compared to carboxylato-bridging ligands.[4,5,8] Further experimental and theoretical studies will be needed to assign the electronic transition for this system.

Attempts were made to spectrally characterize the products of the second oxidation step by controlled-potential electrolysis. Unfortunately, isolation of these compounds in the bulk cell was not possible due to their extremely positive potentials, which were close to the anodic limit of CH_2Cl_2. Further attempts in solvents with a greater anodic potential limit are now underway.

In summary, tetrakis(μ-acetato)dirhodium(II) reacts with *N*-phenylacetamide to produce at least two of four possible geometric isomers of tetrakis(μ-*N*-phenylacetamido)dirhodium(II). Each of these complexes undergoes two reversible one-electron-transfer oxidation steps. The first oxidation occurs at a much lower potential than that found for any other dinuclear rhodium(II) complex of similar structure, and the second oxidation step has never been observed before. The visible spectra of the neutral and cationic complexes are also considerably different from those observed for dinuclear rhodium(II) complexes involving other types of bridging ions. Isolation and characterization of all the substitution products o the exchange reactions and the oxidized complexes is presently underway.

Acknowledgment. The support of the Robert A. Welch Foundation (K.M.K. Grant E680, J.L.B. Grant E918) is gratefully acknowledged.

Registry No. II, 82871-03-2; $Rh_2(O_2CCH_3)_4$, 15956-28-2; Rh, 7440-16-6.

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(8) Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.

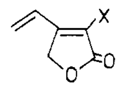
α-(Phenylthio)-β-vinylbutenolide, a Novel Annulating Reagent for the Synthesis of 4-Oxygenated Perhydro-2-oxo-1-benzofuran Derivatives

Fusao Kido, Yoshihiro Noda, and Akira Yoshikoshi*

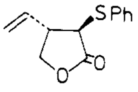
Chemical Research Institute of Non-Aqueous Solutions
Tohoku University, Sendai 980, Japan

Received May 18, 1982

Previously it was reported from this laboratory that β-vinylbutenolide (**1**) and its α-methyl derivative **2** were convenient lactone annulating reagents and that the efficacy in natural product chemistry was illustrated by the successful total synthesis of sesquiterpenes such as frullanolide[1] and furoventalene.[2] In this paper we describe α-(phenylthio)-β-vinylbutenolide (**3**) as a novel and intriguing reagent functionalized to annulate carbonyl compounds for the synthesis of 4-oxygenated perhydro-2-oxo-1-benzofuran derivatives; the perhydroxobenzofuran structure has frequently been found in natural products, in particular, sesquiterpene lactones.



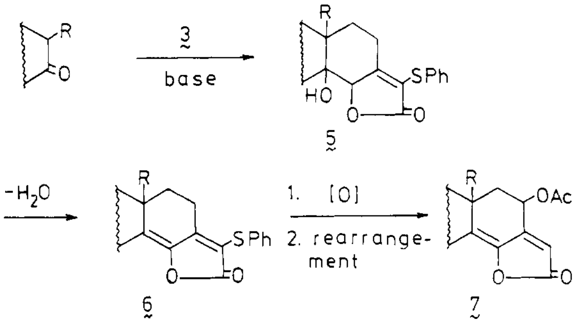
1 X = H
2 X = Me
3 X = SPh



4

The title reagent **3** was readily accessible from α-(phenylthio)-β-vinylbutyrolactone[1] (**4**) by the eliminative Pummerer rearrangement[3,4] as follows: a solution of mCPBA (4.5 mmol) in CH_2Cl_2 (15 mL) was added to a stirred solution of **4** (4.5 mmol) in the same solvent (10 mL) at 0 °C over 15 min. The mixture was stirred at the same temperature for 1 h and then filtered. The filtrate was successively washed with aqueous $NaHCO_3$, water, and brine. The crude sulfoxide thus obtained was dissolved in trifluoroacetic anhydride (1.0 mL) at 0 °C, and then the mixture was stirred at room temperature overnight. The solvent was removed, and the residue, diluted with CH_2Cl_2, was washed with aqueous $NaHCO_3$, water, and brine and dried. Evaporation of the solvent left crystals, which were recrystallized from ether to give pure **3** (694 mg, 71% yield from **4**), mp 70 °C. Unlike **1** and **2**,[1,2] this butenolide is stable and can be stored at ambient temperature in the dark.

The annulation of carbonyl compounds with **3** and the subsequent transformation of the products into the oxygenated perhydroxobenzofurans are shown by the equation: a carbonyl compound adds to **3** under basic conditions in the fashion of exclusive 1,6-conjugate addition followed by consecutive aldol-type cyclization to afford annulated product **5**. Some examples of the annulation are summarized in Table I, which demonstrates that the reaction with this reagent **3** proceeds in much higher yields in comparison with those of **1** and **2**.[1,2]



The product **5** is dehydrated to **6** ($SOCl_2$, py), which is then oxidized to sulfoxide (mCPBA). Under reaction conditions for allylic sulfoxide–sulfenate rearrangement (Ac_2O, py),[4] the sulfoxide yields acetoxyperhydroxobenzofuran **7** as a mixture of epimers with respect to the acetoxyl group (Table II). Judging from limited examples (**13–16**), stereoselectivity in the rearrangement appeared to depend on the bulkiness of angular substituents in the tricyclic system.

A sequence of reactions starting with 2-methylcyclohexane-1,3-dione are illustrative of the typical procedure of the annulation and of the subsequent transformation of the annulation product into **7**.

A solution of **3** (0.5 mmol) in DME (0.8 mL) was added dropwise to a stirred solution of the dione (1 mmol) and KF (0.55 mmol) in a mixture of Me_2SO and DME (1 mL of each) at 0 °C over 3–5 min. Stirring was continued at the same temperature for an additional 1 h, and the mixture was then acidified with dilute HCl. The product was extracted with CH_2Cl_2, and the extract was successively washed with water, aqueous $NaHCO_3$, water, and brine and dried. Removal of the solvent left the crude product, which was chromatographed on a silica gel column using 5:1 ether–petroleum ether as solvent to afford **8** (135 mg) sufficiently pure for the next step. An analytically pure sample was obtained by recrystallization from ether.

Thionyl chloride (0.06 mL) was added dropwise to a stirred solution of **8** (0.41 mmol) in dry pyridine (7.5 mL) at 0 °C. After stirring for an additional 30 min at the same temperature, the mixture was diluted with CH_2Cl_2, and the solution was washed with dilute HCl and water and dried. Removal of the solvent gave an oil, which was chromatographed on a silica gel column using CH_2Cl_2 as solvent to give the oily dehydration product (120 mg).

A solution of mCPBA (0.71 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of the above dehydration product (0.68 mmol) in the same solvent at 0 °C. Stirring was continued

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(1) Kido, F.; Tsutsumi, K.; Maruta, R.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6420.

(2) Kido, F.; Noda, Y.; Maruyama, T.; Kabuto, C.; Yoshikoshi, A. *J. Org. Chem.* **1981**, *46*, 4264.

(3) Sharma, A. K.; Swern, D. *Tetrahedron Lett.* **1974**, 1503. Hagiwara, H.; Nakayama, K.; Uda, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3769.

(4) Yamagiwa, S.; Sato, H.; Hoshi, N.; Kosugi, H.; Uda, H. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 570.

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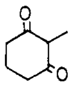
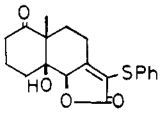
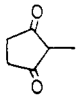
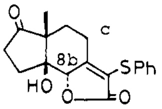
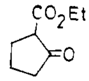
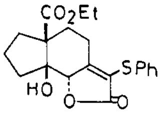
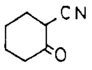
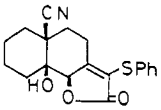
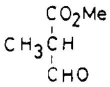
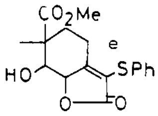
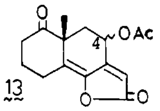
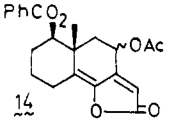
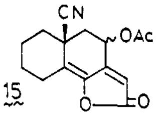
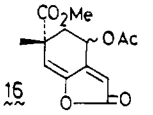
Table I. Annulation of Carbonyl Compounds with α-(Phenylthio)-β-vinylbutenolide

substrate	reaction conditions: base	solvent	temp. (°C)	time (h)	product[a]	m.p. (°C)	isolated yield (%)[b]
	KF	Me_2SO + DME	0	1	 8	193-194	78
	KF	Me_2SO + DME	room temp.	3	 9 [c]	163-164	80[d]
	NaH	DME	room temp.	3	 10	liquid	78
	Na	DME	0-15	12	 11	202-203	53
 $CH_3CH(CO_2Me)CHO$	KF	Me_2SO + DME	room temp.	2	 12 [e]		76

[a] The stereochemistry of the product was assigned in a manner similar to that described in the previous paper (ref 1). [b] Based on the reagent. [c] The ${}^1H$ NMR spectra of the crude product indicated that the major product under reaction conditions described here was the epimer of 9 at C(8b); however, attempted chromatographic separation on silica gel caused ready isomerization to an epimer mixture in which 9 was predominant in the ratio 85:15. The reaction of longer duration also gave 9 as the major product (85:15) in a comparable yield. [d] Combined yield of the C(8b) epimers. [e] Diastereomeric mixture. Three diastereomers were isolated therefrom.

Table II. Transformation of the Annulation Products into Acetoxyperhydroxobenzofurans

annulation product	rearranged product[a]	yield (%)[b]: dehydration	oxidation and rearrangement	epimer ratio (α-OAc: β-OAc)
8	 13	90	56	80:20
	 14 [c]		59	76:24
11	 15	79	53	55:45
12	 16 [d]	69	63	50:50[e]

[a] The stereochemistry at C(4) was assigned by coupling patterns of protons at this position. [b] Isolated yield. [c] The dehydration product of 8 was reduced ($NaBH_4$, THF-MeOH) and then benzoylated (PhCOCl, py; overall yield from 8, 49%). The benzoate, after peracid oxidation, was submitted to the rearrangement. [d] Inseparable mixture. [e] Determined by ${}^1H$ NMR analysis.

for an additional 30 min at the same temperature, and the mixture was filtered. The filtrate was washed with aqueous $NaHCO_3$ and water and dried. The crude product obtained on evaporation was dissolved in a mixture of Ac_2O (2 mL) and pyridine (1 mL) and heated at 30–40 °C for 3 h. The reaction mixture was diluted with CH_2Cl_2 and washed with dilute HCl and water and dried. The residue obtained on evaporation was separated by preparative silica gel TLC using CH_2Cl_2 as solvent, affording crystalline **13** α-acetate (80 mg), mp 173 °C (from MeOH), and oily **13** β-acetate (20 mg) from less polar and polar fractions, respectively.

Although high stereoselectivity was not observed in the rearrangement, this approach seemed promising as a novel entry toward sesquiterpene lactones oxygenated on their six-membered rings neighboring the γ-lactone moiety.[5]

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research 00554156 and 56430010.

Registry No. 3, 81470-07-7; *trans*-**4**, 81470-06-6; **8**, 82891-21-2; didehydro-**8**, 82891-27-8; didehydro-**8** sulfoxide, 82891-30-3; **9**, 81470-09-9; **10**, 82891-22-3; **11**, 82891-23-4; didehydro-**11**, 82891-28-9; didehydro-**11** sulfoxide, 82891-32-5; **12**, 81470-12-4; didehydro-**12**,

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(5) On this approach we have recently completed the total synthesis of paniculide A, which will be published elsewhere.

82891-29-0; didehydro-**12** sulfoxide, 82891-33-6; **13** (α-OAc), 82891-24-5; **13** (β-OAc), 82891-25-6; **14** (α-OAc), 81470-13-5; **14** (β-OAc), 82891-26-7; **15** (α-OAc), 81470-14-6; **15** (β-OAc), 81470-18-0; **16** (α-OAc), 81470-16-8; **16**, 81470-19-1; 2-methyl-1,3-cyclohexanedione, 1193-55-1; 2-methyl-1,3-cyclopentanedione, 765-69-5; ethyl 2-oxocyclopentanecarboxylate, 611-10-9; 2-oxocyclohexanecarbonitrile, 4513-77-3; methyl 2-methyl-3-oxopropanoate, 51673-64-4; 5aβ-methyl-6β-benzoyloxy-3-phenylsulfoxide 2,4,5,5a,6,7,8,9-octahydro-2-naphtho[1,2-*b*]furanone, 82891-31-4.

Supplementary Material Available: Spectroscopic data for compounds **3** and **8–16** (2 pages). Ordering information is given on any current masthead page.

Electron Paramagnetic Resonance Detection of Electric Field Effect on the Nucleation of the Ferroelectric Phase of KD_2PO_4

N. S. Dalal

Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506

Received May 3, 1982

We report here, to our knowledge, the first study by electron paramagnetic resonance (EPR) spectroscopy of the growth of one structural phase into another and the feasibility of influencing the nucleation kinetics of not only a phase but also a domain with a certain polarization. The paraelectric–ferroelectric phase transition[1] of KD_2PO_4 at $T_c = 221$ K was chosen as an example, and the growth rate of the ferroelectric phase was investigated as a function of temperature and externally applied electric field.

KD_2PO_4 was chosen since it is a typical member of a family of hydrogen-bonded compounds whose paraelectric–ferroelectric phase-transition mechanism is not fully understood,[1] and its ferroelectric property made it possible to influence the structural ordering via easily accessible electric fields. The deuteration was employed because the smaller hyperfine splittings from deuterons (as compared to protons) result in simpler EPR spectra. For this reason, KD_2PO_4 was prepared from a vacuum line synthesis from K_2CO_3, P_2O_5, and D_2O. The value of T_c (221 K), determined[2] via microwave dielectric loss at 9.4×10^9 Hz, indicated that the deuteration level was $\sim$99%.[1]

Since KD_2PO_4 is diamagnetic, the EPR studies were carried out on samples into which SeO_4^{3-} radicals were introduced by γ irradiation of KD_2PO_4 crystals doped with $\sim$1 mol % of K_2SeO_4, as described earlier.[3-6] The SeO_4^{3-} probe was preferred over AsO_4^{4-} and CrO_4^{3-}, the other two paramagnetic probes which have been widely used[7] for studying ferroelectric transitions, since SeO_4^{3-} has the same electric charge and site symmetry as a PO_4^{3-} unit in the original lattice, as has been shown by detailed ENDOR (electron nuclear double resonance) measurements.[5] The AsO_4^{4-} probe, formed by doping KD_2PO_4 with $\sim$5% KD_2AsO_4 and γ irradiation,[5,7] has an extra negative charge compared to the substituted (PO_4^{3-}) unit. This excess charge alters local electric field gradients and hence modifies the local ionic displacements near T_c. Similarly detailed ENDOR measurements have shown[8] that the site symmetry of CrO_4^{3-} is distinctly lower (C_s) than that (D_{2d}) of PO_4^{3-} in KH_2PO_4.

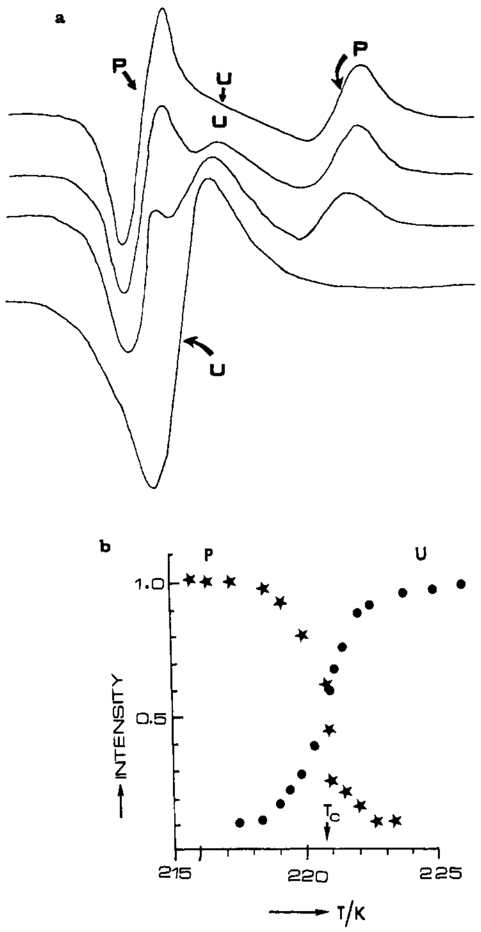

Figure 1. (a) Temperature dependence of the low-field ^{77}Se hyperfine component of the SeO_4^{3-} radical in KD_2PO_4 near $T_c = 221$ K. The signals labeled U and P refer to those from the "unpolarized" and the "polarized" regions. (b) Temperature dependence of the intensity of the P and the U signals, reflecting the growth of the polarized regions in the paraelectric sample in the vicinity of T_c.

The D_{2d} symmetry of SeO_4^{3-} in KD_2PO_4 was verified by analyzing the angular dependence of its EPR spectrum in terms of the electron Zeeman tensor (**g**) and the hyperfine tensor (**A**) with a numerical diagonalization procedure.[5] The results for the ferroelectric phase are as follows:[5b] $g_{xx} = 2.002 \pm 0.005$, $g_{yy} = 2.001 \pm 0.005$, $g_{zz} = 2.001 \pm 0.003$; $A_{xx} = 2988 \pm 8$ MHz, $A_{yy} = 3138 \pm 8$ MHz, $A_{zz} = 3486 \pm 6$ MHz. Here the *z* direction coincides with the *c* axis and the *x* axis is oriented at 30 ± 2° with respect to the *a* axis of the tetragonal crystal *abc* system. These results are essentially identical with those for KH_2PO_4,[5,9] where this probe was identified via ENDOR, thus confirming its formation in KD_2PO_4.

Spectral changes relevant to the nucleation phenomenon are observed within 5 K of T_c. Figure 1a shows the temperature dependence of the low-field component of the ^{77}Se hyperfine line labeled U (for "unpolarized"). At $T = T_c + 3$, the signal is a singlet exhibiting axial symmetry on crystal rotation about the *c* axis, conforming with the tetragonal symmetry of the paraelectric phase of KD_2PO_4. On approaching T_c (from $T > T_c$), this signal is seen to be flanked by two sharper signals, labeled P (for "polarized"). As the temperature is lowered further the P signals increase in intensity at the expense of the U signals and at $\sim$2.5

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(1) Lines, M.; Glass, A. M. "Principles and Applications of Ferroelectrics and Related Materials"; Clarendon Press, Oxford, 1977.

(2) The experimental procedure for determining T_c via microwave dielectric loss measurements was similar to that described by Gough et al. (Gough, S. R.; Ripmeester, J. A.; Dalal, N. S.; Reddoch, A. H. *J. Phys. Chem.* **1979**, *83*, 664). A temperature hysteresis of 1.5 K (maximum) was noted. Temperature was controlled to within 0.5 K and measured with a copper–constantan thermocouple. The temperature gradient across the sample was less than 0.5 K, as judged by the EPR and T_c measurements on samples of widely different sizes.

(3) Hukuda, K. *J. Phys. Soc. Jpn.* **1975**, *38*, 150. Hukuda, K.; Nakagawa, Y. *Ibid.* **1978**, *44*, 1588.

(4) Kawano, T. *J. Phys. Soc. Jpn.* **1974**, *37*, 848.

(5) (a) Dalal, N. S.; Hebden, J. A.; Kennedy, D. E.; McDowell, C. A. *J. Chem. Phys.* **1977**, *66*, 4425. (b) Due to a printing error in 5a, the parameters for KD_2PO_4:SeO_4^{3-} for $T < T_c$ were incorrect. The present work corrects this error.

(6) Dalal, N. S. *Ferroelectrics* **1981**, *39*, 1060.

(7) (a) Adriaenssens, G. J. *J. Magn. Reson.* **1977**, *25*, 511. (b) Dalal, N. S. *Adv. Magn. Reson.*, in press.

(8) Gaillard, J.; Gloux, P.; Muller, K. A. *Phys. Rev. Lett.* **1977**, *38*, 1216.

(9) The corresponding values for SeO_4^{3-} in KH_2PO_4 are as follows: $g_x = 1.9997$, $g_y = 2.0158$, $g_z = 2.0036$; $A_x = 2986$ MHz, $A_y = 3055$ MHz, $A_z = 3490$ MHz. For details see ref 5.

0002-7863/82/1504-5511$01.25/0