Table II. Comparison of Epoxy Alcohols[a]

Grignard reagent	ratio of 1,3-diol:1,2-diol 3	 4	 2	 5
 [b]	7:1 87%, 12.5%	c 72%, 0%	4:1 72%, 18%	5.1:1 76%, 15%
 [b]	6.1:1 82%, 13.5%	5.2:1 70%, 13.5%	4.9:1 83%, 17%[d]	4:1 71%, 17.7%
n-BuMgBr[e]	2.6:1 60%, 23%	6:1 75%, 12.5%	3.4:1 68%, 20%	5:1 72%, 14.4%
CH_3MgI[e]	4.8:1 72%, 15%[d]	6:1 72%, 12%[f]	2.2:1 58%, 26%[g]	3.3:1 68%, 20.6%

[a] For all reactions a mixed solvent of tetrahydrofuran and ether, 1:5 to 1:7, was used. Ratios and yields of 1,3-diol:1,2-diol were determined by isolation of both products. [b] Reactions conducted at −20 to −25 °C. [c] None of the 1,2-diol was detected. [d] Yield based on consumed starting material. [e] Reactions conducted at −40 °C. [f] Ratio determined by ^1H NMR. [g] Reaction time was 11 h at −40 °C followed by warming to 23 °C.

reagents at −40 °C. Tetrahydrofuran (THF) was found to be an essential cosolvent. Large amounts of THF inhibited the reaction, possibly because of strong coordination to the metal ions in the reaction medium,[9] but in the absence of THF, mixtures of reaction products were observed. A small percentage of complexing solvent may be necessary to solubilize the reagent.

Our work compliments recent results which show that alanes selectively cleave epoxy alcohols at C-3.[10] The ready availability of enantiomerically pure epoxy alcohols[11] suggests that this procedure will find widespread use in synthesis.

Experimental Section

Tetrahydrofuran and ether were distilled from sodium benzophenone ketyl. Ultrapure cuprous iodide from Alfa was washed with dry tetrahydrofuran in a Soxhlet extractor for 12 h, was vacuum dried for 8 h, and was stored under argon in a desiccator. Nuclear magnetic resonance (NMR) spectra were recorded either at 100 MHz (Varian XL-100 spectrometer) or at 300 MHz (Oxford magnet, Nicolet data system). Infrared spectra were recorded on a Beckman IR 10 instrument. Electron-impact mass spectra were recorded on a Varian MAT-311 instrument.

General Procedure for Epoxide Ring Opening. To a stirred suspension of 0.57 g (0.03 mol, 0.3 equiv) of cuprous iodide (Alfa, ultrapure) in 100 mL of anhydrous ether under nitrogen at −8 °C was added 0.3 mol of a solution of isopropenyl magnesium bromide in THF (0.43 M, 3 equiv). The light yellow suspension was immediately cooled to −23 °C, and epoxy alcohol **3** (2.0 g, 0.1 mol, 1 equiv) in 5 mL of ether was added slowly via cannula. The yellow heterogeneous mixture was stirred at −23 °C for 8 h. The reaction mixture was partitioned between ether and saturated aqueous NH_4Cl that had been basified to pH 8 by addition of concentrated NH_4OH. The ethereal extract was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and filtered, and the solvent was evaporated. The residue was flash chromatographed on silica gel to provide 2.05 g of 1,3-diol (8.67 mmol, 84%) and 0.29 g of 1,2-diol (1.23 mmol, 12%).

^1H NMR of 1,3-diol (1) (100 MHz, $CDCl_3$): δ 7.32 (s, 5 H), 4.98 (br s, 1 H), 4.85 (br s, 1 H), 4.54 (s, 2 H), 3.98 (m, 1 H), 3.75–3.40 (m, 4 H), 2.42 (m, 3 H, includes both OH), 1.78 (br s, 3 H). ^1H NMR of 1,2-diol (100 MHz, $CDCl_3$): δ 7.31 (s, 5 H), 4.96 (br s, 1 H), 4.84 (br s, 1 H), 4.50 (s, 2 H), 3.75–2.40 (m, 5 H), 2.51 (m, 1 H), 2.18 (br s, 2 H, both OH), 1.76 (br s, 3 H). The aldehyde derived from cleavage of the 1,2-diol with $NaIO_4$ shows an aldehyde proton in the 100-MHz NMR spectrum at δ 9.57 as a doublet, J = 2.1 Hz.

Acknowledgment. We thank the National Institutes of Health (Grant GM 30390-01) for generous financial support. Support from the American Cancer Society, administered by the Cancer Center of Hawaii, Grant IN-145, is also acknowledged. NSF Grant CHE 81-00240 supported the purchase of the 300-MHz NMR spectrometer.

Registry No. 1, 87116-66-3; 2, 73814-97-8; 3, 87172-27-8; 4, 84621-89-6; 5, 87205-38-7; CuI, 7681-65-4; $H_2C{=}C(CH_3)MgBr$, 13291-18-4; $H_2C{=}CHMgBr$, 1826-67-1; *n*-BuMgBr, 693-03-8; CH_3MgI, 917-64-6; $(CH_3)_2CuLi$, 15681-48-8; $[H_2C{=}C(CH_3)]_2CuLi$, 21329-14-6; $(i\text{-}Bu)_2[H_2C{=}C(CH_3)]_2AlLi$, 87136-17-2; $[H_2C{=}C(CH_3)]_2Cu(CN)Li_2$, 87136-18-3.

Supplementary Material Available: Experimental details of the preparation of epoxy alcohols 2–5 and spectroscopic data of the corresponding acetonides (9 pages). Ordering information is given on any current masthead page.

(9) Herr, R. W.; Wieland, D. M.; Johnson, C. R. *J. Am. Chem. Soc.* **1970**, *92*, 3813.
(10) Pfaltz, A.; Mattenberger, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 71. Suzuki, T.; Saimoto, H.; Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 3597. Roush, W. R.; Adam, M. A.; Peseckis, S. M. *Tetrahedron Lett.* **1983**, *24*, 1377.
(11) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464.

Reaction of Some Azolopyrido[2,3-*d*]pyrimidines with Active Methylene Compounds

Andrej Petrič, Branko Stanovnik, and Miha Tišler*

Department of Chemistry, E. Kardelj University, 61000 Ljubljana, Yugoslavia

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Quinazolines or pteridines react with active methylene compounds in several ways. Quinazolines and some pteridines undergo addition of active methylene compounds across the 3,4-double bond. Many adducts have been isolated,[1] but in a further transformation the pyrimidine part is opened, a nitrogen atom is eliminated, and subsequent ring closure gives a condensed pyridine ring. In this way quinazolines were transformed into quinolines[2]

(1) E. Hayashi and T. Higashino, *Chem. Pharm. Bull*, 12, 1111 (1964); E. Hayashi and T. Higashino, *ibid.*, 13, 291 (1965); T. Higashino, K. Suzuki, and E. Hayashi, *ibid.*, 26, 3485 (1978); A. Albert and C. F. Howell, *J. Chem. Soc.*, 1591 (1962); A. Albert and J. J. McCormack, *J. Chem. Soc. C*, 1117 (1966); A. Albert and J. J. McCormack, *ibid.*, 63 (1968).
(2) T. Higashino, H. Ito, and E. Hayashi, *Chem. Pharm. Bull*, 20, 1544 (1972).

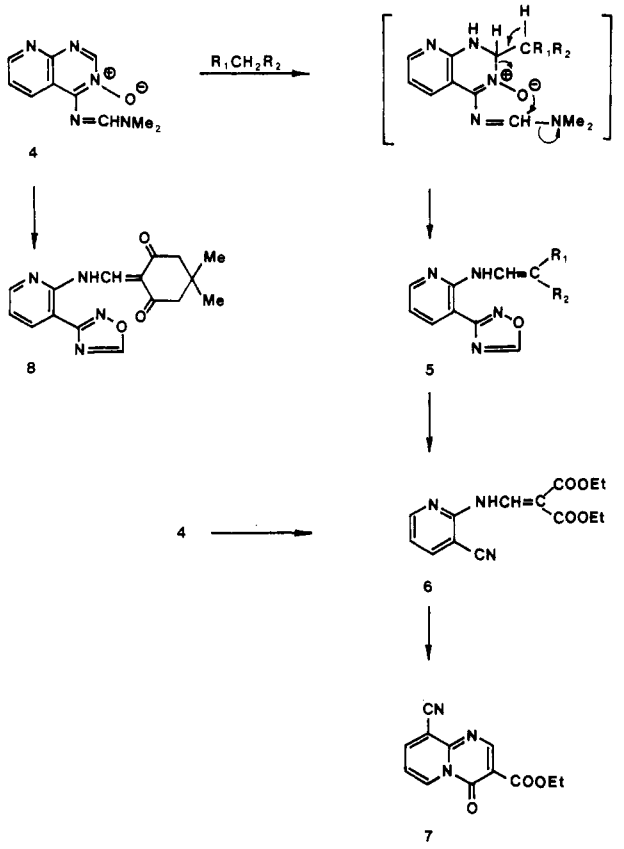
0022-3263/83/1948-4132$01.50/0

Table I. Reaction of Azolopyrido[2,3-*d*]pyrimidines 1 with Reactive Methylene Compounds

starting compound	reactive methylene compounds[a]	reaction time, h (room temperature)	product R_1	product R_2	overall yield, %	mp, °C	recrystallization solvent	MS, M^+
1a	DM	12	2a, COOEt	COOEt	86	176-180 then 245	*n*-PrOH	331
1a	ECA	12	2a, CN	COOEt	93[b]	198-202	EtOH	284
1a	MD	12	2a, CN	CN	40	199-205 dec	EtOH	237
1a	DCD	96	3a,		70	242-246 dec	EtOH	285
1a	PD	2	2a, COMe	COMe	89	213-215[c]	EtOH	271
1b	DM	1	2b, COOEt	COOEt	63	245-250	EtOH	332
1b	ECA	1.5	2b, CN	COOEt	82[b]	190-195	$CHCl_3$/hexane	285
1b	MD	1.5	2b, CN	CN	77	224 dec	EtOH/DMF	238
1b	PD	2.5	2b, COMe	COMe	37	205 dec	EtOH/DMF	272
1b	DCD	2.5	3b		64	240-249 dec	EtOH/DMF	312

[a] DM = diethyl malonate, ECA = ethyl cyanoacetate, MD = malonodinitrile, DCD = 5,5-dimethyl-1,3-cyclohexanedione, PD = 2,4-pentanedione. [b] Mixture of *E* and *Z* isomers. [c] The compound melts at 213-215 °C, crystals are formed, and they melt at 245-250 °C. At heating, the compound decomposed into 2,4-pentanedione and the starting pyrido[2,3-*d*]-*s*-triazolo[3,4-*f*]pyrimidine.

Scheme I

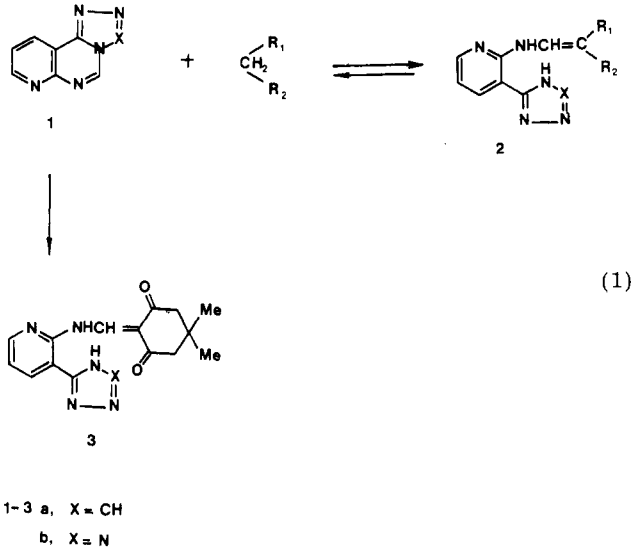


and pteridines into the corresponding pyridopyrazines.[3,4] In another type of addition, which is observed only with pteridines, the addition takes place across the 5,6- and 7,8-double bonds, and in some cases furopteridines are formed.[3-5]

Our recent results of investigations in the pyridopyrimidine series[6] and their 3-oxides[7,8] and pteridine 3-oxides[9,10] have shown that several transformations involve additions across the 1,2- or 2,3-bond, resulting in ring opening. These results prompted us to investigate more in detail the reactivity of position 2 in condensed pyrimidines toward various nucleophiles, in particular toward active methylene compounds.

Results and Discussion

Pyrido[2,3-*d*]-*s*-triazolo[3,4-*f*]pyrimidine (**1a**) and pyrido[2,3-*d*]tetrazolo[5,1-*f*]pyrimidine (**1b**) were treated with active methylene compounds such as diethyl malonate, ethyl cyanoacetate, malonodinitrile, 2,4-pentanedione, and 5,5-dimethyl-1,3-cyclohexanedione (eq 1). The transformation proceeds easily in the presence of sodium ethoxide at room temperature to give the ring-opened products **2** and **3** (Table I). It appears that the annelated five-membered ring influences the reactivity at the unsubstituted position of the pyrimidine part. The tetrazolo analogue **1b** reacted more readily as consequence of the stronger electron-withdrawing property of the tetrazolo



1-3 a, X = CH
b, X = N

(1)

(3) A. Albert and H. Mizuno, *J. Chem. Soc., Perkin Trans. 1*, 1615 (1973).
(4) A. Albert and H. Mizuno, *J. Chem. Soc., Perkin Trans. 1*, 1974 (1973).
(5) A. Albert and J. J. McCormack, *J. Chem. Soc.*, 6930 (1965).
(6) M. Debeljak-Šuštar, B. Stanovnik, M. Tišler, and Z. Zrimšek, *J. Org. Chem.*, **43**, 393 (1978).
(7) B. Verček, I. Leban, B. Stanovnik, and M. Tišler, *Heterocycles*, **7**, 1327 (1978).
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(9) M. Kočevar, B. Stanovnik, and M. Tišler, *Heterocycles*, **15**, 293 (1981); M. Kočevar, B. Verček, B. Stanovnik, and M. Tišler, *Monatsh. Chem.*, **113**, 731 (1982).
(10) M. Kočevar, B. Stanovnik, and M. Tišler, *Tetrahedron*, **38**, 823 (1983).

Table II. Reaction of 4-[[(Dimethylamino)methylene]amino]pyrido[2,3-*d*]pyrimidine 3-Oxide with Reactive Methylene Compounds

reactive methylene compound[a]	reaction time,[c] h	product		overall yield,[b] %	mp, °C	MS, M^+
		R_1	R_2			
DM	1,5; RT	**6**		61	134–135	289
DM	10 min; 0 °C	**5**, COOEt	COOEt	73	163–165	332
ECA	10 min; 0 °C	**5**, COOEt	CN	55	155–185	285
PD	1; RT	**5**, COMe	COMe	18	183–189	272
DCD	4; RT	**8**		46	198–201 dec	312

[a] DM = diethyl malonate, ECA = ethyl cyanoacetate, PD = 2,4-pentanedione, DCD = 5,5-dimethyl-1,3-cyclohexanedione. [b] All products were crystallized from ethanol. [c] RT = room temperature.

part as compared with the triazolo ring. From ^1H NMR spectral data it can be concluded that the reaction of **1a** or **1b** with ethyl cyanoacetate afforded a mixture of *Z* and *E* isomers. Of interest is also the behavior of the ring-opened product **2a** ($R_1 = R_2 =$ COMe), resulting from the reaction between **1a** and 2,4-pentanedione. When heated, the product eliminated 2,4-pentanedione and the starting tricyclic compound (**1a**) was formed. Such thermal reversibility could not be observed with other products.

As another model compound with blocked position 4 of the pyrimidine ring, the functionalized amino derivative of pyrido[2,3-*d*]pyrimidine 3-oxide (**4**) was treated with active methylene compounds. Depending on the active compound used, two types of transformations were observed (Scheme I).

Compound **4** reacted with carbon nucleophiles at position 2, and after ring opening of the pyrimidine ring simultaneous 1,2,4-oxadiazole ring formation occurred to give compounds **5** and **8** (Table II). Evidently, the five-membered ring is formed easily through participation of the [(dimethylamino)methylene]amino and *N*-oxide functions. Also, with diethyl malonate at 0 °C the 1,2,4-oxadiazolyl derivative **5** ($R_1 = R_2 =$ COOEt) is formed readily, indicating that this product is formed first in the reaction sequence leading to product **6**, which is obtained as the sole product when the reaction between **4** and diethyl malonate is conducted at room temperature. Moreover, compound **6** is obtained from **5** ($R_1 = R_2 =$ COOEt) under the influence of sodium salt of diethyl malonate at room temperature. The formation of the cyanopyridine derivative **6** is not surprising since thermal instability of 1,2,4-oxadiazoles and their decomposition into cyano compounds in solution has been observed in several cases,[11] and oxadiazolylpyrazines were transformed into the corresponding cyanopyrazines, usually as byproducts, under various reaction conditions.[9,10] As a synthetic tool, this transformation has been used to convert some oxadiazolyl-*s*-triazolo[1,5-*a*]pyrazines or -*s*-triazolo[1,5-*a*]-pyridines into the corresponding cyano derivatives.[8,10]

Compound **6**, which could be prepared also from 2-amino-3-cyanopyridine and diethyl (ethoxymethylene)-malonate, can be cyclized thermally into the pyrido[1,2-*a*]pyrimidone derivative **7**. The structure of **7** follows from its ^1H NMR and IR spectra as well as from analytical data.

The above results show the so far unrevealed high reactivity at position 2 of the pyrimidine ring in fused pyrido[2,3-*d*]pyrimidines or pyrido[2,3-*d*]pyrimidine 3-oxides, in both cases the position 4 of the pyrimidine part being blocked.

Experimental Section

Melting points were taken on a Kofler micro hot stage. All ^1H NMR spectra were recorded on a JEOL JNM C60-HL spectrometer, IR spectra were recorded on a Perkin-Elmer spectrometer 727B, and mass spectra were recorded on Hitachi-Perkin-Elmer RMU-6L instrument. Chemical shifts are reported in parts per million on the δ scale relative to internal tetramethylsilane. Unless otherwise noted, the NMR solvent was Me_2SO-d_6.

General Procedure for Reaction of Pyrido[2,3-*d*]-*s*-triazolo[3,4-*f*]pyrimidine or Pyrido[2,3-*d*]tetrazolo[5,1-*f*]pyrimidine with Reactive Methylene Compounds. The corresponding compound with an active methylene group (0.5 mmol) was treated with an ethanolic solution of sodium ethylate, prepared from 0.5 mmol of sodium and ethanol (3 mL), and the corresponding pyridoazolopyrimidine (**1**, 0.05 mmol) was added. After a certain reaction period (Table I), the solvent was evaporated in vacuo, water (10 mL) was added, the mixture was acidified with hydrochloric acid (1:1), and the product filtered. The reaction time and spectroscopic and other data are presented in Table I.

General Procedure for Reaction of 4-[[(Dimethylamino)methylene]amino]pyrido[2,3-*d*]pyrimidine 3-Oxide with Reactive Methylene Compounds. To an ethanolic solution of sodium ethylate, prepared from sodium (1 mmol) and ethanol (5 mL) was added the reactive methylene compound (1 mmol) followed by 4-[[(dimethylamino)methylene]amino]-pyrido[2,3-*d*]pyrimidine 3-oxide[8] (1 mmol). After a certain reaction period (Table II), the separated product was filtered and crystallized from an appropriate solvent.

3-Cyano-2-[[2,2-bis(ethoxycarbonyl)vinyl]amino]pyridine (6). A. A mixture of 2-amino-3-cyanopyridine (0.516 g) and diethyl (ethoxymethylene)malonate (0.864 g) was heated at 130–140 °C for 4 h. Upon cooling, the product was filtered, washed with cold ethanol, and crystallized from ethanol to give 1.18 g (82%) of the product, identical as described in Table II.

B. The same product was obtained when compound **5** ($R_1 = R_2 =$ COOEt) was treated with an equimolar quantity of ethanolic diethyl malonate sodium salt at room temperature for 1.5 h: ^1H NMR (Me_2SO-d_6) δ 1.26 (t, Me), 4.17 (q, CH_2), 7.21 (dd, H_5), 8.25 (dd, H_4), 8.57 (dd, H_6), 9.00 (s, HNC*H*), $J_{Et} = 7.0$, $J_{4,5} = 7.8$, $J_{5,6} = 5.0$, $J_{4,6} = 1.8$ Hz). Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53; Found: C, 58.25; H, 5.25; N, 14.44.

9-Cyano-3-(ethoxycarbonyl)pyrido[1,2-*a*]pyrimidin-4-one (7). Compound **6** (0.2 g) was mixed with diphenyl ether (2 mL), and the mixture was heated to boiling for 10 min. From the cold reaction mixture the product was precipitated by addition of petroleum ether to give 0.14 g (83%) and crystallized from ethanol: mp 154–157 °C; ^1H NMR (Me_2SO-d_6) δ 8.88 (s, H_2), 9.24 (dd, H_6), 7.54 (deg dd, H_7), 8.77 (dd, H_8), 1.29 (t, Me), 4.25 (q, CH_2), $J_{6,7} = J_{7,8} = 7.2$, $J_{6,8} = 1.6$ Hz; mass spectrum, m/e 243 (M^+); IR 2205 (CN) and 1725 cm^{-1} (CO). Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28; Found: C, 59.17; H 3.93; N, 17.20.

Registry No. **1a**, 52196-54-0; **1b**, 53511-68-5; **2a** ($R_1 = R_2 =$ COOEt), 87156-21-6; (*E*)-**2a** ($R_1 =$ CN; $R_2 =$ COOEt), 87156-22-7; (*Z*)-**2a** ($R_1 =$ CN; $R_2 =$ COOEt), 87156-23-8; **2a** ($R_1 = R_2 =$ CN), 87156-24-9; **2a** ($R_1 = R_2 =$ COMe), 87156-25-0; **2b** ($R_1 = R_2 =$ COOEt), 87156-26-1; (*E*)-**2b** ($R_1 =$ CN; $R_2 =$ COOEt), 87156-27-2; (*Z*)-**2b** ($R_1 =$ CN; $R_2 =$ COOEt), 87156-28-3; **2b** ($R_1 = R_2 =$ CN), 87156-29-4; **2b** ($R_1 = R_2 =$ COMe), 87156-30-7; **3a**, 87156-31-8; **3b**, 87156-32-9; **4**, 68640-81-3; **5** ($R_1 = R_2 =$ COOEt), 87156-33-0; **5** ($R_1 =$ COOEt; $R_2 =$ CN), 87156-34-1; **5** ($R_1 = R_2 =$ COMe), 87156-35-2; **6**, 87156-36-3; **7**, 87156-37-4; **8**, 87156-38-5; DM, 105-53-3; ECA, 105-56-6; MD, 109-77-3; DCD, 126-81-8; PD,

(11) L. B. Clapp, *Adv. Heterocycl. Chem.*, **20**, 66 (1976).

123-54-6; 2-amino-3-cyanopyridine, 24517-64-4; diethyl (ethoxymethylene)malonate, 87-13-8.

Supplementary Material Available: ^{1}H NMR and analytical data for all compounds of the type **2**, **3**, **5**, and **8** (3 pages). Ordering information is given on any current masthead page.

One-Pot Conversion of Olefins to α,β-Unsaturated Carbonyl Compounds. An Easy Synthesis of 2-Cyclopentenone and Related Compounds

Edward D. Mihelich*† and David J. Eickhoff

The Proctor & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45247

Received April 26, 1983

There are few compounds that have more potential and versatility in organic synthesis than 2-cyclopentenone[1] and its higher homologues. Yet the available sources of these materials are generally tedious, multistep synthetic routes[2] or expensive commercial suppliers.[3] A conceptually attractive synthetic entry to this general class of compounds lies in the direct conversion of their parent olefins[4] through an allylic oxidation pathway. While an impressive amount of research has demonstrated the utility of such a stratagem with a variety of substrates,[4c] no approach has been generally applicable to the simple C-5 through C-8 cycloalkenes. We now report an exceedingly efficient, one-pot synthesis of the 2-cycloalkenones and other α,β-unsaturated carbonyl compounds by an in situ photooxygenation–elimination procedure.

Our synthesis is based on the decades-old observations of Schenck and co-workers,[5] which demonstrated (1) that allylic hydroperoxides are handily prepared by reaction of alkenes with photochemically generated singlet oxygen and (2) that these materials are easily converted to enones under mild conditions. More recently, other research groups[6] have shown that *activated olefins* are especially good substrates for such a conversion but simple 1,2-disubstituted ethylenes have been uniformly ignored.[7] We have found that the cycloalkenes, exemplified by cyclopentene as shown in Scheme I, are readily photooxygenated in the presence of acetic anhydride and base to yield directly cycloalkenones after aqueous workup and distillation. The examples shown in Table I illustrate that this one-pot method is general and readily applied to even those alkenes normally considered to be too unreactive toward $^1O_2$ to be useful in a preparative sense (e.g., cyclohexene). Furthermore, it has been applied to a variety of cyclic and acyclic olefins to produce α,β-unsaturated ketones, aldehydes, and esters. The last example is a replication of the work done by Conia et al. in a two-step sequence.[6a] The yield of product that we obtained by the one-pot method was somewhat higher.

In all cases examined, we found this catalyzed oxidation exceptionally easy to carry out, even on the mole scale. For some of the substrates, the two intermediates could be observed by TLC during the course of the reaction, and complete conversion to unsaturated carbonyl product required the solution to stand overnight prior to isolation. The acylation catalyst, 4-(dimethylamino)pyridine, was incorporated into the general procedure to hasten these steps of the conversion.

Scheme I

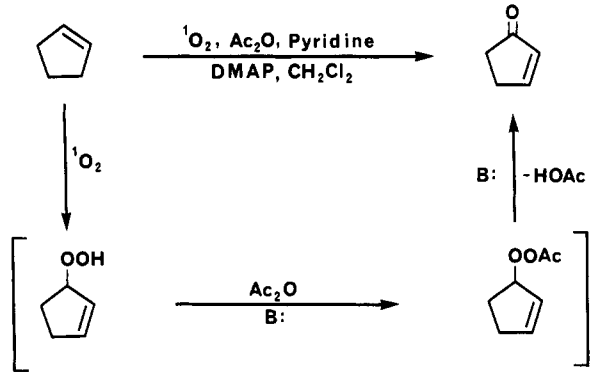
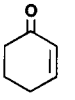
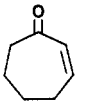
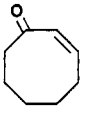
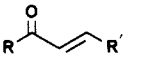
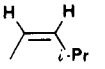
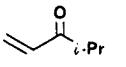
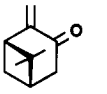
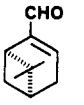
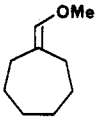
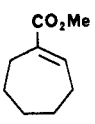


Table I. Direct Synthesis of α,β-Unsaturated Carbonyl Compounds from Olefins

olefin	product	irradiation time, h	yield,[a] %
		2	71
		10	78
		2.3[b]	85
		9[b]	88
Methyl Oleate		2	97[c]
		4.5	58
		1.5	97[d]
		2.5[b]	58[e]
		0.5[b]	77

[a] Yields are based on starting olefin and indicate the amount of distilled product obtained of ≥95% purity as judged by GC analysis. [b] In addition to the photooxygenation time, these reactions were allowed to stand overnight to ensure completion of the reaction sequence. [c] Product consists of an equal mixture of R = $(CH_2)_7CO_2CH_3$, R′ = C_7H_{15} and R = C_8H_{17}, R′ = $(CH_2)_6CO_2CH_3$. [d] Measured rotations were α-pinene $[\alpha]_D$ +47.1° (neat), pinocarvone $[\alpha]_D$ −64.5° (neat). [e] Measured rotations were β-pinene $[\alpha]_D$ −21° (neat) myrtenal $[\alpha]_D$ −14.7° (neat).

Clearly, the success of this approach lies in the lack of reactivity of the intermediates as well as the product to

† Present address: Eli Lilly & Co., Indianapolis, IN.

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