Collection and Isolation of Sulfircin (1). The sponge was collected at a depth of 119 m off Fresh Creek, Andros, Bahamas in August of 1985, by using the Harbor Branch Oceanographic Institution's submersible the Johnson Sea-Link I. One hundred grams of the frozen sponge (wet weight) was extracted exhaustively by homogenization with methanol in a blender. The extract was filtered and then concentrated by distillation under reduced pressure to yield 1.27 g of a pale yellow oil. The oil was chromatographed under reverse phase vacuum liquid chromatographic conditions by using a C-18 stationary phase and a step gradient of acetonitrile/water as eluent. The fraction eluting with acetonitrile/water (4:1) contained a microcrystalline solid, which after recrystallization from dichloromethane/methanol yielded 90 mg of sulfircin (1): colorless needles, mp 199–200 °C (dichloromethane/methanol); $[\alpha]^{20}_D$ +5° (*c* 0.006, ethanol); UV (EtOH) λ_{max} 208 nm (ϵ 1024); IR (KBr) ν (cm^{-1}) 3340, 3200, 2920, 1620, 1445, 1380, 1360, 1210, 1050, 1020, 960, 900, 870, 820, 746, 775; ^1H NMR (360 MHz, $CDCl_3/CD_3OD$ (4:1)) δ 7.25 (t, J = 1.2 Hz, H19), 7.13 (br s, H25), 6.17 (d, J = 1.2 Hz, H18), 5.27 (br s, H7), 4.45 (dd, J = 11.3, 3.1 Hz, H12), 2.84 (6 H, s, H27abc and H28abc), 2.34 (2 H, t, J = 7.5 Hz, H16ab), 2.21 (m, H13), 2.16 (m, H9), 1.84 (2 H, m, H6ab), 1.72 (m, H1a), 1.61 (3 H, br s, H23abc), 1.60 (m, H15a), 1.54 (m, H11a), 1.47 (m, H15b), 1.42 (m, H2a), 1.36 (m, H2b), 1.33 (m, H14a), 1.29 (m, H3a), 1.17 (m, H5), 1.14 (m, H14b), 1.09 (m, H3b), 1.07 (m, H1b), 0.87 (3 H, d, J = 7.0 Hz, H24abc), 0.79 (3 H, s, H20 or H21abc), 0.76 (3 H, s, H21 or H20abc), 0.66 (3 H, s, H22abc); ^{13}C NMR (90 MHz, $CDCl_3/CD_3OD$ (4:1)) 158.3 (s, C26), 142.8 (d, C19), 138.9 (d, C25), 135.8 (s, C8), 125.2 (s, C17), 122.2 (d, C7), 111.1 (d, C18), 83.9 (d, C12), 50.1 (d, C5), 48.8 (d, C9), 42.3 (t, C3), 38.7 (t, C1), 37.8 (q, 2 C, C27 and C28), 37.0 (d, C13), 36.6 (s, C4 or C10), 33.2 (q, C20), 33.1 (s, C4 or C10), 33.1 (t, C14), 28.3 (t, C15), 26.6 (t, C11), 24.9 (t, C16), 23.9 (t, C6), 22.4 (q, C23), 21.9 (q, C21), 18.9 (t, C2), 13.6 (q, C22), 13.1 (q, C24); FAB MS (magic bullet) m/z 781.4, 627.4, 613.4, 599.5, 562.3, 177.0.

Acknowledgment. Mass spectral determinations were performed at the University of Illinois. This is Harbor Branch Oceanographic Institution Contribution no. 712.

Registry No. 1, 120927-18-6.

Supplementary Material Available: Positional parameters, B(eq) values, bond angles and distances, torsion or conformation angles, and U values for compound 1 (7 pages). Ordering information is given on any current masthead page.

Selective Decarbalkoxylation of β-Keto Esters

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Received November 3, 1988

Decarbalkoxylation of a β-keto ester is a common synthetic manipulation. A wide variety of procedures have been developed for this transformation.[2] We now report a novel observation: the rate of decarbalkoxylation of a substituted β-keto ester is a predictable function of the substitution pattern.[3]

Scheme I

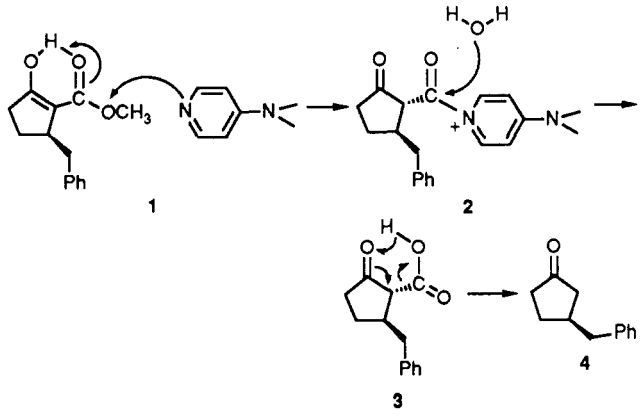
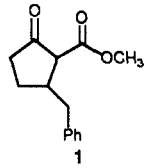
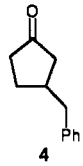
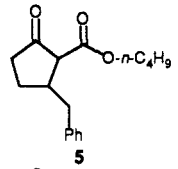
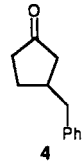
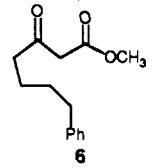
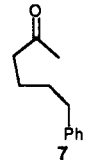
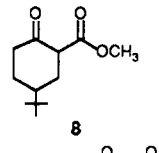
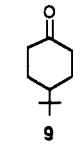
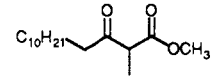


Table I

reactant	product	pH	half-life	yield, %
 1	 4	5	2.5 h	70
		7	6 h	70
		9	2.5 h	58
 5	 4	7	6 h	71
 6	 7	7	1 day	68
 8	 9	7	8 days	61
 10		7	no reaction	

The genesis of this project was the chance observation that 4-(dimethylamino)pyridine (4-DMAP), which we had shown to be an effective catalyst for transesterification of β-keto esters (toluene, 90 °C),[4] effects smooth decarbalkoxylation (1 → 4, Scheme I) of those same β-keto esters[5] if the toluene contains a little water.

The mechanism of this transformation is straightforward. Acylation of 4-DMAP by the ester 1, to give 2, is assumed to be the first step in the transesterification. Interception of the acylated pyridinium species by water would give 3, which at the elevated reaction temperature would spontaneously decarboxylate, to give the product.

To delineate the generality of this procedure, we submitted a representative series of β-keto esters to the reaction conditions (Table I). To our surprise, a substantial difference in rate appeared. As with the transesterification,

(1) Science and Engineering Scholar, University of Delaware Honors Program.

(2) A variety of reagent combinations have been used to effect decarbalkoxylation of β-keto esters. For leading references, see: (a) DMSO/NaCl: Krapcho, P. A.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138. (b) DABCO: Huang, B. S.; Parish, E. J.; Miles, D. H. *J. Org. Chem.* **1974**, *39*, 2647. (c) Al_2O_3/dioxane: Greene, A. E.; Cruz, A.; Crabbe, P. *Tetrahedron Lett.* **1976**, 2707. (d) $Ba(OH)_2$: Miller, R. B.; Nash, R. D. *Tetrahedron* **1974**, *30*, 2961. (e) TMSI: Ho, T.-L. *Synth. Commun.* **1979**, *9*, 233. (f) Boric acid: Ho, T.-L. *Synth. Commun.* **1981**, *11*, 7. (g) $MgCl_2 \cdot nH_2O$/HMPA: Tsuda, Y.; Sakai, Y. *Synthesis* **1981**, 119. (h) Propane-1,2-diol: Aneja, R.; Hollis, W. M.; Davies, A. P.; Eaton, G. *Tetrahedron Lett.* **1983**, *24*, 4641.

(3) The enhanced lability of cyclopentanone carboxylates has been noted previously: Greene, A. E.; Luche, M.-J.; Serra, A. A. *J. Org. Chem.* **1985**, *50*, 3957, and ref. 2c, above.

(4) Taber, D. F.; Amedio, J. C., Jr.; Patel, Y. K. *J. Org. Chem.* **1985**, *50*, 3618.

(5) In the absence of 4-DMAP, no decarbalkoxylation is observed.

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nonenolizable β-keto esters (not shown) were unreactive. Of the enolizable β-keto esters, the cyclopentanone derivative was much faster than the cyclohexanone, which in turn was much faster than the α-substituted acyclic ketone. An α-unsubstituted acyclic ketone was intermediate in reactivity.

We speculate that formation of the pyridinum species **2** is the rate-determining step in this decarbalkoxylation. Formation of **2** could be faster with the enol form of the keto ester, since the enol could hydrogen bond to the ester carbonyl, activating it for 1,2-addition. It would follow that enol content of the keto ester would dictate reactivity in this process, a suggestion certainly in keeping with the data in Table I.

Other factors were briefly probed. The reaction is significantly accelerated at higher or lower pH. On the other hand, no difference in reactivity was seen between a methyl and an *n*-butyl ester. Neither DABCO,[2b] *N,N*-dimethylaniline, pyridine, nor tetrapentylammonium bromide was an effective mediator of decarbalkoxylation under these conditions.

It should be noted that neither isolated esters nor malonates are reactive under these conditions. Thus, in addition to being of interest mechanistically, this method for the decarbalkoxylation of enolizable β-keto esters could prove to be of preparative utility.

Experimental Section[6]

3-Benzylcyclopentanone (4). A 1-mL reaction vial charged with 133 mg (0.488 mmol) of **1**,[7] 24 mg (0.4 equiv) of 4-(dimethylamino)pyridine, 0.5 mL of 1.0 M phosphate buffer (pH 7), and 0.5 mL of toluene was maintained with stirring at 90 °C for 6 h. The reaction mixture was partitioned between aqueous NH_4Cl and ethyl acetate. The organic phase was dried ($MgSO_4$), concentrated in vacuo, and chromatographed[8] on 3 g of TLC mesh silica gel to give 61 mg (0.348 mmol, 71%) of **4** as a yellow oil. ^1H NMR: δ 7.3–7.1 (m, 5 H), 2.7 (d, J = 7.8, 2 H), 2.5–1.5 (m, 7 H). ^{13}C NMR: δ 219 (s), 140.0 (s), 128.8 (d, 2), 128.5 (d, 2), 126.2 (d), 44.9 (t), 41.5 (t), 38.8 (d), 38.3 (t), 29.1 (t). IR: 2920, 2875, 1760, 705 cm^{-1}. MS: *m/e* 91 (100), 115 (22), 117 (38), 174.104 (66) $(M + H)^+$.

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Registry No. 1, 120853-06-7; **4**, 85163-16-2; **5**, 120853-07-8; **6**, 120853-08-9; **7**, 14171-89-2; **8**, 74851-58-4; **9**, 98-53-3; **10**, 120853-09-0; 4-DMAP, 1122-58-3.

(6) For general experimental procedures, see: Taber, D. F.; Deker, P. B.; Fales, H. M.; Jones, T. H.; Lloyd, H. A. *J. Org. Chem.* **1988**, *53*, 2968.
(7) Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808.
(8) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

Quantitative Rearrangement of Monocyclic Endoperoxides to Furans Catalyzed by Co(II)

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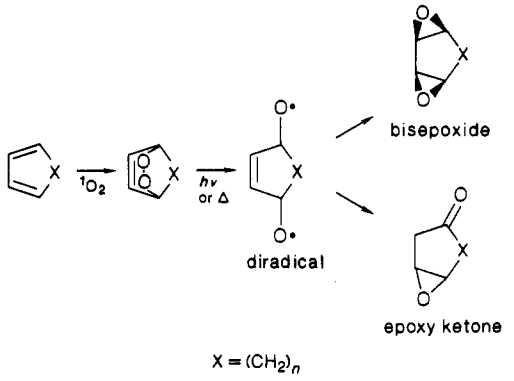
Cycloaddition of singlet oxygen to conjugated dienes provides a synthetically useful method of introducing oxygen at the 1,4-positions of 1,3-dienes.[1,2] The resulting unsaturated bicyclic endoperoxides can be converted both thermally and photolytically to a variety of stereospecifically oxygenated compounds[3] including bisepoxides. Rearrangement to the bisepoxide is usually favored over the competing retro-Diels–Alder reaction unless loss of oxygen leads to a particularly stable product (as with endoperoxides of polycyclic aromatic hydrocarbons).[4] Both thermal and photolytic paths appear to go via a biradical medium and give substantial amounts of side products such as epoxy ketone.[5]



Boyd et al.[6] reported that cobalt(II) tetraphenylporphyrin (CoTPP) catalyzes the rearrangement of unsaturated bicyclic endoperoxides to bisepoxides in high yield. Balci[7] applied this reaction to unsaturated bicyclic endoperoxides from strained dienes and proposed a diradical mechanism. Noyori[8] used iridium and palladium to catalyze the rearrangement.

These reactions have previously been applied only to bicyclic endoperoxides. We now report that CoTPP-catalyzed rearrangement of monocyclic endoperoxides gives furans in quantitative yield.

cis-3,6-Dimethyl-1,2-dioxene was prepared from the reaction of (*E,E*)-2,4-hexadiene with singlet oxygen.[9] Treatment of the endoperoxide with 5–10 mol % CoTPP in chloroform at room temperature yielded a 1:1 mixture of hemiketals **1** and **2**. These compounds were characterized by a variety of NMR experiments, including 2D ^1H–^1H homonuclear correlation, 2D ^1H-^{13}C heteronuclear correlation, DEPT, and homonuclear decoupling experiments. The results are summarized in Table I (assignments of positions 2 and 3 are ambiguous). The hemiketals decompose on further standing at room temperature to give 2,5-dimethylfuran in quantitative yield (see paragraph at the end of the paper about supplementary material). Treatment of *cis*-3,6-diphenyl-1,2-dioxene with CoTPP gave 2,5-diphenylfuran,[10] also in nearly quantitative yield.

Several cobalt(II) complexes were investigated to help gain insight into the mechanism. Spin state, geometry, and

(1) Balci, M. *Chem. Rev.* **1981**, *81*, 91.

(2) (a) Adam, W.; Balci, M. *Tetrahedron* **1980**, *36*, 833. (b) Frimer, A. A. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 201.
(3) Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1980**, *102*, 1961.
(4) Gollnick, K.; Schenck, G. O. In *1,4-Cycloaddition Reactions*; Hamer, J., Ed.; Academic Press: New York, 1967.
(5) (a) Maheshwari, K. K.; DeMayo, P.; Wiegand, D. *Can. J. Chem.* **1970**, *48*, 3265. (b) Carless, H. A. J.; Atkins, R.; Fekarurhobo, G. K. *Tetrahedron Lett.* **1985**, *26*, 803.
(6) Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641.
(7) (a) Sütbeyaz, Y.; Sacen, H.; Balci, M. *J. Org. Chem.* **1988**, *53*, 2312. (b) Sütbeyaz, Y.; Balci, M. *Tetrahedron Lett.* **1983**, *24*, 311, 4135.
(8) (a) Suzuki, M.; Oda, Y.; Noyori, R. *Tetrahedron Lett.* **1981**, *44*, 4413. (b) Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1982**, *104*, 2024.
(9) O'Shea, K.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 7167.
(10) Matsumoto, M.; Dobashi, S.; Kuroda, K.; Konda, K. *Tetrahedron* **1985**, *11*, 2154.

0022-3263/89/1954-3475$01.50/0