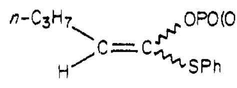
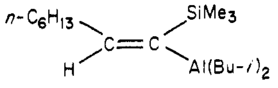
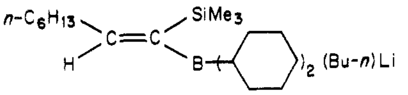


9



10



11

the α-(thioalkenyl) metal reaction such as that shown in eq 2. However, the reported reaction as such does not provide a stereoselective route to alkenyl sulfides. Fourth, the dienes 4 and 5 were prepared by the Pd-catalyzed reaction of 10, that was obtained by hydroalumination of 1-octynylsilane with i-Bu_2AlH in ether[12] for 2 h under reflux, with vinyl bromide and (*E*)-1-iodo-1-heptene, respectively, in the presence of 1 equiv of dry $ZnCl_2$.[13] In its absence, no desired product was produced. These dienes were also obtained by the corresponding reactions of the alkenylborate 11. Interestingly, unlike a recently reported related organoborane reaction requiring the temperature of refluxing benzene,[14] the above reactions were complete within 1-3 h at 22 °C. The major difference in rate between the two related reactions could be due to (a) different bases used in these two related reactions, i.e., n-BuLi in one and alkali metal alkoxides, or hydroxides, in the other,[14] (b) the presence of α-Me_3Si group in one and its absence in the other, and/or (c) the presence of $ZnCl_2$ in one and its absence in the other. The yield of 4 obtained by the Pd-catalyzed reaction of 11 with vinyl bromide increased from 37% to 61% by the addition of 1 equiv of $ZnCl_2$. The fact that this reaction did proceed, albeit unsatisfactorily, at room temperature in the absence of $ZnCl_2$ suggests that this factor alone cannot account for the major difference mentioned above. It should also be noted that the product yields realized in the organoalane reactions are considerably higher than the corresponding organoborate reactions. A few minor unidentified byproducts having GLC retention times similar to those of 4 or 5 were formed in the reaction of 11, while no more than traces ($\leq 1\%$) of such byproducts were detectable in the organoalane reactions.

The following procedure for preparing (6*E*,8*Z*)-8-(trimethylsilyl)-6,8-pentadecadiene is representative. To 1-(trimethylsilyl)-1-octyne (1.82 g, 10 mmol) in 20 mL of ether was added, under nitrogen atmosphere, diisobutylaluminum hydride (1.82 mL, 10 mmol). The reaction mixture was refluxed for 2 h. To this was added a mixture of (*E*)-1-iodo-1-heptene[15] (2.24 g, 10 mmol), $Pd(PPh_3)_4$[16] (0.57 g, 0.5 mmol), and $ZnCl_2$ (1.36 g, 10 mmol), freshly dried at 50 °C and ≤ 1 mm, in 20 mL of THF. The resultant mixture was stirred for 3 h at room temperature, quenched with 3 N HCl (30 mL), and extracted with pentane. The organic extracts were washed with brine, dried over $MgSO_4$, and distilled to give 1.90 g (68%) of 5: bp 92-95 °C (0.05 mm); $n^{24}{}_D$ 1.4650; IR (neat) 1595 (m), 1250 (s), 960 (s), 840 (s), 755 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 0.88 (t, J = 7 Hz, 6 H), 1.1-1.7 (m, 14 H), 1.8-2.4 (m, 4 H), 5.47 (dt, J = 15, 7 Hz, 1 H), 6.01 (d, J = 15 Hz, 1 H), 6.11 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.34, 13.79, 22.36, 22.44, 28.94, 29.24, 29.97, 31.26, 31.70, 32.82, 128.55, 135.00, 138.26, 143.06. High-resolution MS calcd for $C_{18}H_{36}Si$: 280.2586. Found: 280.2600.

Acknowledgment is made to the National Science Foundation and the National Institutes of Health for support of this work. We thank Vahid Bagheri of our laboratories for sharing the preparation of 7. We also thank Professor L. S. Hegedus of Colorado State University for informing us of their unpublished results and Professor R. K. Boeckman, Jr., of University of Rochester for helpful discussions.

Registry No. 1, 85318-56-5; 2, 7326-63-8; 3, 85318-57-6; 4, 85318-58-7; 5, 85318-59-8; 6, 6230-62-2; 7, 6230-80-4; 8, 22914-07-4; 11, 60366-85-0; CH_2=CHOEt, 109-92-2; CH_2=CHSEt, 627-50-9; $Pd(PPh_3)_4$, 14221-01-3; $ZnCl_2$, 7646-85-7; C_6H_5I, 591-50-4; p-ClC_6H_4I, 637-87-6; vinyl bromide, 593-60-2; 1-(trimethylsilyl)-1-octyne, 15719-55-8; (*E*)-1-iodo-1-heptene, 60595-37-1.

Supplementary Material Available: ^1H and ^{13}C NMR and IR spectral data as well as boiling points and n_D data for compounds 1-8 and the experimental procedures for preparing 3 (Zn) and 4 (B) (2 pages). Ordering information is given on any current masthead page.

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Facile and Regioselective Epoxidations of Olefins with a Peroxysulfur Intermediate Generated from Superoxide Anion ($O_2^{-}\bullet$) and Nitrobenzenesulfonyl Chlorides

Summary: A peroxysulfur intermediate generated from the reaction of o- or p-nitrobenzenesulfonyl chloride with superoxide anion ($O_2^{-}\cdot$) is found to be an excellent oxidizing reagent for the facile and regioselective epoxidation of olefins at -35 °C.

Sir: Recently intensive research interests[1] in physical properties and chemical reactivities of superoxide ion have stimulated the development of organic synthesis using superoxide anion. Only a few works on the oxidation of sulfur compounds such as thiols,[2] thiouracils,[3] disulfides,[4] and sulfur halides[5] have been reported. Earlier, peroxysulfonate intermediate was postulated by Berger[6] to be the key in alkaline autoxidation of thiols to the sulfonate.

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[9] When the reactions of superoxide anion with **1a**, **1b**, and **1c** were stopped after 45 min, starting materials of **1a** (41%), **1b**(46%), and **1c** (71%), respectively, were recovered: this results suggest that the formation rate **2a** and **2b** is not so different but the **2a** is more stable than **2b** because the epoxidation using **2a** afforded better yield of epoxide (**8'**, X = H, 84% 1.5 h) than that using **2b** (**8'**, = H, 75%, 3.0 h).

[10] ^1H NMR (60 MHz, $CDCl_3$) δ 2.97 (1 H, epoxide), 1.3 (3 H, Me, epoxide), 1.92 (3 H), 1.10-1.60 (4 H), 1.60 (3 H, Me, =C—), 4.75 (2 H, =C—).

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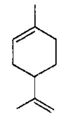
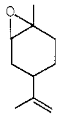
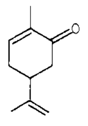
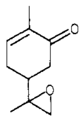
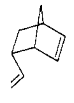
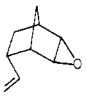
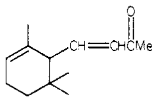
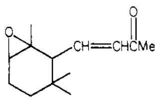
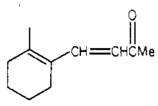
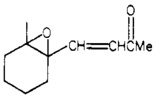
Table I. Epoxidations of Olefins at Ca. -30 °C

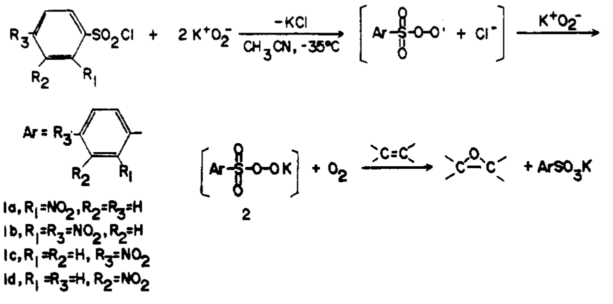
$ArSO_2Cl$	substrates	reaction time, h	epoxides	yield,[b] %	recovery, %
1a	 3	4.5	 3'[10]	87	trace
1b	 4	3.0	 4'[11]	83	c
1a	 5	5.0	 5'[12]	78	c
1a	 6	3.0	 6'[13]	85	ca. 12
1a	 7	2.5	 7'[14]	84	ca. 10
1a	$PhCH{=}CHCOC_6H_4X$-*p* 8, X = H	1.5	$PhCHCHCOC_6H_4X$-*p* 8',[5] X = H[5]	84	5
1a	8, X = Br	2.5	8',[5] X = Br[5]	82	c
1a	8, X = OMe	2.5	8',[5] X = OMe[5]	90	trace
1a	8, X = Me	2.0	8',[15] X = OMe[5]	90	c
1a	$PhC({=}CH_2)Ph$, 9	5.0	1,1-diphenylethylene oxide[16]	82	trace
1a	$PhCH{=}CHPh$	3.0	1,2-diphenylethylene oxide[17]	68	c
1b	8, X = H	3.0	8',[5] X = H	75	8
1b	8, X = OMe	3.0	8',[5] X = OMe	78	c
1c	8, X = H	3.0	8',[5] X = H	60	c
1c	3	6.0	3'[10]	68	c
1c	4	4.0	4'[11]	72	22
1c	7	4.0	7'[14]	70	21
1d	5, X = H	4.0	5'[12]	60	32

[a] Molar ratio: $ArSO_2Cl$:olefin:KO_2 = 1.0:0.7:3.0. [b] Isolated yield. [c] Not determined.

Though the conceivable peroxysulfur intermediate that seems to have potential oxidizing abilities has neither been isolated nor detected, it has been demonstrated to be an unstable intermediate of oxidizing reagents in the oxidation of disulfide-related compounds[4] and sulfonyl chloride.[5] Our previous works on the oxidations of sulfoxide[4] and olefins[5] using superoxide anion suggested that if the peroxysulfur intermediate like **2** is stable enough at low temperature, it might be broadly useful for the synthesis of various epoxides by oxidations of olefins.

We report that oxidations of various olefins containing two double bonds with a peroxysulfonate intermediate (**2**) generated from the nitrobenzenesulfonyl chloride and potassium superoxide afforded high regioselective epoxidations in excellent yields under mild conditions (Scheme I).

Scheme I



In a general procedure, a solution of 2-nitrobenzenesulfonyl chloride (0.22 g, 1.0 mmol) and L-carvone (4, 0.09 g, 0.6 mmol; CH_3CN, 2.0 mL) was added to a heterogeneous solution of potassium superoxide (0.222 g, 3.0 mmol, CH_3CN, 1.0 mL) at ca. -35 °C under dry argon atmosphere. After being stirred for ca. 4 h at ca. -35 °C, the reaction mixture was concentrated and then extracted with $CHCl_3$; concentration of the $CHCl_3$ layer gave highly pure epoxide 4' (0.078 g, 87%). Further purification by preparative TLC afforded pure 4'[11] (0.0748 g, 83%). Results obtained are summarized in Table I, and spectral data are listed in ref 10–17. Regioselective epoxidations of olefins

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(11) ^1H NMR (60 MHz, $CDCl_3$) δ 2.67 (2 H, epoxide), 1.40 (3 H, Me, epoxide), 2.1–2.8 (5 H), 6.7 (1 H, =C—), 1.8 (3 H, Me, =C—).

(12) ^1H NMR (60 MHz, $CDCl_3$) δ 3.0 (2 H, epoxide), 0.75–1.80 (5 H), 2.45 (2 H, 4.85 (1 H, C=C), 4.95 (1 H, C=C), 5.65 (1 H, C=C).

(13) ^1H NMR (60 MHz, $CDCl_3$) δ 3.0 (1 H, epoxide), 1.20 (3 H, Me, epoxide), 1.00–2.40 (5 H), 0.9 (3 H, Me), 1.0 (3 H, Me), 2.2 (3 H, Me), 5.92 (1 H, C=C), 6.52 (1 H, =CCO—).

containing an α,β-unsaturated ketone moiety such as 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone, **6**), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone, **7**), and L-*p*-mentha-6,8-dien-2-one (L-carvone, **4**) afforded their corresponding epoxides **6′**, **7′**, and **4′**, respectively in mostly quantitative yields; no epoxidation of the double bond in the α,β-unsaturated ketone moiety was detected. Earlier work[7] demonstrated that epoxidations of α- and β-ionone (**6** and **7**) with hydrogen peroxide or phthalic monoperacid afforded the epoxides **6′** and **7′**, respectively, as the major products whose yields are lower than those obtained by our method using the reaction of nitrobenzenesulfonyl chloride with $O_2^{-}\cdot$. Epoxidations of chalcones or stilbene yielded excellent yields of their epoxides at −35 °C. Recently, Curci et al. reported that epoxidation of olefins involved peroxide-reactive intermediate of dioxirane generated in the reaction of potassium caroate ($KHSO_5$) with ketones.[8] In the presence of dimethyl sulfoxide as a trapping agent for an activated oxygen of **2**, dimethyl sulfone was obtained quantitatively along with 2-nitrobenzenesulfonate (quantitative yields). Without olefins, the oxidation of nitrobenzenesulfonyl chloride with $O_2^{-}\cdot$ gave the nitrobenzenesulfonates. In the absence of nitrobenzenesulfonyl chlorides, olefins **4** and **6** were recovered quantitatively under the same reaction conditions: no direct epoxidations between olefins and $O_2^{-}\cdot$ occurred. Thus, the obtained results can be accounted by the formation of an oxidizing reagent such as peroxysulfonate intermediate **2** in this oxidation system, though the reaction mechanism is not clear. When the epoxidations using **1a**, **1b**, and **1c** were compared with each other, **1a** gave the better yield of epoxide (**8**, X = H), in the shorter reaction time than those from **1b** and **1c**.[9]

Acknowledgment. We gratefully acknowledge financial support from the Asan Foundation.

Registry No. **1a**, 1694-92-4; **1b**, 1656-44-6; **1c**, 98-74-8; **1d**, 121-51-7; **3**, 5989-27-5; **3′**, 1195-92-2; **4**, 6485-40-1; **4′**, 56423-45-1; **5**, 25093-48-5; **5′**, 2886-87-5; **6**, 127-41-3; **6′**, 37677-81-9; **7**, 79-77-6; **7′**, 23267-57-4; **8** (X = H), 94-41-7; **8** (X = Br), 2403-27-2; **8** (X = OMe), 959-23-9; **8′** (X = H), 5411-12-1; **8′** (X = Br), 29425-81-8; **8′** (X = OMe), 40327-51-3; **9**, 530-48-3; 1,1-diphenylethylene oxide, 882-59-7; 1,2-diphenylethylene oxide, 17619-97-5; potassium superoxide, 12030-88-5; PhCH═CHPh, 588-59-0.

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(14) ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.00 (3 H, Me, epoxide), 1.10–1.60 (6 H), 1.05 (6 H, Me), 2.17 (3 H, Me, CO), 5.92 (1 H, C═C), 6.52 (1 H, ═CCO).

(15) ^{1}H NMR (60 MHZ, $CDCl_3$) δ 4.05, 4.15 (2 H, epoxide), 2.50 (3 H, Me).

(16) ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.30 (2 H, epoxide), 7.40 (10 H, C_6H_5).

(17) "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, Vol. 4, p 103.

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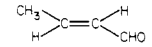
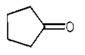
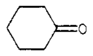
Regioreversed Addition of Crotylmagnesium Chloride to Carbonyl Compounds in the Presence of $AlCl_3$

Summary: The reaction of carbonyl compounds with crotylmagnesium chloride in the presence of $AlCl_3$ at −78 °C gives predominantly products in which the allylic group is attached at the less substituted position (α-adduct).

Sir: The reaction of unhindered carbonyl compounds with substituted allylic organometallic reagents (**1**) such as M = Li,[1] Mg,[1,2] Cu,[3] Zn,[1] Cd,[1] B,[4] Al,[1] Si,[5] Sn,[6] Ti,[7] Zr,[8] Cr,[9] and Mn,[10] generally results in products in which the allylic group is attached at the more highly substituted position (γ-adduct) (eq 1). The reaction of this type is becoming increasingly important as a basic synthetic strategy for stereoregulated synthesis of acyclic systems.[11] With hindered ketones such as di-*tert*-butyl ketone and di-isopropyl ketone, α-adduct is sometimes obtained because of the reversible addition of allylic organometallic reagents.[12]

Table I. Reaction of Carbonyl Compounds with Crotylmagnesium Chloride in the Presence of $AlCl_3$[a]

	product ratio,[b] %		
carbonyl compd	α-adduct (E:Z)	γ-adduct (*erythro*: *threo*)	total yield,[c] %
C_6H_5CHO[d]	85 (83:17)	15 (50:50)	92
C_6H_5CHO	87 (78:22)	13 (50:50)	92
C_6H_5CHO[e]	80 (95:5)	20 (50:50)	(95)
C_6H_5CHO[f]	84 (77:23)	16 (50:50)	(88)
CH_3CHO	83 (84:16)	17 (41:59)	(90)
CH_3CH_2CHO	94 (81:19)	6 (17:83)	85
$CH_3(CH_2)_2CHO$[g]	83 (84:16)	17 (31:69)	90
$CH_3(CH_2)_2CHO$	85 (84:16)	15 (40:60)	(95)
$CH_3(CH_2)_2CHO$[e]	78 (96:4)	22 (40:60)	(95)
$CH_3(CH_2)_3CHO$	86 (81:19)	14[h]	90
$CH_3(CH_2)_8CHO$	89 (83:11)	11[h]	82
$(CH_3)_2CHCHO$	84 (92:8)	16 (44:56)	90
$(CH_3)_2CHCH_2CHO$	87 (87:13)	13 (50:50)	88
	83 (85:15)	17 (44:56)	90
	84 (67:33)	16	90
	83 (66:34)	17	92
$C_6H_5C(O)CH_3$	70 (62:38)	30 (50:50)	94

[a] All reactions were carried out on a 1-mmol scale as described in the text, except where otherwise indicated. [b] By GLC analyses using a column of CW-6000-5%-2m. The ratio of *erythro*/*threo* was determined by ^{1}H NMR and/or GLC. [c] Isolated combined yield (GLC yield). [d] One equivalent of $AlCl_3$ was used. [e] THF was used as a solvent. [f] HMPA (1 equiv) was added to the Mg-Al mixture. [g] Two equivalents of $AlCl_3$ were used. [h] Not determined.

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