohol to an equimolar amount of commercially available $VOCl_3$ in hexane while bubbling nitrogen into the reaction mixture at room temperature and was distilled under the reduced pressure (e.g., bp $VO(OEt)Cl_2$, 52–54 °C/2 mmHg; $VO(OPr\text{-}i)Cl_2$, 68–70 °C/4 mmHg). $VO(OEt)_3$ was obtained from Shinko Chemical Co., Ltd.

Representative Procedure for $VO(OR)Cl_2$-Induced Aromatization Reactions. A mixture of 2-cyclohexen-1-one (**1a**, 0.192 g, 2.0 mmol) in ethanol (2 mL) was treated with $VO(OEt)Cl_2$ (0.732 g, 4.0 mmol) under oxygen. The resulting solution was refluxed for 0.5 h. Small amounts of concentrated HCl and saturated aqueous NaCl were added to the mixture, which was extracted with ether (3 × 40 mL). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was an almost pure product **2a** by ^1H NMR, which was purified by silica gel column chromatography if required.

The other reactions were carried out in the same manner, and the conditions are shown in Scheme I, eq 2 and 3, and Table I. Yields were determined by GLC (10% PEG 20M 2.1-m column, 180 °C) based on **1**. The products **2** were identified by comparison of spectral data with those of authentic compounds reported or prepared by alkylation of the corresponding phenols.[5]

Oxidative Ring-Opening of 4,4-Dimethyl-2-cyclohexen-1-one (1m). The ketone **1m** (0.248 g, 2.0 mmol) was treated with $VO(OEt)Cl_2$ (1.098 g, 6.0 mmol) in ethanol (2 mL) under oxygen at 80 °C for 2 h. Workup was carried out as above. GLC analysis showed that **5m** was produced in 35% yield. **5m**: IR (neat) 2980, 1732, 1642, 1422, 1182, 1034, 964, 940, 828 cm^{-1}; ^1H NMR ($CDCl_3$ with TMS, 90 MHz) δ 1.24 (t, 3 H, J = 6.9 Hz), 1.29 (s, 6 H), 1.30 (t, 3 H, J = 6.9 Hz), 2.73 (s, 2 H), 4.10 (q, 2 H, J = 6.9 Hz), 4.17 (q, 2 H, J = 6.9 Hz), 5.71 (d, 1 H, J = 13.3 Hz), 6.18 (d, 1 H, J = 13.3 Hz); MS, m/z 228 (M^+).

Acknowledgment. This study was partly supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan.

Registry No. **1a**, 930-68-7; **1f**, 1193-18-6; **1g**, 1123-09-7; **1h**, 99-49-0; **1i**, 5323-87-5; **1l**, 78-59-1; **1m**, 1073-13-8; **2a**, 103-73-1; **2b**, 100-66-3; **2c**, 2741-16-4; **2d**, 2206-38-4; **2e**, 1746-13-0; **2f**, 621-32-9; **2g**, 18102-49-3; **2h**, 123507-46-0; **2i**, 2049-73-2; **2j**, 79128-08-8; **2k**, 123507-48-2; **2l**, 123507-47-1; **3a**, 13619-73-3; **4**, 504-02-9; **5m**, 123507-45-9; $VO(OEt)Cl_2$, 1801-77-0; $VO(OEt)_3$, 1686-22-2; $VO(CH_3CO\text{-}CHCOCH_3)_2$, 3153-26-2; $VO(OSiPh)_3$, 18822-50-9; $VO(OPr\text{-}i)Cl_2$, 1636-01-7; $VO(OPr\text{-}i)_2$, 119254-23-8; cyclohexanol, 108-93-0; 2-propen-1-ol, 107-18-6.

Supplementary Material Available: Listing of spectral data (IR, ^1H NMR, and MS) of the products reported (2 pages). Ordering information is given on any current masthead page.

(5) Vogel, A. I. *J. Chem. Soc.* **1948**, 616. Bodroux, D. *Ann. Chim.* **1929**, *11*, 511. Smith, L. I.; Hoehn, H. H.; Whitney, A. G. *J. Am. Chem. Soc.* **1940**, *62*, 1863. Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. Bates, R. B.; Siahaan, T. J.; Suvannachut, K.; Vasey, S. K.; Yager, K. M. *Ibid.* **1987**, *52*, 4605. So, Y. H.; Miller, L. L. *Synthesis* **1976**, 468. Sweeny, W.; Singh, G. *J. Org. Chem.* **1988**, *53*, 1819. Baciocchi, E.; Cort, A. D.; Eberson, L.; Mandolini, L.; Rol, C. *Ibid.* **1986**, *51*, 4544.

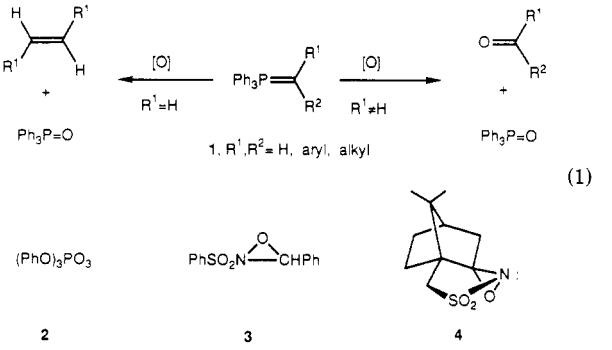
Chemistry of Oxaziridines. 12.[1] Oxidation of Alkylidenetriphenylphosphoranes with *N*-Sulfonyloxaziridines

Franklin A. Davis* and Bang-chi Chen

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received June 16, 1989

The oxidation of alkylidenephosphoranes (ylides) to alkenes and ketones has been explored by Bestmann and co-workers.[2] Ylides of type **1** (R^1 = H) gave alkenes while



(1)

bis(ylides) afforded cycloalkenes. Two molecules of vitamin A were oxidized to β-carotene by using this methodology.[3] Ketones are formed on oxidation of **1** ($R^1 \neq H$) making possible the synthesis of acylsilanes from silyl ylides (R^1 = aryl, R^2 = $SiMe_3$).[2b,4] Triphenyl phosphite–ozone (**2**) was generally used in these oxidations because of its aprotic nature. Although this reagent is readily prepared by treatment of triphenyl phosphite with O_3 at −78 °C, it is inconvenient to use because above −35 °C it decomposes to $^1O_2$ and triphenyl phosphate.[5] Symmetrical carotenoids have been prepared by oxidation of resonance-stabilized ylides using 50% hydrogen peroxide.[6] More recently Wassmerman and co-workers reported useful methodology for the preparation 1,2,3-tricarbonyl compounds via oxidation of phosphorane keto ylide carboxylates with ozone or singlet oxygen.[7]

(1) Davis, F. A.; Towson, J. C.; Weismiller, M. C.; Lal, S.; Carroll, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 8477.
(2) (a) Bestmann, H. J.; Pfuller, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 508. (b) Bestmann, H. J.; Kisielowski, L.; Distler, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 298.
(3) Bestmann, H. J.; Kratzer, O.; Armsen, R.; Maekawa, E. L. *Liebigs Ann. Chem.* **1973**, 760.
(4) Ricci, A.; Fiorenza, M.; Degl'Innocenti, A.; Seconi, G.; Dembech, P.; Witzgall, K.; Bestmann, H. J. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1068.
(5) Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* **1969**, *91*, 5358.
(6) Nurrenbach, A.; Paust, J.; Pommer, H.; Schneider, J.; Schulz, B. *Liebigs Ann. Chem.* **1977**, 1146.
(7) For leading references see: Wasserman, H. H.; Rotello, V. M.; Williams, D. R.; Benbow, J. W. *J. Org. Chem.* **1989**, *54*, 2785.

0022-3263/90/1955-0360$02.50/0