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Chiral Carbenoids: Effect of TMEDA

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In recent publications we have reported the results of our studies on the formation and reactions of chiral carbenoids.[1] We were able to demonstrate that chiral carbenoids can be prepared from chiral vinyl and cyclopropyl halides in ether solvents by metalation at *ca.* −70 °C or halogen−metal exchange reactions at *ca.* −90 °C and that subsequent reaction with external nucleophiles yielded optically active products with overall inversion of configuration.[2] In order to explain these results we postulated that metal-assisted ionization (MAI) of the halogen occurs leading to the formation of a chiral intermediate with a positive charge located at the central carbon atom. This chiral electrophilic intermediate can then undergo nucleophilic substitution reactions leading to optically active products with inversion of configuration[2] (Scheme 1).

In our continued investigation of the chemistry of chiral carbenoids we have conducted the current study of their behavior in the presence of a strong solvating agent, *N,N,N',N'*-tetramethylenediamine (TMEDA). TMEDA is probably the most commonly used solvating agent in organometallic chemistry and is known to dramatically increase the reaction rates of organolithium reagents, improve yields, and alter products distributions.[3,4] The crystallographic literature is replete with reports of lithium−TMEDA chelate substructure;[5] occasionally, η^1-bound solvates are formed, and these have also been characterized.[6] Unfortunately, X-ray data give little insight into solution thermodynamics of aggregation and solvation. The prevailing belief that TMEDA in ether solvents (THF, diethyl ether) is always a good ligand for lithium has recently been challenged.[7] It has been shown in several cases that TMEDA cannot compete with bulk THF in solvating lithium.[8] In general, behavior of the frequently used THF/TMEDA system is very complicated and still not fully understood. In order to obtain a clearer picture of the interaction between TMEDA and chiral carbenoids we decided to conduct our study in a nonpolar and nonsolvating solvent such as pentane and to compare the solvation by TMEDA with the solvation by (bulk) THF.

Table 1. Reaction of (*R*)-(−)-(4-Methylcyclohexylidene)chloromethane (1) with *tert*-Butyllithium in Pentane in the Presence of TMEDA

expt	time	*T*, °C	% of **1**	% of **2**	% of **3**	% of **4**
1	1 h	−70	37	44	6	13
2	15 min	−100	51	25	3	21

Results and Discussion

When (*R*)-(−)-(4-methylcyclohexylidene)chloromethane (**1**) was reacted with *tert*-butyllithium in pentane followed by deuterolysis no reaction could be detected at −70 °C, −10 °C, and even room temperature. The starting material was recovered in each case in essentially quantitative yield and with no detectable deuterium incorporation. However, when 1 equiv of TMEDA was present in the reaction mixture a fast reaction was observed at both −70 °C and −100 °C (Scheme 2). The reaction conditions and product distributions are given in the Table 1.

In a subsequent experiment (1 equiv of TMEDA, 3 equiv of t-BuLi, pentane, −100 °C, quenching with MeOH) products **2** (H) and **3** (H) were isolated and they were both found to be racemic. When the same reaction was run in THF instead of pentane in the presence of TMEDA the "substitution" product **2** was isolated in 65% yield and it was also found to be racemic.

When the reaction of (*R*)-(−)-(4-methylcyclohexylidene)chloromethane (**1**) with *tert*-butyllithium in pentane was carried out in the presence of cyclohexene as a carbene trap, 2% of 7-(4-methylcyclohexylidene)bicyclo[4.1.0]heptane (**6**) could be isolated after careful chromatography.

6

Carbene **8** was also generated in THF in the presence of TMEDA and an excess of LiCl by the decomposition (**7**) which was prepared, *in situ*, by the Horner reaction of 4-methylcyclohexanone with diethyl diazomethanephosphonate. The carbene was trapped with LiCl present in the resaction mixture as evidenced by the isolation of 16% of (4-methylcyclohexylidene)chloromethane (**1**) upon quenching with methanol (Scheme 3). This experiment demonstrates that carbenoid **5** can also exist in THF.

Finally, a lithium−halogen exchange reaction was carried out between (*R*)-(−)-(4-methylcyclohexylidene)bromomethane (**9**) and *tert*-butyllithium in *pentane* and in the presence of 1 equiv of TMEDA at −100 °C. The reaction mixture was carbonated at −70 °C to yield 4-methylcyclohexylideneacetic acid (**10**) in 78% yield. The acid was found to be racemic (Scheme 4). On the other hand, when the same reaction was repeated in THF in the presence of TMEDA optically active 4-methylcyclohexylideneacetic acid was isolated with 67% retention of configuration.

The results of this study are entirely different from those obtained previously in our laboratory. In ether solvents (THF, diethyl ether) (4-methylcyclohexylidene)-

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[1] (a) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546. (b) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035. (c) Walborsky, H. M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, *26*, 2743. (d) Rachon, J.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 7435.

[2] For a notable exception (retention of configuration) see ref 1d.

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[4] (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (b) Beak, P. *Chem. Rev.* **1984**, *84*, 471. (c) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356. (d) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (e) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.

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[6] (a) Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics*, **1988**, *7*, 552. (b) Tecle', B.; Ilsley, W. H.; Oliver, J. P. *Organometallics*, **1982**, *1*, 875. (c) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A. *J. Organomet. Chem.* **1988**, *339*, 7.

[7] Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448.

[8] (a) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, A.-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 5100.

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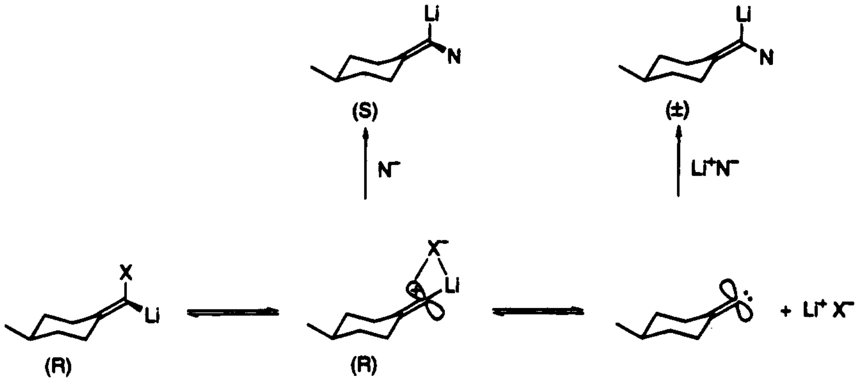
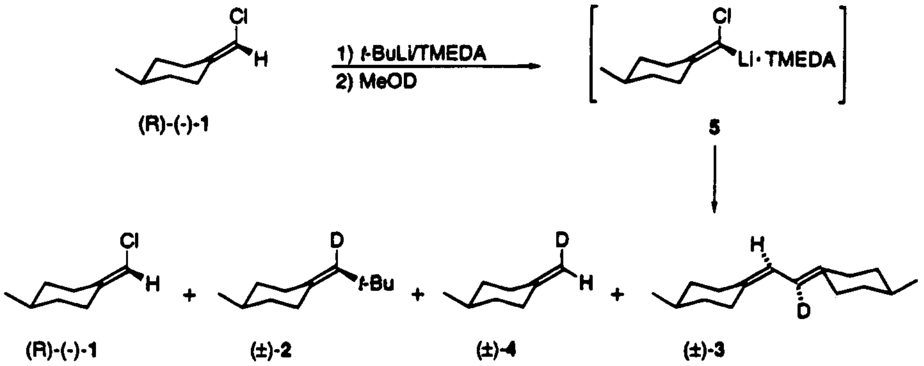
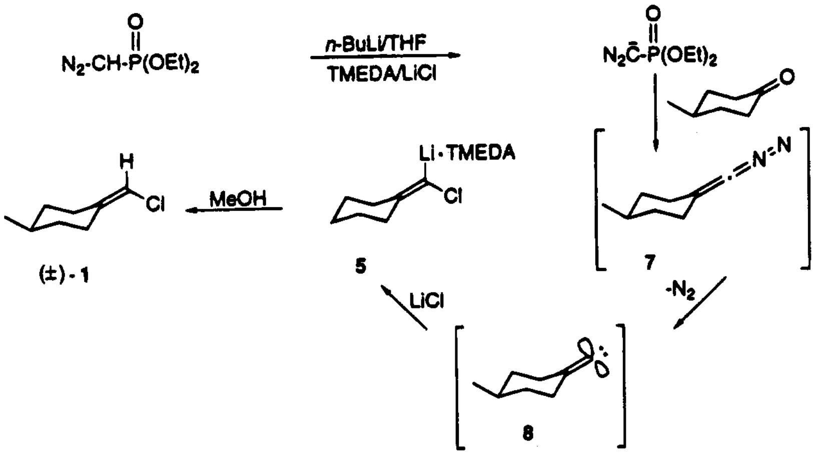
Scheme 1



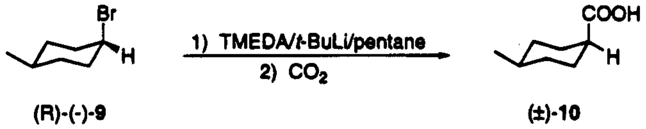
Scheme 2



Scheme 3



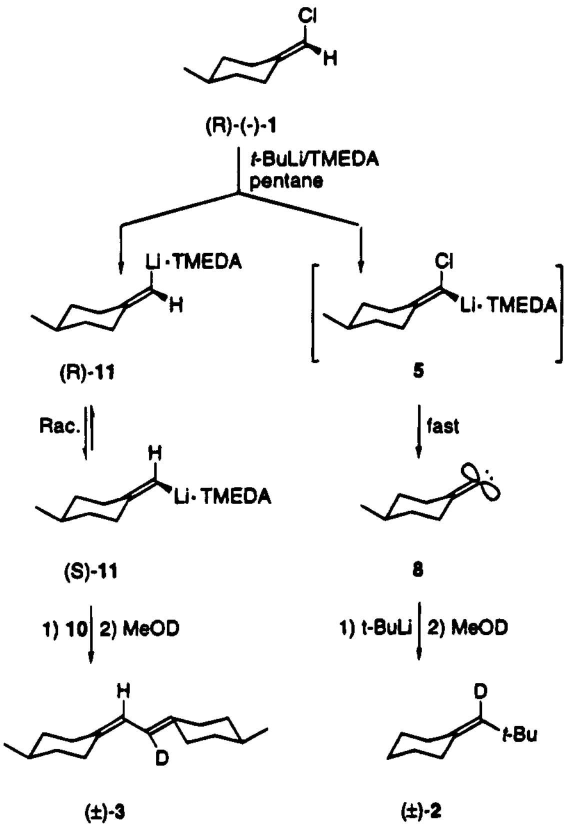
Scheme 4



chloromethane (**1**) is relatively easily metalated with *tert*-butyllithium at −75 °C and above.[1b] In pentane, however, when essentially no solvation is present, no reaction takes place even at room temperature. On the other hand, addition of 1 equiv of TMEDA, a strong solvating agent, leads to a fast reaction at low temperatures. The total unreactivity of (4-methylcyclohexylidene)chloromethane (**1**) toward *tert*-butyllithium in pentane is quite fortunate since it enables one to investigate the influence of TMEDA on the formation and reactivity of the intermediate carbenoid (**5**) and to compare it with solvating effects of common ether solvents. The analysis of product distribution leads to some very interesting conclusions.

First of all, use of 1 equiv of *tert*-butyllithium resulted in recovery of substantial amounts of starting material **1** as evidenced by the lack of deuterium incorporation upon quenching of the reaction with methanol-d_1. At the same time, formation of substitution product **2** and dimer **3** is observed which suggests that secondary reactions are very fast, in fact competitive with metalation (formation of **2** consumes *tert*-butyllithium, thus making it no longer available for metalation of the starting material **1**). Also of interest is the formation of **4**. Obviously, it was formed by deuterolysis of the corresponding vinyllithium reagent, which in turn must have been formed by a lithium−chlorine exchange reaction. This process has previously never been observed in this system using ether solvents, but under these conditions it seems to compete with the metalation reaction, especially at very low temperatures. Moreover, more *tert*-butyllithium is consumed in a side reaction (elimination) involving the

Scheme 5



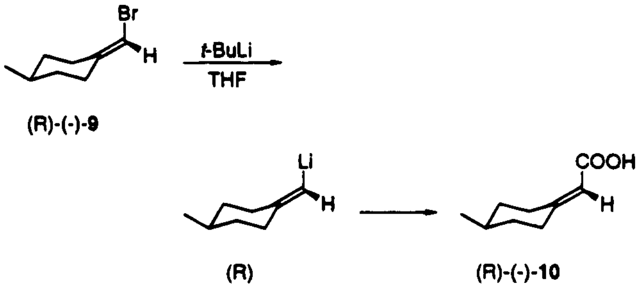
terg-butyl chloride that is formed in the lithium–chlorine exchange reaction.

Products **2** and **3** were isolated and found to be racemic, in contrast to the results previously obtained in ether solvents.[1] The fact that substitution product **2** is found to be racemic can be explained by assuming that TMEDA-solvated carbenoid **5** is not stable and racemizes quickly or almost immediately decomposes to give an achiral carbene **8** which is trapped by *tert*-butyllithium to give racemic **2** (Scheme 5).

Carbene formation was subsequently demonstrated by a trapping experiment with cyclohexene (isolation of the appropriate cyclopropane derivative, 7-(4-methylcyclohexylidene)bicyclo[4.1.0]heptane (**6**).

Even more interesting is the observation that dimer **3** is also racemic. When the reaction is conducted in ether solvents this compound is found to be 50% optically pure, since it is formed by coupling of optically pure vinyllithium with an achiral carbene. The result found in the current work implies that the vinyllithium reagent formed in pentane also racemizes in the presence of TMEDA. This was shown to be the case by performing a lithium–halogen exchange[9] with optically active (*R*)-(−)-(4-methylcyclohexylidene)bromomethane (**9**) and *tert*-butyllithium in the presence of TMEDA in pentane at −100 °C and allowing the reaction mixture to warm to −70 °C at which temperature it was carbonated. The (4-methylcyclohexylidene)acetic acid (**10**) isolated was found to be racemic. This vinyllithium reagent is known to be configurationally stable in THF between −70 and −20 °C[10] (Scheme 6).

Scheme 6



However, when the lithium–halogen exchange reaction in THF is conducted in the presence of TMEDA a partial racemization is observed. Complexation with TMEDA apparently decreases configurational stability of vinyllithium reagent **11** in THF. This observation prompted us to investigate the formation and reactions of TMEDA-coordinated carbenoid **5** in THF and compare the results with those obtained in pentane. In contrast to the results in pentane, this carbenoid seems to show some detectable stability in THF since we were able to generate it by a process reverse to its decomposition. The carbene **8** was produced in this reaction in an independent way, and it was trapped with LiCl in the presence of TMEDA to form the carbenoid. Quenching with MeOH gave **1** in 16% yield. With this result in mind we reacted optically active **1** with *tert*-butyllithium in THF in the presence of TMEDA. We were able to isolate racemic substitution product **2** (65%) accompanied by only traces of dimer **3**. The origin of racemization in this reaction is not entirely clear. Perhaps another mode of racemization different from the carbene pathway operates in this case. Configurational instability of the intermediate *tert*-butyl-substituted vinyllithium coordinated by TMEDA may also contribute.

The results of this study clearly indicate a profound effect of TMEDA on the kinetics of formation of the carbenoid **5** in pentane and on the nature of the carbon–lithium bond. The kinetic effect may be explained in terms of deaggregation of *tert*-butyllithium in pentane by TMEDA. The effect of TMEDA on lithium carbenoids and vinyllithium reagents needs a closer look and speaks to the nature of carbon–lithium bond in these reagents. TMEDA, being a bidentate ligand, binds tightly to lithium and "pulls it off" to the extent that a tight carbanion–lithium ion pair is formed. The latter is expected to have distinctively different properties from a "normal", predominantly covalent carbon–lithium bond. Since no chiral, electrophilic intermediate (Scheme 1) can be detected by stereochemical analysis of the reaction products this implies that carbenoid **5** does not undergo MAI due to the bonding of the lithium by TMEDA. Apparently, the change in carbon–lithium bond character leads to the fast collapse of the carbenoid and production of the achiral carbene **8**.

In the case of vinyllithium reagent **11** charge separation allows the carbanion to racemize via a rapid inversion of the carbanion through a linear sp-type transition state. This result was not unexpected. Early studies by

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(9) The halogen–lithium exchange reaction is known to proceed with complete retention of configuration: (a) Bailey, W. F.; Patricia, J. *J. Organomet. Chem.* **1988**, *352*, 1. (b) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 892. (c) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283. (d) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. (e) Letsinger, R. J. *J. Am. Chem. Soc.* **1950**, *72*, 4842.

(10) (a) Walborsky, H. M.; Banks, R. B. *Bull. Soc. Chim. Belg.* **1980**, *89*, 849. (b) Walborsky, H. M.; Banks, R. B.; Banks, L. A.; Duraisamy, M. *Organometallics* **1982**, *1*, 667. (c) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3252.

Letsinger[11] and Curtin[12] showed that even secondary alkyllithium reagents are capable of maintaining their configuration provided that a hydrocarbon solvent is used. Addition of small amounts of more polar solvent (like ether) would lead to a fast racemization. One might reasonably assume that the same principle should hold[13] for more configurationally stable organolithiums such as cyclopropyl[9c] and vinyllithium[10,14] reagents. The results reported in this work are consistant with such reasoning. We have also provided strong evidence that, in our system, TMEDA binds more strongly to lithium than bulk THF or diethyl ether.

Experimental Section

All reagents were purchased from Aldrich. All bulk solvents were distilled before use. TMEDA was dried by distillation in partial vacuum (about 100 Torr) from lithium aluminum hydride. All reactions were conducted under a dry argon atmosphere.

^{1}H NMR spectra were recorded at 300 MHz using CDCl$_3$ as solvent, with Me$_4$Si and CHCl$_3$ (7.27 ppm) as internal standards.

Optical rotations were measured at the 546.1-nm mercury line. The cell length was 0.17 dm, and the accuracy was ±0.002°.

High-resolution mass spectra were taken by GC/MS in the electron ionization mode at 70 eV.

Column chromatography was carried out by using silica gel (70–230 mesh) (Merck). GC analyses were performed 20% SE-30 as a stationary phase.

Attempted Reactions of (*R*)-(−)-(4-Methylcyclohexylidene)chloromethane (1) with *tert*-Butyllithium in Pentane. To the solution of (*R*)-(−)-(4-methylcyclohexylidene)chloromethane[1] (**1**) (2 mmol, 288 mg; ee = 93%) in pentane (15 mL) was added a solution of *tert*-butyllithium (2 mmol, 1.33 mL of 1.5 M solution in pentane) at, respectively, −70 °C, −10 °C, and rt. In each case the reaction mixture was stirred for 2 h, cautiously quenched with MeOD (5 mL), and washed with water (25 mL), and the organic phase was dried over MgSO$_4$. Upon removal of solvent the starting material was quantitatively recovered with no detectible deuterium incorporation by NMR: ^{1}H NMR δ 0.88 (d, J = 6 Hz, 3H), 0.90–1.02 (m, 2H), 1.40–1.60 (m, 1H), 1.68–1.80 (m, 3H), 1.90–2.05 (m, 2H), 2.18–2.28 (m, 1H), 2.78–2.88 (m, 1H), 5.75 (s, 1H).

Reactions of (*R*)-(−)-(4-Methylcyclohexylidene)chloromethane (1) with *tert*-Butyllithium in the Presence of TMEDA. The reaction described above was repeated in the presence of 1-equiv of TMEDA (2 mmol, 0.3 mL). Reaction conditions and yields of the products (based on GC and NMR analyses) are given in Table 1.

Isolation of 1-(4-Methylcyclohexylidene)-2,2-dimethylpropane (2) and 1,2-Bis(4-methylcyclohexylidene)ethane (3). The reaction was run in this case with 3 equiv of *tert*-butyllithium and 1 equiv of TMEDA at −100 °C and was quenched with MeOH (5 mL). The crude product was separated using column chromatography with pentane as an eluent. Samples of both **2** and **3** were isolated and identified by GC and NMR comparison with authentic materials.[1] Both products were found to be racemic. 1-(4-Methylcyclohexylidene)-2,2-dimethylpropane (**2**): isolated yield 100 mg, 30%; ^{1}H NMR δ 0.84 (d, J = 6 Hz, 3H), 0.88–1.12 (m, 2H), 1.05 (s, 9H), 1.40–1.54 (m, 1H), 1.64–1.80 (m, 3H), 1.88–2.05 (m, 2H), 2.69–2.79 (m, 1H), 5.10 (s, 1H). 1,2-Bis(4-methylcyclohexylidene)ethane (**3**): isolated yield 29 mg, 7%; ^{1}H NMR δ 0.88 (d, J = 6 Hz, 3H), 0.89 (d, J = 6 Hz, 3H), 0.8–2.30 (m, 16H), 2.7–2.85 (m, 2H), 5.98 (s, 2H).

Trapping Experiment. (*R*)-(−)-(4-methylcyclohexylidene)chloromethane[1] (**1**) (2 mmol, 288 mg; ee = 93%) was dissolved in 10 mL of pentane and 10 mL of cyclohexene. *tert*-Butyllithium (2 mmol, 1.33 mL of 1.5 M solution in pentane) and 1 equiv of TMEDA (2 mmol, 0.3 mL) were added and the solution kept at −100 °C for 1 h. The reaction mixture was quenched with MeOH (5 mL) and worked up as previously described. The crude reaction product was carefully separated by column chromatography (pentane) to give 8 mg, 2% yield, of 7-(4-methylcyclohexylidene)bicyclo[4.1.0]heptane (**6**): ^{1}H NMR δ 0.80–1.32 (m, SH), 0.90 and 0.91 (two doublets corresponding to diastereoisomers, 3H, J = 6 Hz), 1.45–1.58 (m, 1H), 1.60–1.82 (m, 6H), 1.92–2.11 (m, 2H), 2.37–2.48 (m, 2H); GC–MS analysis indicates the presence of two diastereoisomers, which gave virtually identical mass specra; HRMS calcd for C$_{14}$H$_{22}$ 190.172, found, 190.171.

Racemization of Chiral Vinyllithium Reagent in the Presence of TMEDA in Pentane. To a solution of (*R*)-(−)-(4-methylcyclohexylidene)bromomethane[10a] (**9**) (7 mmol, 1.35 g; ee = 93%) and TMEDA (7 mmol, 1.1 mL) in pentane (20 mL) was added, at −100 °C, a solution of *tert*-butyllithium in pentane (15 mmol, 10 mL of 1.5 M solution). The temperature was raised to −70 °C, and after additional 30 min at this temperature dry CO$_2$ was passed through the mixture for 1 h. The reaction mixture was then allowed to reach rt and then poured onto an ice–HCl mixture. The crude product was subsequently extracted with ether (3 × 50 mL). The ether phase was washed three times with 50 mL portions of 1 N NaOH, and the alkaline extracts were combined and washed with ether (50 mL). Finally, the alkaline extract was acidified with 6 N HCl to pH = 1. Extraction with ether (3 × 50 mL), followed by evaporation of the solvent, afforded essentially pure product, 4-methylcyclohexylideneacetic acid (**10**) (0.84 g, 78%) which was identified by comparison with an authentic sample[10] and NMR spectroscopy: ^{1}H NMR δ 0.90 (d, 3H, J = 6 Hz), 1.00–1.20 (m, 2H), 1.58–1.75 (m, 1H), 1.80–1.95 (m, 2H), 2.15–2.35 (m, 3H), 3.67–3.78 (m, 1H), 5.64 (s, 1H), 9.90 (s, broad, 1H). This product was found to be racemic.

Optical Stability of Chiral Vinyllithium Reagent in the Presence of TMEDA in THF. The reaction described above was repeated in THF instead of pentane and using (*S*)-(+)-(4-methylcyclohexylidene)bromomethane (**9**) of 85% optical purity. After 1 h at −70 °C the reaction mixture was carbonated and worked up. Essentially pure product (*S*)-(+)-(4-methylcyclohexylidene)acetic acid (identical with an authentic sample) was obtained in 71% yield. $[\alpha]^{25}_{\mathrm{Hg}}$ = +54.1 (c = 1, ethanol), 57% optically pure, which corresponds to 67% retention of configuration, taking into account optical purity of the starting material.

Independent Generation of the Carbene 10 and Its Trapping with LiCl/TMEDA in THF. *n*-Butyllithium (3.13 mL, 5 mmol of 1.6 M solution in hexanes) was added dropwise with stirring to the solution of diethyl diazomethanephosphonate[15] (5 mmol, 0.9 g), LiCl (25 mmol, 1.05 g), and TMEDA (5 mmol, 0.75 mL) in THF (25 mL) at −70 °C. After 15 min 4-methylcyclohexanone (5 mmol, 0.61 mL in 3 mL of THF) was injected, and the reaction mixture was stirred at this temperature for an additional 30 min. During that time slow evolution of nitrogen was observed. The reaction mixture was subsequently quenched with MeOH (2 mL), allowed to reach rt and was then diluted with pentane (50 mL) and washed with water, 5% HCl, and brine. The organic phase was dried with Na$_2$SO$_4$, and the solvents were removed under reduced pressure. Pure (4-methylcyclohexylidene)chloromethane was isolated by using column chromatography with pentane as an eluent: yield 109 mg, 16%; ^{1}H NMR δ 0.88 (d, J = 6 Hz, 3H), 0.90–1.02 (m, 2H), 1.40–1.60 (m, 1H), 1.68–1.80 (m, 3H), 1.90–2.05 (m, 2H), 2.18–2.28 (m, 1H), 2.78–2.88 (m, 1H), 5.75 (s, 1H). Identical with an authentic sample.

Reaction of (*S*)-(+)-(4-Methylcyclohexylidene)chloromethane with *tert*-Butyllithium in THF in the Presence of TMEDA. To the solution of (*S*)-(+)-(4-methylcyclohexylidene)chloromethane (**1**) (8.2 mmol, 1.18 g; ee = 87%) and TMEDA (8.2 mmol, 1.24 g) in THF (25 mL) was added a solution of *tert*-butyllithium (25 mmol, 17.8 mL of 1.5 M solution in pentane) at −70 °C. The reaction mixture was stirred at that temperature for 1 h and cautiously quenched with MeOD (5 mL). It was then washed with water, 5% HCl, and brine (25 mL),

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(11) Letsinger, R. L. *J. Am. Chem. Soc.* **1950**, *72*, 4842.

(12) Curtin, D. Y.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 1967.

(13) For a remarkable exception of higher configurational stability in a more strongly coordinating medium see: Reich, H. J.; Medina, M. A.; Bowe, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 11003.

(14) (a) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. (b) Panek, E. J.; Neff, B. L.; Chu, H.; Panek, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 3996. (c) Knorr, R.; Lattke, E. *Tetrahedron Lett.* **1977**, 3969. (d) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

(15) Seyferth, D.; Marmor, R. S.; Hilbert, P. *J. Org. Chem.* **1971**, *36*, 1379.

and the organic phase was dried over magnesium sulfate. The solvent was then removed under reduced pressure and the residue analyzed by NMR and TLC. No starting material could be detected, and only traces of the dimer **3** were found by NMR. The main product (4-methylcyclohexylidene)-1-deuterio-2,2-dimethylpropane (**2**) was isolated by column chromatography (elution with pentane): yield 890 mg, 65%, 90% deuterium incorporation by NMR; ^{1}H NMR δ 0.84 (d, $J = 6$ Hz, 3H), 0.88–1.12 (m, 2H), 1.05 (s, 9H), 1.40–1.54 (m, 1H), 1.64–1.80 (m, 3H), 1.88–2.05 (m, 2H), 2.69–2.79 (m, 1H), 5.10 (s, residual C-H). This compound was found to be racemic.

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