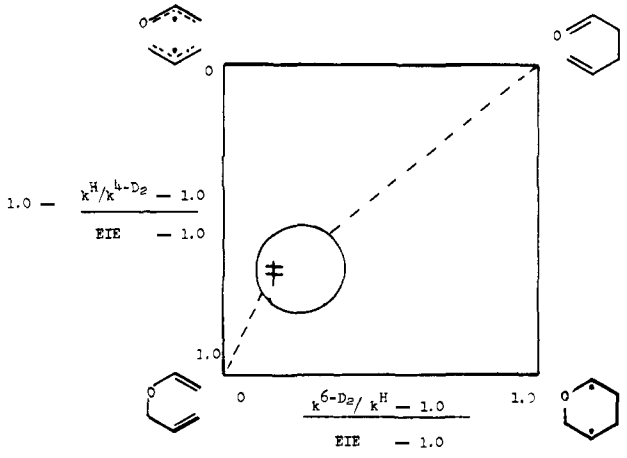
$$k^H/k^{4\text{-}D_2} = 1.092 \pm 0.005$$

$$k^{6\text{-}D_2}/k^H = 1.025 \pm 0.005$$

At 160.3 °C the normal KIE at C_4 is 1.092 ± 0.005 and the inverse KIE at C_6 is 1/1.025 ± 0.005.[8] It is meaningful to compare these KIE's with the maximum possible KIE's at each site which are the appropriate equilibrium IE's—provided that coordination number changes and electronegativities alone are responsible for the KIE's as they are in the EIE's.[12] Since the EIE's cannot be determined in the actual system, the C_6 KIE should be compared with the EIE for fractionation of deuterium between an *exo*-methylene and a saturated methylene flanked by two carbons; for two deuteriums this is 1.16 at 160 °C.[9,10] The EIE of deuterium between *exo*-methylene and a saturated carbon flanked by one carbon and one oxygen is 1.27 ± 0.03 determined from the equilibrium constant for allyl acetate-α,α-γ,γ-d_2 interconversion catalyzed by mercuric acetate at 160 °C.[10,11,17]

The ratio of the KIE to the EIE at the bond breaking site is (1.09-1.0)/(1.27-1.0) or ⅓, while that at the bond making site is only (1.025-1.0/1.16-1.0) or <⅙. A More O'Ferrall-Jencks diagram[13] for the AVE rearrangement using these IE ratios as coordinates[14] is shown in Scheme I where it is clear that the transition state is "early" presumably because of the exothermicity of the reaction.[7]

Scheme I



Since the AVE 3,3 shift involves more bond breaking than making, it appears that the bond-breaking alternative is more stable than the bond-making alternative. An estimate[15] of the relative free energies of the two nonconcerted extremes indicates that the former is more stable than the latter by ~7 kcal/mol primarily because of the greater entropy of the former.

Interestingly, the entropy of activation for the AVE rearrangement is less negative than for the Cope rearrangement,[16] suggesting more bond breaking than making in the former relative to the latter which is consistent with the isotope effects and the analysis of the relative energies of the nonconcerted alternatives.

Finally, the transition state structure suggests that radical stabilizing substituents on C_1, C_4, and C_6 will stabilize the transition state to a greater extent than placement of the same substituents on C_2 and C_5. The relative rates of reaction will, of course, depend on relative transition state and ground state stabilities.[17]

Acknowledgment. We thank the National Science Foundation for support of our work and acknowledge helpful discussions with Professors V. J. Shiner and L. K. Montgomery.

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(9) Log (K_H/K_{O_4}) = 129.5/T − 0.1721 (correlation coefficient, 0.95) for EIE's in eight appropriate but different systems over a temperature range of 55 to 288 °C allows determination of the EIE for two deuteriums at 160 °C: N. D. Conrad, Ph.D. Thesis, Indiana University, Aug 1978. See for example, ref 1.
(10) This assumes that substituents on atoms β to the reacting site have little effect on KIE's or EIE. See ref 12 for a justification.
(11) The equilibrium was approached from both sides. The experimental value agrees well with that calculated by Shiner (1.29 at 160 °C) who assumes the effect of oxygen can be estimated by force field associated with fluorine.[12]
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(14) Usually bond orders or bond distances are the structural coordinates of the MOF-J diagram, but we prefer using parameters which are directly experimentally accessible. A linear relationship between KIE's and bond order changes is often assumed but controversy surrounds this point—see K. D. McMichael and G. L. Korver, *J. Am. Chem. Soc.*, preceding paper in this issue.
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(16) For AVE, log k = 11.70-30 600/2.3RT: F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950). For 1,5-hexadiene log k = 10.36-34 300/2.3RT: W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **21**, 5299 (1971).
(17) Professor K. D. McMichael and G. L. Korver have determined the EIE for allyl acetate-d_2 to be 1.64 ± 0.04 at 38-60 °C which is close to the Hartshorn-Shiner calculation (1.62).[12] Furthermore, McMichael and Korver have determined the bond-breaking and bond-making KIE's for the aryl Claisen rearrangement. See accompanying paper. We thank Professor McMichael for sharing his results and the suggestion that these two papers be published jointly.

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Structure and Stereochemistry of Officinalic Acid, a Novel Triterpene from *Fomes officinalis*

Sir:

Fomes officinalis is a wood-rotting fungus which is found on the trunks of living or dead coniferous trees in the Pacific Northwest United States, Canada and in Europe.[1] A variety of triterpenes from this fungus[2] have been characterized since it was first studied in 1804.[3] Officinalic acid[4] ($C_{30}H_{44}O_6$, mp 272 °C, $[\alpha]_D$ −60° (c 0.5, dioxane)[5] is the trivial name assigned to a plentiful constituent (1.5% by weight) obtained from ether extracts of the ground mycelium.

In addition to bicarbonate solubility **1a** was characterized as a carboxylic acid by conversion (CH_2N_2) to a monomethyl ester, **1b** ($C_{31}H_{46}O_6$, HR, mp 236 °C, $[\alpha]_D$ −54 ° (c 0.15 dioxane)), and by its IR spectra (**1a**, 3210, 1730, 1709 cm^{-1}; **1b**, no OH, 1736 cm^{-1}). The presence of three carbonyls was established by the ^{13}C NMR spectrum of **1b** ($CDCl_3$) (δ 205.3, 172.6, 168.5). Compound **1b** was inert to monoperphthalic and *m*-chloroperbenzoic acids, gave negative unsaturation tests, and showed only a single ^{13}C NMR peak at δ 105.3 which is assigned to a ketal carbon with nothing further in the δ 100-150 region.

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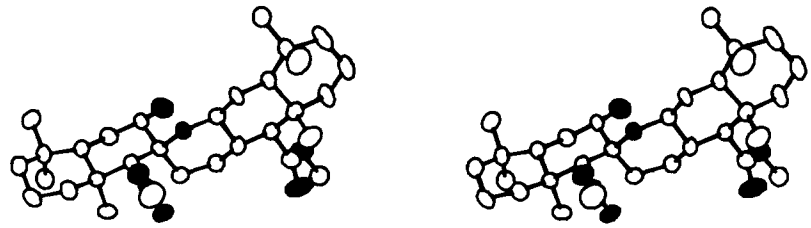
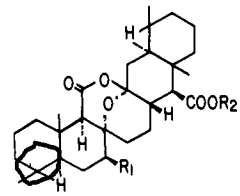


Figure 1. Stereoscopic projection of **2a**.



1

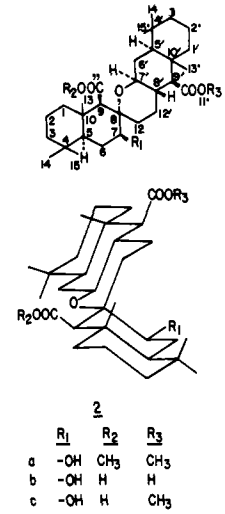
	R_1	R_2
a	=O	H
b	=O	CH_3
c	(H)-OH	H
d	(H)-OH	CH_3
e	(H)-OAc	H
f	(H)-OAc	CH_3

The NMR spectrum of methyl officinalate (**1b**) showed six methyl resonances (220 MHz, $CDCl_3$) (δ 0.82, 0.84, 0.85, 0.89, 1.04, 1.29, all singlets). A 1 H doublet (δ 2.84, J = 13 Hz), and two 2 H singlets at δ 3.24 and 2.49 were the only low-field NMR absorptions other than the OCH_3 of the ester.

Selective reduction of **1a** or **1b** with borohydride (100 mg of $NaBH_4$, 50 mg of **1a** or **1b**, in 25 mL of 95% EtOH, 2 h at room temperature) gave dihydroofficinalic acid **1c** (mp 316 °C) or methyl dihydroofficinalate **1d** (mp 247 °C); **1c** could be converted into **1d** (CH_2N_2). Acetylation of **1c** or **1d** gave monoacetates **1e** or **1f**, respectively, while methylation of **1e** also gave **1f.** These data coupled with the ^{13}C NMR peak at δ 205.4 verified the presence of the ketone. The ^1H NMR spectra of dihydro derivatives **1e–f** varied slightly from the spectra of **1a** and **1b;** one methyl singlet was shifted from δ 1.29 in **1b** to 1.14 in **1d** suggesting the deshielding of a single methyl group by the carbonyl in **1b.** One of the 2 H singlets in the NMR of **1b** (δ 2.49) was absent in spectra of dihydro derivatives **1c–f,** consistent with assignment of $-CH_2CO-$ to this signal. The other low-field NMR peaks in **1b** were superimposable with similar absorptions in the spectra of dihydro compounds **1c–f.**

Compounds **1a–d** could be reduced further with borohydride (3 mg of $NaBH_4$/1 mg of compound in EtOH, 24 h) or by catalytic reduction (PtO_2, HOAc, 12-20 h) to give the corresponding tetrahydro derivatives. Catalytic reduction of officinalic acid (above conditions) yielded one major product **2b** (mp 368 °C) identical with that obtained by 24-h borohydride reduction of officinalic acid (**1a**) or further reduction of dihydroofficinalic acid (**1c**). Compounds **2b** or **2c** (**2c,** mp 185 °C) were converted into the same dimethyl ester (**2a**) ($C_{32}H_{52}O_6$, HR, mp 290 °C). Thus, the complete reduction of **1a** or **1b** first involves the reduction of a ketone, followed by a reduction to form a second carboxyl. The presence of a cyclic ether was suggested by reduction of **2a** ($LiAlH_4$-THF, 48-h reflux under N_2) to give a pentacyclic triol ($C_{30}H_{52}O_6$, HR, mp 260 °C).

A labile lactone in **1** is postulated as the source of the second carboxyl group formed during reduction. Evidence for the lactone linkage of **1** at C-7′ is found in the NMR spectra (no resonances in δ 3.5-4.5 region except OCH_3) of **1a** or **1b** as well as the ^{13}C NMR spectrum of **1b** where the resonance at δ 105.3 in **1b** shifts to 83.7 in **2a.** A γ-lactone involving the carboxyl group at C-9′ is precluded in **1** by IR and stereochemical considerations while the C-9 carboxyl can be part of a δ-lactone if C-7′ undergoes inversion upon reduction.



2

	R_1	R_2	R_3
a	-OH	CH_3	CH_3
b	-OH	H	H
c	-OH	H	CH_3

Single-crystal X-ray diffraction analysis was used to determine structure of **2a.** Crystals of **2a** grown from acetone yielded the following data: from diffractometer measurements on 25 reflections in the range $20° < \theta < 30°$ (Cu Kα, λ = 1.5418 Å), a = 14.997 (6), b = 7.304 (3), c = 13.951 (5) Å and β = 93.08 (2)°; monoclinic, space group $P2_1$; Z = 2; d_{obsd} = 1.163 (by flotation in CCl_4-hexane mixture), d_{calcd} = 1.159 g cm^{-3}. The crystal used for intensity measurements had dimensions 432 × 128 × 96 μm.

Intensity data were collected on a computer-controlled automatic diffractometer[6] using the θ-2θ scan method with graphite-monochromatized Mo Kα radiation. In the range $0 < \theta < 26°$, 2950 independent reflections were measured of which 2605 were classified as observed by the criterion $I > \sigma(I)$ where I was determined from counting statistics. No absorption corrections were applied.

A trial structure consisting of 35 nonhydrogen atoms was obtained using the MULTAN[7] program for direct phase determination. Preliminary isotropic refinement provided difference electron density maps in which the remaining major atoms were located. The six oxygen atoms were selected on the basis of chemical reasonableness and low temperature parameters when compared with neighboring carbon atoms. Bond distances obtained at the end of refinement confirmed the assignments. Isotropic refinement of the complete structure gave $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] = 0.11$. Coordinates for 45 of the 52 hydrogen atoms were obtained from the difference map calculated at this stage; peaks corresponding to the hydroxyl hydrogen and six methyl hydrogens could not be located. Further refinement in which nonhydrogens were treated anisotropically and the hydrogens were refined isotropically led to a final R value of 0.057 for the observed reflections.[8]

As can be seen in the stereoscopic projection[9] (Figure 1), derivative **2a** consists of a *trans*-decalin section connected by

a spiro link at C-8 to a tricyclic portion. All the rings are joined trans except the spiro ring, and all have chair conformation. The carboxymethyl groups at C-9 and C-9′ are equatorial while at the spiro C-8 the oxygen is equatorial and C-12 is axial. The hydroxyl at C-7 is equatorial but the peak corresponding to the C-7 hydrogen was large enough (approximately three electrons at a distance of 1.22 Å) to suggest that there might be some disorder at C-7 involving axial attachment of the hydroxyl.

The structure of officinalic acid is unique in comparison with those of known triterpenes, but it has some similarity to the onoceranes. While the onoceranes are likely derived from squalene, extensive rearrangement of a squalene precursor would be required to give the carbon skeleton of officinalic acid.

Supplementary Material Available: Lists of atomic coordinates, temperature parameters, torsion angles, and bond distances (17 pages). Ordering information is given on any current masthead page.

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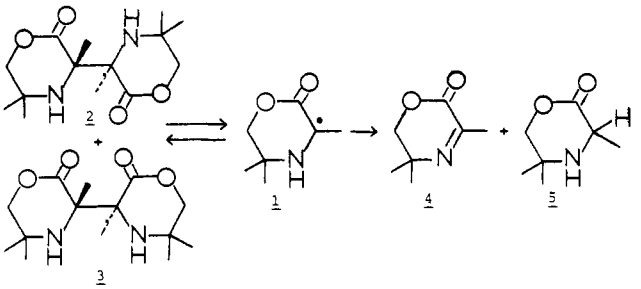
Electron-Transfer Chemistry of the 3,5,5-Trimethyl-2-morpholinon-3-yl Radical

Sir:

Previously we have reported that the 3,5,5-trimethyl-2-morpholinon-3-yl radical (**1**) is formed when a mixture of the meso and *dl* dimers (**2** and **3**, respectively) of the radical are dissolved in benzene, chloroform, or ethanol solvent at ambient temperature.[1,2] Upon being heated to 80 °C **1** disproportionates to a 50:50 mixture of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**4**) and 3,5,5-trimethyl-2-morpholinone (**5**). The methylmorpholinonyl radical **1** is analogous to some free radicals described by Katritzky as merostabilized radicals.[3]



We now report (1) that the morpholinonyl radical **1** is capable of serving as a mild reducing agent by formally transferring a hydrogen atom to an appropriate acceptor, (2) that as a hydrogen atom donor it is capable of generating other stable free radicals and serving as a selective reducing agent for some functional groups, and (3) that the mechanism of hydrogen atom transfer is actually a rate-controlling electron transfer followed by a rapid proton transfer.

When a degassed mixture of the meso and *dl* radical dimers **2** and **3** and 5,6-dihydro-5,5-dimethyl-3-phenyl-1,4-oxazin-2-one (**6**)[4] is dissolved in methanol solvent, a new radical species is observed in the EPR spectrum which has been identified as the 5,5-dimethyl-3-phenyl-2-morpholinon-3-yl radical (**7**). The spectrum has a *g* value of 2.00399 and the following splitting pattern N, 1:1:1, 6.52; N-H, 1:1, 3.95; ortho and para H, 1:3:3:1, 2.01; meta H, 1:2:1, 0.81 G. The phenylmorpholinonyl radical **7** is persistent at ambient temperature for a period of days, does not dimerize, and is further reduced quantitatively to 5,5-dimethyl-3-phenyl-2-morpholinone (**8**) upon prolonged heating.

A mechanism for the production of the phenylmorpholinone **8** is shown in Scheme I and is suggested by the following evidence. The intensity of the EPR spectrum of the phenylmorpholinonyl radical **7** at ambient temperature is directly proportional to the square root of the concentration of the phenyloxazinone **6** and the fourth root of the concentration of the radical dimers **2** and **3**. Furthermore, the intensity of the EPR spectrum of **7** is significantly diminished upon the addition of trimethyloxazinone **4**. Under the conditions of the intensity

Scheme I