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Alkylation, Aldol, and Related Reactions of *O*-Alkanoyl- and 2-AlkenoylTEMPOs (2,2,6,6-Tetramethylpiperidine-*N*-oxyl): Insight into the Reactivity of Their Anionic Species in Comparison with Esters and Amides

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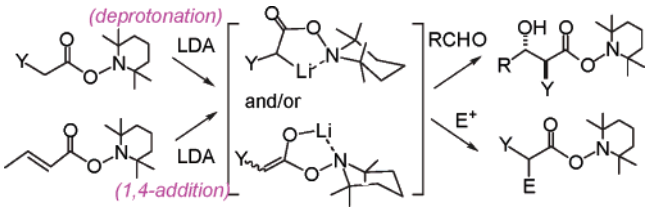

The lithium anionic species generated from *O*-alkanoylTEMPOs upon treatment with LDA were first employed as a nucleophile for alkylation, Michael addition, direct aldol reaction, and others. The alkylation occurred smoothly at the methylene carbon, and no alkylation was found in the isobutyryl analogue, while silylation was scarcely attainable. Substitutions of the heteroatom were achieved by reaction with PhSSPh and DEAD. The reactivity of these anionic species is successfully extended to aldol reactions in which moderate anti or syn selectivity was executed with propionyl derivatives. Tandem Michael addition of lithium amide followed by aldol reaction was performed on the *O*-crotonoylTEMPOs.

Enolates of carboxylic acid derivatives such as esters, thioesters, and amides are one of the pivotal intermediates in the carbon−carbon bond-making process in alkylation, aldol reaction, Michael addition, and others,[1] and their potential is well demonstrated by the key role played in the synthesis of biologically significant compounds such as taxol and epothilones.[2] Furthermore, the choice of the acyl substituent is important for the ensuing elaboration of the acyl functionality to a more versatile form. For instance, the aldol derivatives comprised of *N*-methoxy-*N*-methylamides (Weinreb amide), accessible either directly by aldol reaction[3] or indirectly by transamidation of *β*-hydroxycarboxylic derivatives,[4] are often utilized as a precursor of aldehydes or ketones through the reduction or alkylation process.[5] In this context, we succeeded in selective reduction of *O*-acylTEMPOs,[6] extended carboxylic acid derivatives with a hetero−hetero bond-like peroxyesters[7] and Weinreb amides,[8] to the corresponding aldehydes upon treatment with DIBALH.

In our continuing studies on exploring TEMPO substitution as a reaction-controlling element,[9] we examined the reactivity of *O*-alkanoylTEMPOs **A**, easily accessible by acyl substitution with the TEMPO anion, in the C−C bond-making reaction at the C2 position including alkylation, direct aldol reaction, Michael addition, as well as related reactions. Thus far scant attention has been paid to characterization of the anionic species **B** and/or **C** possibly accessible by deprotonation of **A**, though compound **A** poses as carboxylic derivatives (Scheme 1).[10] In the meantime, we also discussed the effect of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as an auxiliary on the stereochemistry of the aldol reactions.

As shown in Table 1, deprotonation of the *O*-acylTEMPO **2a** was easily achieved on treatment with LDA in THF at −78 °C, and reaction of the resulting anionic species with iodomethane (MeI) and benzyl and allyl bromides led to the corresponding **3a**,**b**,**c** (E = Me, $PhCH_2$, allyl) in 74−87% yields (entries 1−3). The same alkylation was also achieved with *tert*-butyl bromoacetate as an electrophile at 0 °C, affording the desired mixed *tert*-butyl/TEMPO-1-yl succinate **3d** (E = $CH_2CO_2Bu^t$) in 64% yield (entry 4).[11] On the other hand, our attempts for the alkylation of 2,2-dialkylated **3a** were unsuccessful. Furthermore, silylation of the anionic species from *O*-aceylTEMPO (**1**), **2a**, and **3a** with TMSCl at −10 °C resulted in the recovery of the starting *O*-acylTEMPOs, which is different from that of *tert*-butyl isobutyrate, forming the corresponding enol silyl ether even at −78 °C.[12]

Subsequently, we examined the reactivity of this anionic species toward other electrophiles such as nitroolefin and

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(10) *O*-AcetylTEMPO (**1**) shows C=O absorption at 1759 cm^{-1} in IR spectra, which is distinguishable from that of Weinreb amide at 1668 cm^{-1} and ethyl acetate at 1741 cm^{-1}.

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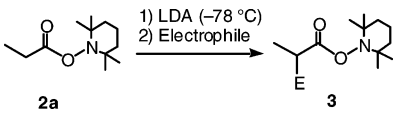
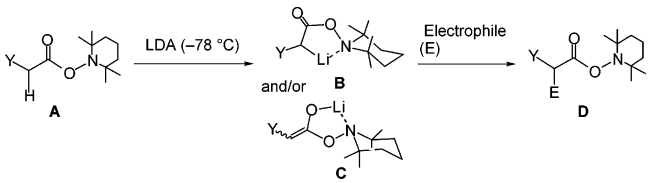
TABLE 1. Alkylation, Michael Addition, and Sulfenylation of *O*-PropionylTEMPO with LDA[a]



entry	electrophile (E−X)	conditions	product	%[b]
1	MeI	−78 to −10 °C/3.5 h	**3a**	74[c]
2	$PhCH_2Br$	−78 to −25 °C/4 h	**3b**	87[c]
3	allyl-Br	−70 to −20 °C/2 h	**3c**	83[c]
4	t-BuO_2CH_2Br	−70 to 0 °C/8 h	**3d**	64
5	$PhCH{=}CHNO_2$	−70 to −7 °C/2.5 h	**3e**[d]	83[e]
6	$(EtO_2CN{=})_2$	−78 to −15 °C/4.5 h	**3f**[f]	65
7	PhSSPh	−70 to +6 °C/3.5 h	**3g**[g]	69

[a] Carried out by reaction of **2a** (1 mmol) with LDA (1.5−2 equiv) at −78 °C for 45 min followed by addition of the electrophiles (2 equiv). [b] On the basis of isolated products. [c] Contaminated with 1−3% of **2a** by ^{1}H NMR analyses. [d] E = $PhCH{-}CH_2NO_2$. [e] A 1:1 diastereomeric mixture. [f] E = $EtO_2CNH{-}N(CO_2Et)$. [g] E = PhS.

SCHEME 1. Possible Anionic Species from *O*-AcylTEMPOs and Their Reactions

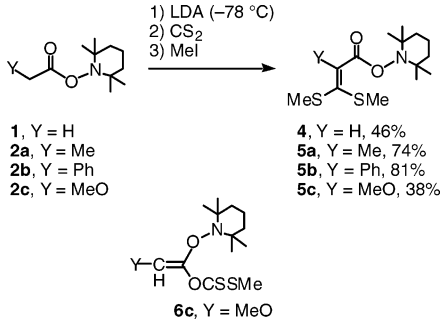


hetero−hetero atoms bonds. Thus, 1,4-addition of this anionic species to nitroolefin,[13] (*E*)-$PhCH{=}CHNO_2$, smoothly proceeded, giving the corresponding adducts **3e** as a 1:1 diastereomeric mixture in 83% yield (entry 5). However, our efforts for the 1,4-addition to *tert*-butyl acrylate and acrylonitrile by a similar treatment as described above were unsuccessful.

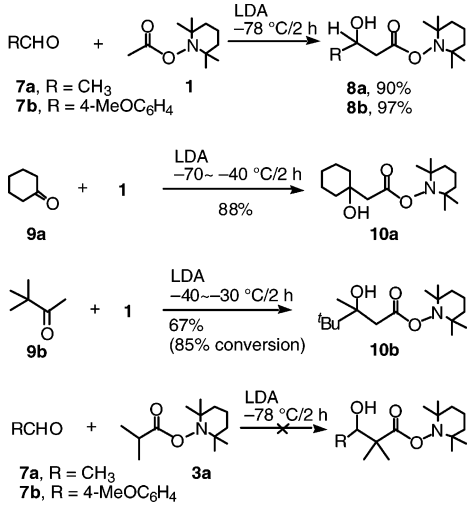
Introduction of hetero atoms such as nitrogen and sulfur at the C2 carbon of **2a** was also achieved by treatment of the anionic species with diethyl azodicarboxylate (DEAD)[14] and diphenyl disulfide ($(PhS)_2$),[15] giving the corresponding **3f** (E = $EtO_2CNH{-}N(CO_2Et)$) and **3g** (E = PhS) in 65% and 69% yields, respectively (entries 6 and 7).

The reaction of ester enolate with carbon disulfide (CS_2) is known to undergo either *C*- or *O*-alkylation depending on the carbon-skeleton of the C2 position,[16] that is, a methylene or methine structure. Accordingly, anionic species from *O*-acylTEMPOs **1** and **2** were submitted to the reaction with CS_2 followed by methylation with MeI, giving the desired 2-bis(methylthio)-methylenealkanoylTEMPOs **4** and **5** in moderate to good yields. In this case, a trace amount of the *O*-alkylation, that is **6c**, besides the *C*-alkylated **5c** as a major product was found in the case of methoxyacetylTEMPO **2c** (Scheme 2).

SCHEME 2. Reaction of *O*-AcylTEMPOs with CS_2 and MeI



SCHEME 3. Aldol Reactions of *O*-AcylTEMPOs with Various Aldehydes and Ketones



Subsequently, we examined aldol reactions of *O*-acetylTEMPO (**1**) with various aldehydes **7** and ketones **9** using LDA as a base. As shown in Scheme 3, it turned out that the deprotonated species from **1** reacted smoothly with common aldehydes and ketone such as acetaldehyde (**7a**), anisaldehyde (**7b**), and cylohexanone (**9a**), giving the corresponding aldols **8a** and **8b** in 90% and 97% yields and **10a** in 88% yield, respectively. The reaction of **1** with sterically hindered pinacolone (**9b**) was slightly sluggish, but a fairly good yield (67% yield, 85% conversion) of the adduct **10b** was obtained by raising the temperature to between −40 and −35 °C for 2 h. On the other hand, our attempts for the aldol reaction of *O*-isobutyrylTEMPO (**3a**), the 2,2-dimethylated analogue of **1**, with **7a** and **7b** were unsuccessful, resulting in recovery of **3a**. Thus, although no significant steric hindrance of the TEMPO group was observed in aldol reaction of the anionic species from *O*-acetylTEMPO (**1**), the disubstituents at the C2 carbon, that is **3a**, exerted depression on their reactivity in aldol and related alkylation processes.

We next examined the chemoselective aldol reaction of **1** with various functionalized carbonyl compounds **9c**−**e**, since the inertness of the *O*-acylTEMPO moiety toward $LiAlH_4$ at low temperature and to Grignard reagents would allow further elaboration of the aldol products into functionally diverse derivatives with chemo- and regioselectivity.[9b] Thus, the aldol reaction of **1** with 2-cyclohexenone (**9c**) afforded the 1,2-adduct **10c** in 79% yield with no 1,4-adduct being detected. Diacid alkyl/TEMPO-1-yl esters **10d** and **10e** were obtained by the aldol reaction of **1** with keto esters such as pyruvate **9d** and levulinate **9e**, respectively (Scheme 4).

(12) (a) Otera, J.; Fujita, Y.; Sato, T.; Nozaki, H.; Fukuzumi, S.; Fujita, M. *J. Org. Chem.* **1992**, *57*, 5054−5055. (b) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Duniz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403−5409.

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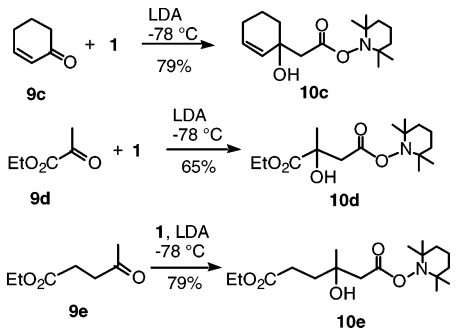
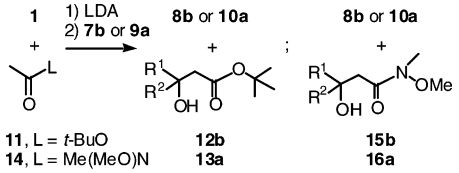
SCHEME 4. Chemoselective Aldol Reactions of *O*-AcetylTEMPO (1) with Various Ketones



SCHEME 5. Competitive Aldol Reactions of 1 vs 11 and 1 vs 14 with LDA as a Base



In order to estimate the relative reactivity of the *O*-acylTEMPOs in comparison with usual alkyl esters and amides, competitive aldol reactions of **1** vs *tert*-butyl acetate (**11**) or **1** vs Weinreb amide **14** were attempted (Scheme 5). Thus, a 1:1 mixture of **1** and **11** was treated with 1 equiv of LDA at −78 °C for 1.5 h, and then the resulting reaction mixture was allowed to react with an excess amount of either anisaldehyde (**7b**) or cyclohexanone (**9a**). In each case, the products were a ca. 1:1 mixture of the corresponding aldol adducts, **8b** + **12b**, and **10a** + **13a**, as well as the starting carboxylic derivatives **1** and **11**. Thus, these results tell that the acidities of **1** and **11** are similar. Furthermore, similar results were also obtained in a competitive aldol reaction of **1** vs **14**. Thus, *O*-acetylTEMPO (**1**) can be used as a viable alternative of carboxylic derivatives in terms of its comparable nucleophilicity on the C2 carbon.

Subsequently, the competitive aldol reaction was extended to diacid derivatives comprised of *O*-acylTEMPO and the Weinreb amide to compare the reactivity of the anionic species from the viewpoint of its regioselectivity.[17] Thus, treatment of glutaric derivative **17** with LDA (2.5 equiv) at −70 °C for 3 h followed with anisaldehyde (**7b**) at −70 to −30 °C for 3 h afforded the aldol product **18b** as a major product[18] along with several byproducts (Scheme 6).[19] Similar regioselectivity was found in the reaction of **17** with **7c** and **9a**, producing **18c** and **19a**, respectively. Contrary to our expectation based on the acidity of the α-methylene of *O*-acylTEMPO compared with

(17) According to absorptions due to CO groups in IR spectra of **17**, the α-proton of *O*-acylTEMPO (1762 cm^{-1}) is considered to be more acidic than that of the Weinreb amide (1668 cm^{-1}).

(18) Compound **18b** was confirmed by transformation to the corresponding enal **ii** by the successive treatment with $LiAlH_4$, giving **i**, followed with MsCl and DBU.

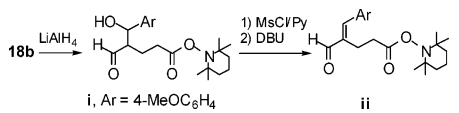
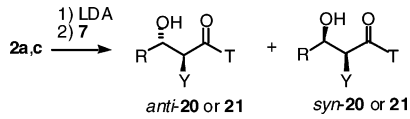


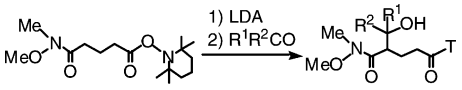
TABLE 2. Anti/Syn Selectivity of Aldol Reactions of *O*-AcylTEMPOs[a]



entry	**2a,c** Y	RCHO **7**	product, %[b]	anti/syn[c]
1	Me	**c**, Me_2CHCHO	**20c**, 91	9/1(10/1)
2	Me	**a**, MeCHO	**20a**, 86	2.5/1(2/1)
3	Me	**d**, (*E*)-MeCH=CHCHO	**20d**, 82	2.3/1
4	Me	**e**, PhCHO	**20e**, 92	5.4/1(3/1)
5	Me	**b**, 4-$MeOC_6H_4CHO$	**20b**, 95	7/1
6	MeO	**b**, 4-$MeOC_6H_4CHO$	**21b**, 41	1/3

[a] Carried out using YCH_2COT (**2a**, Y = Me; **2c**, Y = MeO, 2 mmol), RCHO (**7**, 2.0−2.5 equiv), and LDA (1.5 equiv) in THF at −78 °C for 15 min: **20**, Y = Me; **21**, Y = MeO, T = TEMPO. [b] Yields are based on isolated products. [c] Determined by ^1H NMR. Numbers in parentheses are of data of alkoxyalkyl propionate taken from ref 20a.

SCHEME 6. Regioselective Aldol Reactions of Glutaric Derivative Bearing *O*-AcylTEMPO and Weireb Amide



R^1R^2CO		products, yield (%)	
4-$MeOC_6H_4CHO$	**7b**	**18b**	46
trans-C_6H_5CH=CHCHO	**7c**	**18c**	60
c-$C_6H_{10}CO$	**9a**	**19a**	59

T = TEMPO

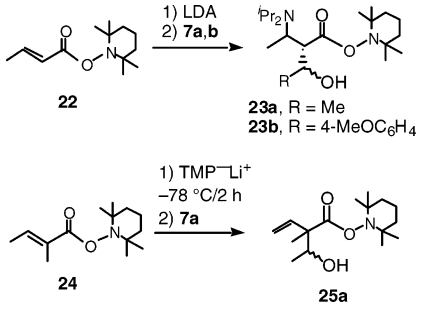
that of Weinreb amide, the aldol reaction occurred at the C2 position of the Weinreb amide predominantly. This can be best explained by formation of a dianion species, generated on both α positions of the two carbonyl groups of **17** due to excess LDA followed by a fast addition reaction at the enolate of the amide, since the enolate of the Weinreb amide is considered to be more reactive than the anionic species available from the *O*-alkanoylTEMPO moiety.

We next examined the aldol reaction of *O*-propionylTEMPO (**2a**) or 2-hetero-substituted *O*-acetylTEMPO **2c** with various aldehydes **7** in order to explore the effect of the TEMPO group toward anti/syn selectivity.[20] As shown in Table 2, aldol reactions of **2a** proceeded smoothly to afford the corresponding adducts **20** as an anti/syn diastereomeric mixture in good yields. The anti/syn ratio was determined by ^1H NMR; the *anti*-aldol **20b**, for example, showed a doublet at 4.74 ppm (J = 8.2 Hz) due to the β-CH, while the *syn*-isomer of **20b** was at 5.05 ppm (J = 4.7 Hz). Almost the same or higher selectivities compared with that obtained from other alkyl esters bearing an internal chelating group were attained with *O*-acylTEMPO **2a** with aliphatic aldehydes (entries 1−3).[20a] Similar anti selectivity was also obtained by the reaction with aromatic aldehydes **7e** and **7b** (entries 4 and 5). Aldol reaction of methoxyacetylTEMPO

(19) Decomposition of Weinreb amide with a strong base was found in the reaction products: Graham, S. L.; Scholz, T. H. *Tetrahedron Lett.* **1990**, *31*, 6269−6272.

(20) (a) Meyers, A. I.; Reider, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 2501−2502. (b) Pirrung, M. C.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1727−1728. (c) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975−3978.

SCHEME 7. Aldol Reactions of CrotonoylTEMPOs



2c with **7b** proceeded smoothly to give the corresponding adducts **21b** with a reverse anti/syn ratio of 1:3 (entry 6).

In the course of our examination on the γ-alkylation or α-alkylation with the vinylogous anionic species accessible from *O*-2-alkenylTEMPOs,[21] we encountered facile Michael addition of LDA,[22] employed as a base, to the crontonyl derivative **22** and subsequent aldol reaction of the resulting anionic species with aldehydes **7a** and **7b**, giving the corresponding adducts **23a** (R = Me) in 82% yield and **23b** (R = 4-MeOC$_6$H$_4$) as a separable 3:1 diastereomeric mixture in 71% yield (Scheme 7). On the other hand, treatment of **24** with bulky lithium amide from 2,2,6,6-tetramethylpiperidine (TMP) as a base for deprotonation followed by reaction with **7a** afforded the α-addition products **25a** as a ca. 4:1 diastereomeric mixture in 37% yield (Scheme 7). In this case, no γ-addition was found.

In summary, *O*-alkanoylTEMPOs are easily deprotonated with LDA at −78 °C to generate the corresponding lithium anionic species, which are a potent nucleophiles for carbon−carbon bond-making reactions such as alkylations, Michael additions, aldol reactions, etc. Fairly good anti or syn selectivities were attained in aldol reactions of *O*-propionoyl derivatives owing to the TEMPO moiety as an auxiliary, whose selectivities are comparable with those reported.[20] CrotonoylTEMPOs, more electron deficient than usual alkyl crotonates, are prone to undergo 1,4-addition of lithium amide, and the subsequent aldol reactions of the resulting anionic species lead to the three-component combined products smoothly.

Experimental Section

General Procedure for Aldol Reaction of *O*-AcylTEMPOs Using LDA. To an LDA solution, prepared from BuLi (1.58 N in hexane, 1.9 mL) and $(Me_2CH)_2NH$ (0.42 mL, 3.0 mmol) in THF (5 mL), cooled to −78 °C, was added dropwise over 5 min a solution of *O*-propionylTEMPO (**2a**, 426 mg, 2.0 mmol) in THF (3 mL). After stirring at −78 °C for 5 min, was added a solution of acetaldehyde (**7a**, R = Me, 370 mg, 8.4 mmol) in THF (2 mL). The mixture was stirred at the same temperature for 15 min, the reaction was quenched with cold aqueous NH_4Cl, and the products were extracted with AcOEt. The extracts were washed with brine, dried ($MgSO_4$), and concentrated. The products were analyzed by ^{1}H NMR and purified by LC (SiO_2, hexane−AcOEt 5:1, by increasing the gradient from 10:1 to 1:2) to give 440 mg (86%) of the aldol **20a** as a 2.5:1 diastereomeric mixture. An analytical sample of the anti isomer (contaminated with a small amount of the syn isomer) was obtained by recrystallization from hexane−AcOEt. *anti*- **20a** (R_f = 0.50, hexane−AcOEt 2:1): mp 105−106 °C (from hexane−AcOEt); IR (KBr) 3419, 3012, 2941, 1741, 1456, 1383, 1367, 1257, 1163, 1115, 1099, 999, 905 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.07 (s, 6H), 1.16, 1.17 (s, 6H), 1.25 (d, J = 6.4 Hz, 3H), 1.28 (d, J = 7.3 Hz, 3H), 1.38−1.44 (m, 1H), 1.50−1.75 (m, 5H), 2.50 (quin, J = 7.3 Hz, 1H), 2.82 (brs, 1H), 3.90 (m, 1H); ^{13}C NMR (75.5 MHz) δ 14.8, 16.9, 20.51 (2C), 20.75, 31.79 and 31.91, 38.95 and 39.07, 46.1, 59.96 and 60.19, 69.3, 175.6. HRMS (EI) calcd for $C_{14}H_{27}NO_3$ 257.1991, found 257.2025.

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Supporting Information Available: Spectral data including IR, ^{1}H NMR, and ^{13}C NMR spectra of **3a**−**g**, **4**, **5a**−**c**, **8a**,**b**, **10a**−**e**, and **17** and starting material of **17**, **18b**,**c**, **19a**, **20a**−**d**, **21b**, **23a**,**b**, and **25a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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