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Deprotonation of 5,6-Dihydro-5-methylene-4*H*-1,2-oxazines and Regioselective Reactions with Electrophiles

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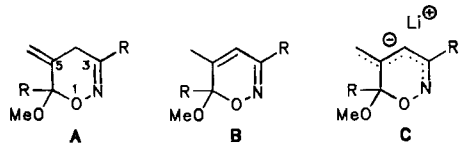
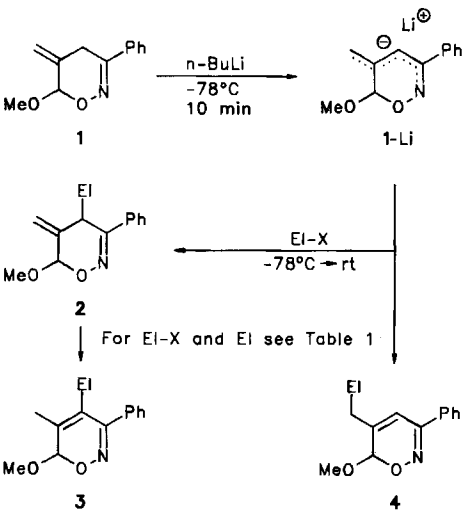
5,6-Dihydro-5-methylene-4*H*-1,2-oxazine **1** is smoothly converted by *n*-butyllithium into **1**-Li which reacts with electrophiles such as D_2O, carbonyl compounds, dimethyl sulfide, or an azo diester to give the γ-adducts **4a** – **4i**. On the other hand, alkylation of **1**-Li occurs exclusively at C-4 of the heterocycle and provides the α-adducts **3g** and **3h**. These reactions require the activation of **1**-Li by tetramethylethylenediamine. Treatment with allyl bromide and methyl acrylate affords mixtures of regioisomers **3** and **4**. 1,2-Oxazine **5** with a conjugated C=C bond is less acidic than **1** but is also converted into **1**-Li, whilst compound **6**, lacking the 6-methoxy group, is not deprotonated under standard conditions. The dianion of 1,2-oxazine **7** is generated by employing an excess of *n*-butyllithium. This dianion displays a similar regiochemical behavior as **1**-Li. Deuterium is exclusively incorporated into the γ-position to give product **8**, while methylation occurs at C-4 to produce **9**. 1,2-Oxazine **3g** with an additional 4-methyl group can also be metalated and affords γ-adducts **10** and **11** upon reaction with D_2O or acetone. Treatment with methyl iodide gives a 3:1 mixture of regioisomers **12** and **13**. Deuteration of 1,2-oxazines **14** and **16** bearing a 3-CF_3 or 3-CO_2Et substituent requires more severe deprotonation conditions to provide the γ-adducts **15** and **17** in moderate yields. MNDO calculations of neutral 1,2-oxazines, the corresponding carbanions, and the lithium compounds allow an insight into the structure and charge distribution of these species, and also an estimation of the relative acidities. The regioselectivity of reactions of **1**-Li is discussed on the basis of these semiempirical calculations and comparison with related ambident nucleophiles.

1,2-Oxazines of type **A** or **B** are easily accessible by hetero Diels-Alder reactions of nitroso alkenes with methoxyallene or derivatives thereof[4]. These heterocycles can be transformed into new 1,2-oxazines by Lewis acid promoted substitution of the 6-methoxy group[5], or they may be converted into acyclic compounds, e.g. by various reductive ring cleavage methods[2,6]. In this paper we describe the generation of carbanions **C** and their reactions with different electrophiles. Since deprotonated unsaturated oxime ethers[7] have not been studied so far, the regioselectivity of the ambident carbanion **C** has been examined in some detail. Intermediate **C** can react at the nitrogen atom or at two different carbon positions (C-4: α-selectivity; 5-CH_2: γ-selectivity). Also, MO calculations have been performed to compare the acidities of various 1,2-oxazines and to gain an insight into the structure and charge distribution of **C** and related lithiated 1,2-oxazines.



Results with 5,6-Dihydro-5-methylene-3-phenyl-4*H*-1,2-oxazine (1)

1,2-Oxazine **1** is smoothly deprotonated at C-4 by a slight excess of *n*-butyllithium in tetrahydrofuran (THF). After 10 min at −78 °C, the dark green color of the resulting solution of **1**-Li does not deepen further, and quenching with D_2O provides the monodeuterated compound **4a** in 80% yield. Deuterium is exclusively introduced into the 5-methyl group as indicated by the ^{1}H-NMR signal integrals. Thus, this reaction of **1**-Li occurs with very high (>95%) γ-selectivity. This is also true for carbonyl compounds used as electrophiles; thus, the reactions with benzaldehyde, acetone, or



r. t.: room temperature.

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benzophenone afford the expected 1,2-oxazines **4b**–**4d** in good yields (Table 1, entries 2–4). The benzaldehyde adduct **4b** is formed as a 1:1 mixture of two diastereomers.

Table 1. Reaction of **1**-Li with electrophiles

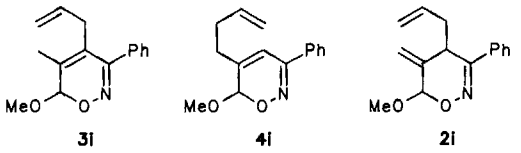
Entry	Electrophile El-X	γ-Addition 4	El	α-Addition 3
1	D_2O	**4a** 80%	D	-
2	PhCHO	**4b** 82% (1:1) [a]	PhCHOH	-
3	Me_2CO	**4c** 70%	Me_2COH	-
4	Ph_2CO	**4d** 63%	Ph_2COH [c]	-
5	Me_2S_2	**4e** 73%	MeS	-
6	E-N=N-E [b]	**4f** 34%	EHN-NE [b]	-
7	MeI [c]	-	Me	**3g** 82%
8	EtI [c]	-	Et	**3h** 42%
9	CH_2=$CHCH_2Br$ [c]	**4i**	CH_2=$CHCH_2$ 1:3, 66%	**3i** [d]
10	CH_2=CH-CO_2Me	**4j**	MeO_2C-CH_2CH_2 3:1, 5%	**3j**

[a] Ratio of diastereomers. – [b] E = CO_2tBu. – [c] Addition of 1.1 equivalents of TMEDA. – [d] Crude and purified product mixtures contain approximately 5% of **2i**.

Dimethyl disulfide and di-*tert*-butyl azodicarboxylate are also electrophilic components which add to **1**-Li to give γ-adducts **4e** and **4f** (Table 1, entries 5 and 6). These hetero-electrophiles therefore allow selective introduction of functional groups at the 5-methyl substituent of 1,2-oxazines. Of special interest is the electrophilic amination[8] by employing the azo ester[9], since product **4f** is an equivalent of a 1,4-diamino compound.

In all reactions of **1**-Li described (entries 1–6) the also possible α-adducts **2** or **3** cannot be detected even in the crude material. In contrast, the alkylations with methyl iodide or ethyl iodide exclusively afford 1,2-oxazines **3g** and **3h** bearing the new alkyl group at C-4 (Table 1, entries 7 and 8). The primary products **2** of α-alkylations apparently isomerize during workup to the more stable conjugated 6*H*-1,2-oxazines **3**[4]. The reactions of **1**-Li with alkyl halides are considerably slower than those with other electrophiles. Thus, methylation under the usual conditions leads to the recovery of approximately 50% of unalkylated compound **5** arising from protonation of **1**-Li[2]. However, activation of intermediate **1**-Li by the addition of 1.1 equivalents of tetramethylethylenediamine allows smooth methylation, whilst the reaction with ethyl iodide is still not complete and gives a mixture of **3h** (42% yield) and **5** (26% isolated).

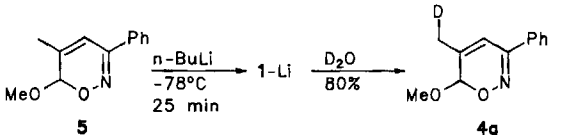
The reaction of **1**-Li with allyl bromide provides α- *and* γ-products. 1,2-Oxazines **3i** and **4i** are isolated as a 3:1 mixture in 66% yield. This distribution is the result of kinetic control, since the conceivable equilibration of **3i**/**4i** by a Cope rearrangement via **2i** does not occur. Even during distillation at 120°C, the product ratio does not change. Treatment of **1**-Li with methyl acrylate also affords a mixture of α-adduct **3j** and γ-adduct **4j** (1:3), but the yield of 5% is very low due to polymerization of the olefin.



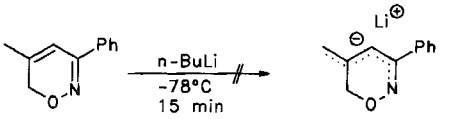
3i **4i** **2i**

Deprotonation of Other 1,2-Oxazines

The conjugated 1,2-oxazine **5**, obtained by isomerization of **1**[4], seems to be less acidic as indicated by a considerably slower appearance of the dark green color of the **1**-Li solution. Addition of D_2O after a deprotonation period of 25 min also provides the deuterated compound **4a**, thus proving that an identical intermediate is generated from **1** and **5**. On the other hand, the related 1,2-oxazine **6**[5], which lacks the 6-methoxy substituent, is not converted into the corresponding lithiated species **6**-Li. Quenching with D_2O leads to reisolation of **6**, thus indicating that the conditions chosen for metalation are not strong enough.



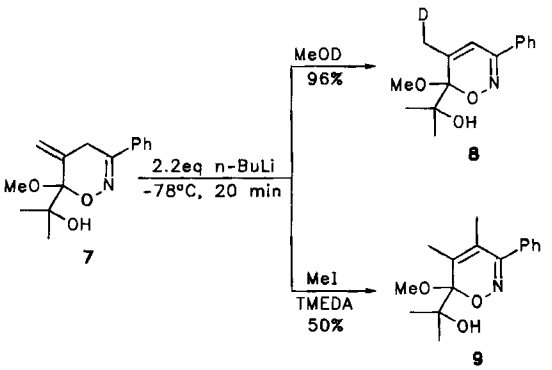
5 **4a**



6 **6**-Li

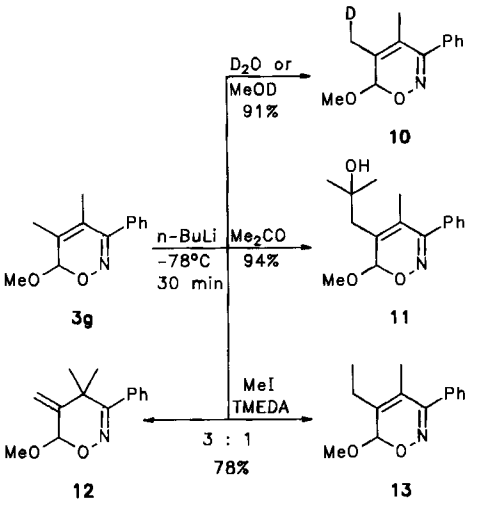
Interestingly, the 1,2-oxazine **7** bearing a 6-(hydroxyalkyl) group can smoothly be transformed into an intermediate dianion. This species seems to display a pattern of regioselectivity comparable with that of **1**-Li. Deuteration gives **8** (γ-addition), whereas methylation affords the highly substituted 1,2-oxazine **9** (α-addition).

The 1,2-oxazine **3g** is available by methylation of the parent compound **1**. It can also be deprotonated to give a carb-

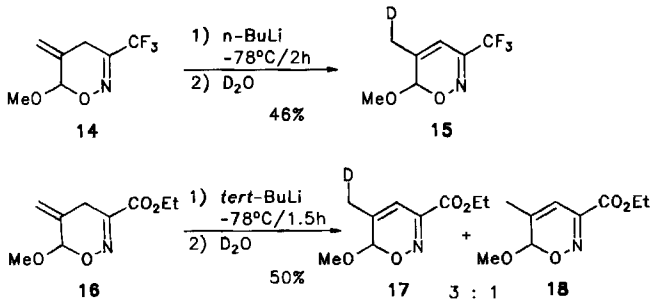


7 **8** **9**

anion which provides γ-adducts **10** or **11** upon treatment with D_2O or acetone as electrophiles. Reaction with monodeuterated methanol as a deuteron source does not exhibit a divergent regioselectivity compared with D_2O[10]. Interestingly, not only the expected α-product **12** is isolated after reaction with methyl iodide, but compound **13**, bearing a 5-ethyl group, has also been identified. The ratio of about 3:1 in favor of **12** illustrates that notwithstanding steric hindrance of the 4-methyl group in **3g**-Li α-alkylation is still preferred.

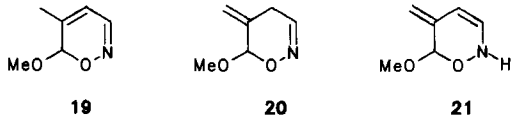


Preliminary experiments with the 5,6-dihydro-5-methylene-4*H*-1,2-oxazines **14** and **16** demonstrate that the metalation is not restricted to 3-phenyl-substituted 1,2-oxazines like **1**. However, both compounds seem to be less acidic than **1** and **5**. To achieve complete deprotonation of **14**, a metalation time of two hours is required, and deprotonation of **16** is brought about to an extent of 75% only even with *tert*-butyllithium. In both experiments the material balance is rather low, and therefore addition of the organolithium compounds may to some degree have occurred. Attempts to alkylate or hydroxyalkylate these lithiated 1,2-oxazines have so far not been very successful[1] and require further optimization.



MNDO Calculations

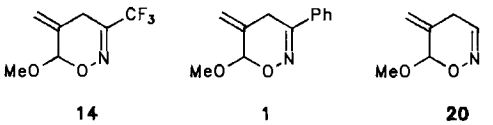
MNDO calculations of compounds **19**–**21** reveal that the conjugated 6*H*-1,2-oxazine **19** is by 4.5 kcal/mol more stable than the deconjugated isomer **20**, while the dienamine **21** is by far the least stable compound in this series. Thus, thermodynamics will favor the formation of conjugated 6*H*-1,2-oxazines like **19** (γ-selectivity). On the other hand, the generation of a carbanion should be more easily achieved by starting from deconjugated compounds like **20**.



	19	**20**	**21**
H_f = (kcal/mol)	-33.6	-29.1	-16.3

Inspection of the structure of **19** shows an almost planar six-membered heterocycle with C-6 slightly out of plane and the 6-methoxy group in a pseudoaxial position. This structural feature is also found for the corresponding carbanions, e. g. $\mathbf{19}^-$ ($\triangleq \mathbf{20}^-$). Calculation of the reaction enthalpies, as demonstrated for $\mathbf{20} \rightarrow \mathbf{19}^- + H^+$ (equation 1), allows a comparison of the relative *thermodynamic* acidities of the 1,2-oxazines **14**, **1**, **20**, **19**, and **22**.

	20	→	$\mathbf{19}^-$	+	H^+	(1)
ΔH_f =	−29.1		−45.0		367.2 kcal/mol	
ΔH_r =	−351.3 kcal/mol					



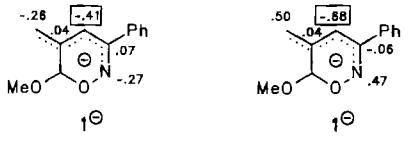
	14	**1**	**20**
rel. ΔH_R (kcal/mol)	0	12.15	14.7

19	**22**
19.2	20.4

The CF_3-substituted 1,2-oxazine **14** should exhibit the highest acidity, which is in disaccord with our observations indicating slower deprotonation. However, competition and equilibration experiments are required to determine the relative kinetic and thermodynamic acidities of **14** and **1**. The higher acidity of **20** compared with **19** is in accord with the apparently faster deprotonation of 1,2-oxazine **1** (compared to **5**). Also, the lower acidity of **22** might explain our failure to deprotonate compound **6** which lacks the 6-methoxy group.

For a discussion of the regioselectivities observed for reactions of **1**-Li the charge distribution and the HOMO coefficients of carbanion $\mathbf{1}^-$ are of interest. Both sets of parameters show the highest value at C-4 and therefore indicate that orbital and charge control might govern an electrophile to attack this position.

MNDO calculations also reveal that neither the substituent at C-3 (R = Ph, H, CF_3) nor the fragment in position 1 (O, NH, CH_2) has great influence on the HOMO coefficients and charge densities in the 1-azapentadienyl anion part.



To unify experiment and theory the calculation of the *lithiated* species **19**-Li is of particular interest. The most stable structure obtained by MNDO is depicted in Figure 1, and essential geometrical parameters are collected in Table 2. Other structures locating the lithium atom *trans* with respect to the 6-methoxy group or *cis* without an interaction with this substituent are by approximately 2.5 kcal/mol disfavored.

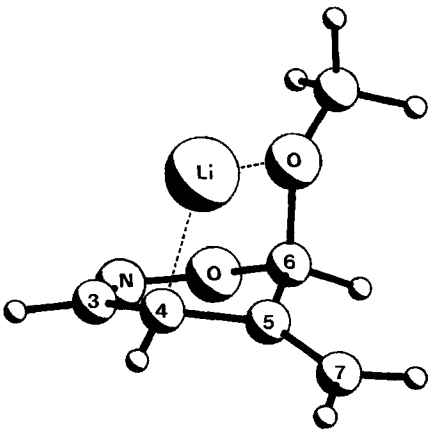


Figure 1. Structure of lithiated 1,2-oxazine (**19**-Li) according to MNDO calculations

Table 2. Characteristic bond lengths and angles of **19**-Li according to MNDO calculations (ΔH_f = −40.5 kcal/mol)

Distance [Å]		Bond Angle [°]	
O – N	1.310	O – N – C-3	120.6
N – C-3	1.325	N – C-3 – C-4	125.6
C-3 – C-4	1.470	C-3 – C-4 – C-5	112.6
C-4 – C-5	1.496	C-4 – C-5 – C-6	111.6
C-5 – C-6	1.557	C-5 – C-6 – O	113.7
C-6 – O	1.415	C-6 – O – N	122.2
C-5 – C-7	1.354	C-4 – C-5 – C-7	126.7
C-6 – OMe	1.440	C-7 – C-5 – C-6	121.7
C-3 – Li	2.747	C-3 – C-4 – Li	105.1
C-4 – Li	1.968	C-5 – C-4 – Li	83.9
C-5 – Li	2.342	4-H – C-4 – Li	120.4
C-6 – Li	2.752	C-5 – C-6 – OMe	105.5
C-7 – Li	3.281		
N – Li	3.373		
O – Li	3.426		
MeO– Li	2.186		

The structure of **19**-Li reveals several interesting features:

a) The 1-azapentadienyl anion moiety acts essentially as an η^1-ligand towards the lithium cation; the distance of C-4 – Li is 1.97 Å and the hybridization of C-4 is close to sp^3.

b) The lithium atom is *cis*-located to the 6-methoxy group, and a strong interaction of the metal atom with the oxygen atom can be deduced from the short O – Li distance of 2.19 Å.

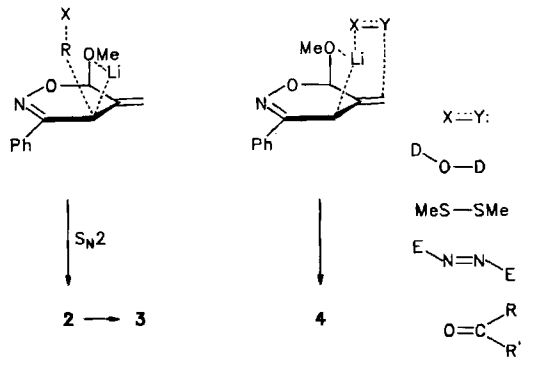
c) The distances of the endocyclic oxygen and nitrogen atoms to the lithium atom are too large for assuming an interaction of these centers[11].

According to this calculation the lithium atom of **19**-Li seems to be highly localized at the almost tetrahedral carbon atom C-4. It exhibits a strong interaction with the methoxy group and a weaker one with the *exo*-methylene unit. Although the actual structure of **1**-Li might be modified by further interaction with solvent molecules and/or by formation of aggregates, the picture obtained by the MNDO calculation can very nicely explain most of the experiments.

Discussion

Our results demonstrate that 1,2-oxazines **1** and **5** are reasonably acidic and that lithiated species **1**-Li may be generated without interfering addition of *n*-butyllithium to the C=N moiety[12]. The deprotonation of **5** occurs regioselectively at the 5-methyl group and not at C-6, which would generate an antiaromatic 8π-system[13]. The acidity of 1,2-oxazines seems to be enhanced by a 6-methoxy substituent. This effect might be of kinetic origin, e. g. primary complexation of the attacking *n*-butyllithium; however, the MNDO calculations also reveal a thermodynamic effect.

The charge distribution and HOMO coefficients in $\mathbf{1}^-$ and the structure of **1**-Li, which is assumed to be very similar to that of **19**-Li (Figure 1), suggest that electrophiles should attack C-4 of this ambident system[14] affording α-products **2**. However, experimental proof for this has only been obtained for alkylations. Since these reactions require further activation by the cation-complexating agent TMEDA, we conclude that a higher carbanionic character of the nucleophile is favorable, and that the interaction of the lithium cation with the leaving group of the electrophile is not essential. Thus, a typical S_N2 process seems to be likely. The crucial question concerning the stereochemistry[7b] at the nucleophilic center C-4 cannot be answered so far because of fast isomerization of the primary products **2** to the conjugated compounds **3**. Assuming retention of configuration – as often albeit not always observed for S_E processes[15] – a



structure as assumed for **1**-Li should lead to a *cis*-substituted 1,2-oxazine **2**.

The other electrophiles investigated are able to react with **1**-Li via a six-membered transition state. This is why the addition of carbonyl compounds, dimethyl disulfide, the azo compound, and D_2O affords exclusively γ-adducts **4**. A similar transition state is not available for alkyl halides, because this would imply a front-side attack at the electrophilic carbon atom. Allyl bromide is a borderline case since it can be attacked in an S_N2 (α-selectivity?) and/or an S_N2' fashion (γ-selectivity?). The observation that mixtures of regioisomers are formed suggests that both processes compete with one another.

γ-Selective additions of electrophiles at the exocyclic carbon atom of **1**-Li directly provide the thermodynamically more stable isomers. γ-Deuteration and γ-methylthiolation of **1**-Li undoubtedly occur under kinetic control. On the other hand, the reaction of **1**-Li with carbonyl compounds might be reversible, a point that has not yet been experimentally proven.

To the best of our knowledge α,β-unsaturated oxime ether carbanions and their reactions with electrophiles have not been described so far[16]. Our results must therefore be compared with related ambident systems, e. g. the carbanions derived from α,β-unsaturated hydrazones[17], imines[18–21], or carbonyl compounds[19,20,22,23]. In all these 1-heteropentadienyl anions alkylation preferentially occurs in the α-position, whereas the regioselectivity when employing carbonyl compounds as electrophiles is often highly dependent on the conditions (thermodynamic versus kinetic control)[21]. We are not aware of deuterations and thiomethylations, but a recent paper reports on the highly γ-selective reaction of deprotonated crotonic ester or similar compounds[23] with di-*tert*-butyl azodicarboxylate. This result is in accord with our observation employing this electrophile. In summary, the regiochemical behavior of **1**-Li is in reasonable agreement with related systems, but for a full understanding of these ambident nucleophiles certain effects deserve further investigation[24]. Notwithstanding these open mechanistic questions, from a preparative point of view, we could remarkably extend the accessibility of substituted and/or functionalized 6*H*-1,2-oxazines.

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Experimental

For general information see ref.[5]. The preparation of the 1,2-oxazines required as starting materials is described in ref.[4]. All reactions were executed in a flame-dried flask under a slight pressure of dry nitrogen. All components were added with a syringe. Tetrahydrofuran (THF) was distilled from potassium/benzophenone immediately before use.

General Procedure for the Deprotonation of 1,2-Oxazines and the Reaction with Electrophiles: The corresponding 1,2-oxazine was dissolved in dry THF (10.0 ml/1.50 mmol of 1,2-oxazine) and treated at −78°C with 1.1 equivalents of *n*-butyllithium (2.5 M in hexane). After the deprotonation time indicated in Table 3, 1.5 equivalents of the electrophile were slowly added within 10 min. The reaction mixture was allowed to warm up to room temperature within 15 h, and then it was quenched with 20 ml of saturated aqueous NH_4Cl solution. Extractive workup with diethyl ether and drying of the organic phases ($MgSO_4$) provided the crude product which was purified by column chromatography [Al_2O_3, neutral, activity III, pentane/ethyl acetate (4:1)] or by Kugelrohr distillation. For NMR data see Tables 4–7.

Further spectroscopic and analytical data of the 6*H*-1,2-oxazines **4** and **3**.

5-[(2-Hydroxy-2-phenyl)ethyl]-6-methoxy-3-phenyl-6H-1,2-oxazine (**4b**): Pale yellow oil (1:1 mixture of diastereomers). – IR (film): $\tilde{\nu}$ = 3660–3120 cm^{-1} (O–H), 3120–2820 (=C–H, C–H), 1655 (C=C), 1530 (C=N).

$C_{19}H_{19}NO_3$ (309.4) Calcd. C 73.76 H 6.19 N 4.53
Found C 73.36 H 6.15 N 4.29

5-[(2-Hydroxy-2-methyl)propyl]-6-methoxy-3-phenyl-6H-1,2-oxazine (**4c**): Colorless liquid. – IR (film): $\tilde{\nu}$ = 3640–3120 cm^{-1} (O–H), 3120–2780 (=C–H, C–H), 1645 (C=C), 1580 (C=N).

$C_{15}H_{19}NO_3$ (261.3) Calcd. C 68.94 H 7.33 N 5.36
Found C 68.51 H 7.20 N 5.16

Table 3. Synthesis of 6*H*-1,2-oxazines **4** and **3** (according to the general procedure)

1,2-Oxazine g (mmol)	Electrophile g (mmol)	Time[a] h	Product	Yield g
1 0.406 (2.00)	D_2O 2.0 ml	1.5	**4a**	80% 0.328
5[b] 0.406 (2.00)	D_2O 2.0 ml	2	**4a**	80% 0.327
1 0.609 (3.00)	Benzaldehyde 0.480 (4.50)	15	**4b**	82% 0.760
1 0.609 (3.00)	Acetone 0.348 (6.00)	12	**4c**	70% 0.551
1 1.22 (6.00)	Benzophenone 1.64 (9.00)[c]	15	**4d**	63% 1.46
1 0.609 (3.00)	Dimethyl Disulfide 0.564 (6.00)	21	**4e**	73% 0.543
1 0.609 (3.00)	Di-*tert*-butyl Azodicarboxylate 1.04 (4.50)[d]	15	**4f**	34% 0.444
1 1.22 (6.00)[e]	Methyl Iodide 1.28 (9.00)	15	**3g**	82% 1.07
1 0.609 (3.00)[e]	Ethyl Iodide 0.700 (4.50)	15	**3h**	42% 0.290[f]
1 0.609 (3.00)[e]	Allyl Bromide 0.550 (4.50)	15	**4i/3i** g) (1:3)	66% 0.485
1 0.609 (3.00)	Methyl Acrylate 0.290 (3.30)	15	**4j/3j** (3:1)	5% 0.040[h]

[a] After addition of the electrophile, slow warming to room temperature. – [b] Deprotonation period 25 min. – [c] Dissolved in 20 ml of THF. – [d] Dissolved in 10 ml THF. – [e] Addition of 1.1 equivalents of TMEDA before treatment with the electrophile. – [f] 0.160 g (26%) of **5** was separated by column chromatography. – [g] Crude and purified product mixtures contained approximately 5% of **2i**. – [h] 0.085 g (14%) of **5** was separated by column chromatography.

Table 4. ^{1}H-NMR data ($CDCl_3$, 300 MHz) of 6*H*-1,2-oxazines **4** and **3**

Compound	Ph (5 H)	4-H (1 H)	6-H (1 H)	OMe (3 H)	Other Signals
4a	7.73-7.69 7.42-7.39, 2 m	6.34 t (1.5)	5.31 s	3.54 s	2.06 (m_c, 2 H, 5-CH_2D)
4b[a]	7.66-7.26, m[b]	6.46, 6.29 2 m_c	5.46, 5.51 2 s	3.54, 3.47 2 s	4.02 (broad s, 1 H, OH), 4.96 (m_c, 1 H, C<u>H</u>PhOH) 2.76, 2.73 (2 m_c, 2 H, 5-CH_2)
4c	7.74-7.70 7.43-7.40, 2 m	6.36 s	5.50 s	3.53 s	2.96 (broad s, 1 H, OH), 2.52, 2.47 (AB-system, J = 12.5 Hz, 2 H, 5-CH_2), 1.31, 1.29 (2 s, 6 H, Me)
4d	7.55-7.22 m[c]	5.93 m_c	5.23 s	3.34 s	4.24 (broad s, 1 H, OH), 3.49, 3.33 (2 d, J = 14 Hz, 2 H, 5-CH_2)
4e	7.76-7.70 7.44-7.39, 2 m	6.42 t (1.0)	5.61 s	3.55 s	3.38 (m_c, 2 H, 5-CH_2), 2.03 (s, 3 H, SMe)
4f[d]	7.73-7.69 7.42-7.39, 2 m	6.47 s	5.46 s	3.51 s	6.35 (broad s, 1 H, NH), 4.50, 4.24 (2 d, J = 16 Hz, 2 H, 5-CH_2), 1.49, 1.47 (2 s, 18 H, CMe_3)
3g	7.45-7.38, m	-	5.26, s	3.52, s	2.00, 1.75 (2 s, 6 H, 4-, 5-Me)
3h	7.50-7.36 m	-	5.24 s	3.51 s	2.30, 2.18 (2 qd, J = 7, 14 Hz, 2 H, 4-CH_2) 2.01 (s, 3 H, 5-Me), 0.77 (t, J = 7 Hz, 3 H, Me)
4i	7.42-7.30 m	6.30 s	5.33 s	3.50 s	5.89-5.68, 5.12, 5.05 (m, 2 m_c, 1 H, 2 H, CH=CH_2) 2.53-2.33 (m, 4 H, CH_2CH_2)
3i	7.42-7.30 m	-	5.25 s	3.49 s	5.76-5.52, 4.94, 4.73 (m, 2 dd, J = 1.5, 10 Hz, J = 1.5, 17 Hz, 1 H each, CH=CH_2), 2.91 (d, J = 5.5 Hz, 2 H, 4-CH_2), 1.96 (s, 3 H, 5-Me)
4j	7.76-7.68 7.48-7.37, 2 m	6.33 t (1.5)	5.34 s	3.53 s	3.69 (s, 3 H, CO_2Me), 2.42, 2.41, 1.95 (t, dt, quint., J = 7.5 Hz, J = 1.5, 7.5 Hz, J = 7.5 Hz, 2 H each, $CH_2CH_2CH_2$)
3j	7.76-7.68 7.48-7.37, 2 m	-	5.24 s	3.51 s	3.57 (s, 3 H, CO_2Me), 2.68, 2.50 (2 m_c, 4 H, CH_2CH_2), 1.66 (s, 3 H, 5-Me)

[a] Two diastereomers. – [b] 10 H. – [c] 15 H. – [d] Spectrum recorded at 373 K.

5-[(2-Hydroxy-2,2-diphenyl)ethyl]-6-methoxy-3-phenyl-6H-1,2-oxazine (**4d**): Very viscous resin. – IR (film): $\tilde{\nu}$ = 3620–3180 cm^{-1} (O–H), 3120–2820 (=C–H, C–H), 1650 (C=C), 1590 (C=N).

$C_{25}H_{23}NO_3$ (385.5) Calcd. C 77.89 H 6.01 N 3.63
Found C 77.05 H 6.16 N 3.20

6-Methoxy-5-[(methylthio)methyl]-3-phenyl-6H-1,2-oxazine (**4e**): Pale yellow oil, b. p. 130°C/0.1 Torr. – IR (film): $\tilde{\nu}$ = 3120–2790 cm^{-1} (=C–H, C–H), 1655 (C=C), 1580 (C=N).

$C_{13}H_{15}NO_2S$ (249.3) Calcd. C 62.63 H 6.06 N 5.62
Found C 62.92 H 6.00 N 5.45

5-{[N,N'-Bis(tert-butoxycarbonyl)hydrazino]methyl}-6-methoxy-3-phenyl-6H-1,2-oxazine (**4f**): Colorless crystals, m. p. 51–53°C. – IR (KBr): $\tilde{\nu}$ = 3700–3140 cm^{-1} (N–H), 3120–2850 (=C–H, C–H), 1740 (C=O), 1690 (C=C), 1590 (C=N).

$C_{22}H_{31}N_3O_6$ (433.5) Calcd. C 60.96 H 7.21 N 9.69
Found C 60.52 H 7.45 N 9.48

6-Methoxy-4,5-dimethyl-3-phenyl-6H-1,2-oxazine (**3g**): Pale yellow oil, b. p. 100°C/0.07 Torr, which slowly crystallizes, m. p. 49–52°C. – IR (film): $\tilde{\nu}$ = 3120–2880 cm^{-1} (=C–H, C–H), 1655 (C=C), 1575 (C=N).

$C_{13}H_{15}NO_2$ (217.3) Calcd. C 71.87 H 6.96 N 6.45
Found C 71.58 H 6.97 N 6.42

4-Ethyl-6-methoxy-5-methyl-3-phenyl-6H-1,2-oxazine (**3h**): Colorless crystals, m. p. 64–66°C. – IR (KBr): $\tilde{\nu}$ = 3120–2880 cm^{-1} (=C–H, C–H), 1655 (C=C), 1530 (C=N).

$C_{14}H_{17}NO_2$ (231.3) Calcd. C 72.70 H 7.41 N 6.05
Found C 72.79 H 7.51 N 5.86

4-Allyl-6-methoxy-5-methyl-3-phenyl-6H-1,2-oxazine (**3i**) *and 5-(3-Butenyl)-6-methoxy-3-phenyl-6H-1,2-oxazine* (**4i**): Crude product distribution **3i**:**2i**:**4i** = 73:5:22; purification by column chromatography did not change the ratio of isomers (pale yellow liquid, 66% yield). A sample purified by Kugelrohr distillation (110–120°C/0.01 Torr) exhibited a very similar isomer distribution (**3i**:**2i**:**4i** = 70:5:25). – IR (film): $\tilde{\nu}$ = 3120–2800 cm^{-1} (=C–H, C–H), 1650 (C=C), 1550 (C=N).

$C_{15}H_{17}NO_2$ (243.3) Calcd. C 74.04 H 7.04 N 5.76
Found C 73.94 H 7.16 N 5.42

^{1}H NMR data for **2i** ($CDCl_3$, 300 MHz): δ = 7.42–7.30 (m, 5H, Ph), 5.92–5.76 (m, 1H, =CH), 5.31 (s, 1H, 6-H), 5.19, 5.14, 5.09, 5.04 (4 m_c, 4H, $=CH_2$), 3.72–3.64 (m, 1H, 4-H), 3.53 (s, 3H, OMe), 2.53–2.33 (m, 2H, 4-CH_2).

Adducts **3j** *and* **4j** *of* **1**-Li *with Methyl Acrylate:* Purification by column chromatography, **3j**:**4j** = 1:3 as yellow liquid (5% yield). – IR (film): $\tilde{\nu}$ = 3080–2800 cm^{-1} (=C–H, C–H), 1730 (C=O), 1660 (C=C), 1560 (C=N).

$C_{16}H_{19}NO_4$ (289.3) Calcd. C 66.42 H 6.62 N 4.84
Found C 66.81 H 6.80 N 4.50

Deuteration of **7**: According to the general procedure, 1,2-oxazine **7** (200 mg, 0.76 mmol) was deprotonated with *n*-butyllithium (1.70 mmol) in 20 ml of THF and after 20 min treated with 0.20 ml of CH_3OD. The usual workup provided 192 mg (96%) of **8** as colorless crystals (m. p. 87–90°C). For ^{1}H-NMR and ^{13}C-NMR data see Tables 6 and 7.

6-[(1-Hydroxy-1-methyl)ethyl]-6-methoxy-4,5-dimethyl-3-phenyl-6H-1,2-oxazine (**9**): According to the general procedure, 1,2-oxazine **7** (200 mg, 0.76 mmol) was deprotonated with *n*-butyllithium (1.70 mmol) in 20 ml of THF. After 20 min, TMEDA (100 mg, 0.85 mmol) and methyl iodide (483 mg, 3.40 mmol) were added. The usual procedure and workup provided after chromatography 105 mg (50%) of **9** as colorless crystals (m. p. 92–94°C). – IR (KBr): $\tilde{\nu}$ = 3550–3100 cm^{-1} (O–H), 3100–3010 (=C–H, C–H), 1660 (C=C), 1580 (C=N).

$C_{16}H_{21}NO_3$ (275.4) Calcd. C 69.79 H 7.69 N 5.09
Found C 68.77 H 7.65 N 4.96

Deuteration Experiment with **3g**: According to the general procedure, 1,2-oxazine **3g** (217 mg, 1.00 mmol) was deprotonated with *n*-butyllithium (1.10 mmol) in 20 ml of THF. After 30 min, the orange solution was quenched with 1.0 ml of D_2O. The usual workup provided 195 mg (90%) of **10** as pale yellow oil, which crystallized at 7°C (m. p. 49–50°C). The experiment with CH_3OD

Table 5. ^{13}C-NMR data ($CDCl_3$) of 6*H*-1,2-oxazines **4** and **3**

Compound	C-3 s	C-4 d	C-5 s	C-6 d	6-OMe q	Ph s, 3 d	Other Signals
4a	153.5	111.9	137.6	97.1	56.0	134.0, 129.8 128.7, 126.2	19.0 (m_c, 5-CH_2D)
4b[a]	154.3 153.9	114.6[b]	140.9 136.9	96.4 95.7	55.9[b]	133.8, 133.7 128.9, 128.8 128.6, 128.5 126.7, 126.2	144.9, 143.0, 128.4, 128.3, 127.6, 127.5, 126.9, 125.9 (2 s, 6 d, Ph), 74.6, 71.7 (2 d, CHPh), 43.9, 42.1 (2 t, 5-CH_2)
4c	154.3	115.0	137.6	97.0	55.7	133.9, 129.9 128.7, 126.2	70.4, 29.8, 29.3 (s, 2 q, CMe_2) 47.9 (t, 5-CH_2)
4d	154.3	116.7	135.3	96.6	55.7	133.5, 129.9 128.6, 126.6	146.4, 146.2, 128.4, 128.3, 128.2, 127.2, 126.1, 125.6 (2 s, 6 d, Ph), 77.7 (s, CPh_2) 46.4 (t, 5-CH_2)
4e	153.9	112.6	136.7	95.1	56.1	133.7, 130.0 128.7, 126.2	35.7 (t, 5-CH_2) 14.9 (q, S-Me)
4f[c]	153.7	113.4	135.4	94.9	55.9	133.5, 129.6 129.5, 126.0	155.0, 81.3, 28.0 (2 s, q, CO_2CMe_3) 51.1 (t, 5-CH_2)
3g	159.6	118.9 s	134.1	98.2	55.8	131.9, 128.9 128.4, 128.2	16.1, 14.1 (2 q, 4-, 5-Me)
3h	159.6	125.1 s	134.2	98.4	55.9	131.3, 128.9 128.6, 128.5	20.4 (t, 4-CH_2), 15.8, 13.2 (2 q, 5-Me, CH_2Me)
4i	154.1	111.1	140.6	96.5	55.8	136.8, 128.5 128.1, 127.9	129.7, 116.0 (d, t, CH=CH_2) 32.1, 30.8 (2 t, 5-CH_2CH_2)
3i	159.4	120.8 s	136.6	98.3	55.9	134.9, 128.5 128.1, 127.9	126.1, 116.1 (d, t, CH=CH_2) 31.1 (t, 4-CH_2), 16.1 (q, 5-Me)
4j	154.2	111.4	140.3	96.4	55.9	133.4, 129.8 128.6, 126.2	173.4, 51.6 (s, q, CO_2Me), 33.1, 32.3, 22.1 (3 t, 5-$CH_2CH_2CH_2$)
3j	159.1	121.9 s	134.0	98.2	56.2	133.8, 129.2 128.5, 128.4	172.5, 51.6 (s, q, CO_2Me) 32.6, 22.4 (2 t, 4-CH_2CH_2), 16.1 (q, 5-Me)

[a] Two diastereomers. – [b] Broad signal. – [c] Recorded at 373 K.

Table 6. ^{1}H-NMR data ($CDCl_3$, 300 MHz) of 6*H*-1,2-oxazines **8**–**13**

Compound	Ph (5 H)	6-H (1 H)	OMe (3 H)	Other Signals
8	7.70-7.66 7.42-7.39, 2 m	-	3.23 s	6.54 (t, J = 1.5 Hz, 1 H, 4-H), 2.58 (broad s, 1 H, OH) 2.16 (m_c, 2 H, 5-CH_2D), 1.46, 1.24 (2 s, 6 H, Me)
9	7.40-7.30 m	-	3.29 s	2.41 (s, 1 H, OH), 2.03, 1.76 (2 s, 6 H, 5-, 4-Me) 1.40, 1.26 (2 s, 6 H, Me)
10	7.45-7.27, m	5.24, s	3.51, s	1.97 (broad s, 2 H, 5-CH_2D), 1.74 (s, 3 H, 4-Me)
11	7.46-7.39 m	5.40 s	3.51 s	3.28 (broad s, 1 H, OH), 2.74, 2.39 (2 d, J = 14 Hz, 2 H, 5-CH_2), 1.75 (s, 3 H, 4-Me), 1.34, 1.30 (2 s, 6 H, CMe_2)
12	7.45-7.31, m	5.25, s	3.53, s	5.24, 5.18 (2 s, 2 H, 5-CH_2), 1.35, 1.31 (2 s, 6 H, 4-Me)
13	7.45-7.31, m	5.32, s	3.50, s	2.36, 1.15 (q, t, J = 7 Hz, 2 H, 3 H, 5-Et), 1.75 (s, 3 H, 4-Me)

Table 7. ^{13}C-NMR data ($CDCl_3$) of 6*H*-1,2-oxazines **8**–**13**

Compound	C-3 s	C-4 s	C-5 s	C-6 d	6-OMe q	Ph s, 3 d	Other Signals
8	149.4	116.9 d	136.8[a]	103.5 s	50.6	133.6[a], 129.7 128.7, 125.6	76.4, 24.5, 23.9 (s, 2 q, 6-CMe_2) 20.3 (m_c, 5-CH_2D)
9	155.6	123.6	134.4[a]	104.5 s	51.0	131.7[a], 128.7 128.3, 128.2	76.9, 24.6, 24.1 (s, 2 q, 6-CMe_2) 15.2, 15.1 (2 q, 3-, 4-Me)
10	159.6	118.9	134.1[a]	98.3	55.9	131.9[a], 129.0 128.5, 128.3	15.9 (m_c, 5-CH_2D) 14.2 (q, 4-Me)
11	159.9	121.5	133.8[a]	97.9	55.3	132.2[a], 128.8 128.1, 125.9	71.3, 29.7, 28.7 (s, 2 q, CMe_2) 44.2 (t, 5-CH_2), 14.7 (q, 4-Me)
12	146.8	36.8	137.2[a]	100.6	55.4	134.3[a], 129.1 128.6, 127.9	111.6 (t, 5-CH_2) 28.3, 26.1 (2 q, 4-Me)
13	159.9	118.3	134.2[a]	96.7	55.8	130.1[a], 128.9 128.5, 128.3	23.3, 12.3 (t, q, 5-Et) 13.8 (q, 4-Me)

[a] Assignment ambiguous; marked signals are exchangeable within the line.

as reagent afforded 198 mg (91%) of **10** as colorless crystals (m. p. 48–50°C).

5-[(2-Hydroxy-2-methyl)propyl]-6-methoxy-4-methyl-3-phenyl-6H-1,2-oxazine (**11**): According to the general procedure, 1,2-oxazine **3g** (217 mg, 1.00 mmol) was deprotonated with *n*-butyllithium (1.10 mmol) in 20 ml of THF. After 30 min, 87.0 mg (1.50 mmol) of acetone was added. The usual workup afforded 260 mg (94%) of **11** as liquid. – IR (film): $\tilde{\nu}$ = 3640–3150 cm^{-1} (O–H), 3140–2800 (=C–H, C–H), 1655 (C=C), 1570 (C=N).

$C_{16}H_{21}NO_3$ (275.4) Calcd. C 69.79 H 7.69 N 5.09
Found C 69.81 H 7.58 N 5.02

5,6-Dihydro-6-methoxy-4,4-dimethyl-5-methylene-3-phenyl-4H-1,2-oxazine (**12**) *and 5-Ethyl-6-methoxy-4-methyl-3-phenyl-6H-1,2-oxazine* (**13**): According to the general procedure, 1,2-oxazine **3g** (217 mg, 1.00 mmol) was deprotonated with *n*-butyllithium (1.10 mmol) in 20 ml of THF. After 30 min, TMEDA (128 mg, 1.10 mmol) and methyl iodide (213 mg, 1.50 mmol) were added. The usual workup provided 180 mg (78%) of **12** and **13** as a 3:1 mixture (colorless crystals, m. p. 58°C). The mixture of **12** and **13** could not be separated by column chromatography and was characterized as received. – IR (KBr): $\tilde{\nu}$ = 3100–2820 cm^{-1} (=C–H, C–H), 1655 (C=C), 1575 (C=N).

$C_{14}H_{17}NO_2$ (231.3) Calcd. C 72.70 H 7.41 N 6.05
Found C 72.87 H 7.64 N 5.56

Deuteration Experiment with **14**: According to the general procedure, 1,2-oxazine **14** (60.0 mg, 0.31 mmol) was deprotonated with *n*-butyllithium (0.35 mmol) in 8 ml of THF. After 2 h, the red-brown solution was quenched with 1.00 ml of D_2O. The usual workup and Kugelrohr distillation (60–70°C/0.08 Torr) provided 28.0 mg (46%) of **15** as colorless liquid. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.06 (t, J = 2.0 Hz, 1H, 4-H), 5.37 (s, 1H, 6-H), 3.54 (s, 3H, OMe), 2.04 (m_c, 2H, 5-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 147.2 (q, $J_{C,F}$ = 34 Hz, C-3), 138.4 (s, C-5), 120.2 (q, $J_{C,F}$ = 274 Hz, CF_3), 107.6 (d, C-4), 97.7 (d, C-6), 56.1 (q, OMe), 18.6 (t, CH_2D).

Deuteration Experiment with **16**: According to the general procedure, 1,2-oxazine **16** (598 mg, 3.00 mmol) was deprotonated with *tert*-butyllithium (3.30 mmol) in 20 ml of THF. After 90 min, the deep red solution was quenched with 1.00 ml of D_2O. The usual workup and Kugelrohr distillation (75–85°C/0.07 Torr) gave a 3:1 mixture of deuterated compound **17** and **18**[4] (302 mg, 50%). Spectroscopic data for **17**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.46 (m_c, 1H, 4-H), 5.38 (s, 1H, 6-H), 4.37, 1.37 (q, t, *J* = 7.0 Hz, 2H, 3H, OEt), 3.52 (s, 3H, OMe), 2.02 (m_c, 2H, 5-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 162.1, 61.9, 13.8 (s, t, q, CO_2Et), 147.9 (s, C-3), 136.3 (s, C-5), 110.2 (d, C-4), 97.4 (d, C-6), 55.7 (q, OMe), 18.5 (t, CH_2D).

MNDO Calculations: See ref.[25].

CAS Registry Numbers

1: 117341-58-9 / **1**$^-$: 134359-49-2 / **2i**: 134359-37-8 / **3g**: 134359-31-2 / **3h**: 134359-32-3 / **3i**: 134359-34-5 / **3j**: 134359-36-7 / **4a**: 134359-24-3 / **4b** (isomer 1): 134359-25-4 / **4b** (isomer 2): 134359-26-5 / **4c**: 134359-27-6 / **4d**: 134359-28-7 / **4e**: 134359-29-8 / **4f**: 134359-30-1 / **4i**: 134359-33-4 / **4j**: 134359-35-6 / **5**: 117341-61-4 / **6**: 117341-66-9 / **7**: 117369-63-8 / **8**: 134359-38-9 / **9**: 134359-39-0 / **10**: 134359-40-3 / **11**: 134359-41-4 / **12**: 134359-42-5 / **13**: 134359-43-6 / **14**: 117341-60-3 / **15**: 134359-44-7 / **16**: 117341-59-0 / **17**: 134359-45-8 / **18**: 117341-62-5 / **19**: 134359-46-9 / **19**-Li: 134359-51-6 / **20**: 134359-47-0 / **21**: 134359-48-1 / **22**: 134359-50-5 / PhCHO: 100-52-7 / Me_2CO: 67-64-1 / Ph_2CO: 119-61-9 / MeS_2Me: 624-92-0 / $tBuO_2CN{=}NCO_2tBu$: 870-50-8 / MeI: 74-88-4 / EtI: 75-03-6 / $H_2C{=}CHCH_2Br$: 106-95-6 / $H_2C{=}CHCO_2Me$: 96-33-3

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