Reactions of β-trimethylstannylcyclohexanones with peracids: investigations into the stannyl-directed Baeyer–Villiger reaction

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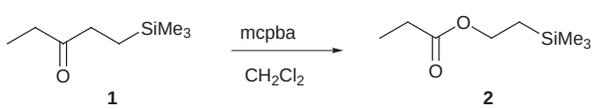
The trimethylstannyl substituent raises the migratory aptitude of a primary β-carbon to be above that of a not otherwise activated secondary or tertiary carbon. This is apparent from the exclusive formation of the alkene acids 9–11 from Baeyer–Villiger reaction of the β-stannyl cyclohexanones 3–5. The stereoelectronic requirements of the stannyl-directed Baeyer–Villiger reaction were investigated using the axial β-trimethylstannylcyclohexanone 20.

Introduction

The remarkable ability of Group IV metal substituents R_3M- (M = Si, Ge, Sn) to stabilise positive charge at the β position has been the subject of recent mechanistic and theoretical studies.[1–11] The stabilisation of β positive charge increases down the group Si < Ge ≪ Sn[6] and is related to the ability of the C–metal bond to donate electrons to the vacant carbenium ion p orbital by hyperconjugation (Scheme 1).

Scheme 1

For example, the silyl substituent has been shown experimentally and by theoretical calculations to stabilise 1° carbenium ions by a remarkable 38 kcal mol^{-1}, and 2° and 3° carbenium ions by 28 and 18 kcal mol^{-1} respectively.[10,11] The Group IV metal substituents, particularly silicon, have proved to be very useful for directing the course of organic reactions and rearrangements which involve carbenium ion (or partly developed carbenium ion) intermediates;[12–27] these reactions proceed in such a way that the positive charge ultimately resides at a position which is β to the metal substituent. Examples of silicon directed reactions include electrophilic addition to vinyl and allyl silanes,[21,22] silicon directed Nazarov[23–25] and Beckman rearrangements,[26] and silicon controlled Bamford–Stevens reaction.[27] In addition to these, β-silicon also enhances the migratory aptitude of groups in the Baeyer–Villiger reaction;[28,29] this is demonstrated by the reaction of 1-trimethylsilylpentan-3-one **1** (Scheme 2) with *m*-chloroperbenzoic



1 **2**

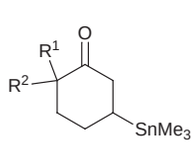
Scheme 2

acid (mcpba) which results in the exclusive formation of 2-trimethylsilylethyl propanoate **2**.

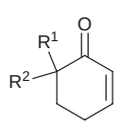
The migratory aptitude of groups in the Baeyer–Villiger reaction is related to the ability of the migrating group to bear a positive charge. The presence of β-silicon enhances this ability, and in fact the migratory aptitude of the primary carbon in $Me_3SiCH_2CH_2$ was shown to be between that of secondary and tertiary alkyl groups. Given that the trimethylstannyl substituent has been demonstrated to stabilise positive charge much more effectively than the trimethylsilyl substituent,[6] we were interested in the question of whether the trimethylstannyl substituent would exert a greater influence on the course of the Baeyer–Villiger reaction than silicon. To this end we chose to investigate the Baeyer–Villiger reaction of the β-trimethylstannyl cyclohexanone derivatives **3**, **4**, and **5**. The primary carbon activated by the β-stannyl substituent competes with a non-activated 1° carbon in **3**, a non-activated 2° carbon in **4**, and a non-activated 3° carbon in **5** as the migrating carbon in the ring expansion.

Results and discussion

The β-stannyl cyclohexanones **3**, **4** (as a *ca.* 1:1 mixture of diastereoisomers), and **5** were prepared by conjugate addition of trimethylstannyllithium to the corresponding cyclohex-2-enones[30] **6**, **7** and **8**. The enone **6** was commercially available, 6-



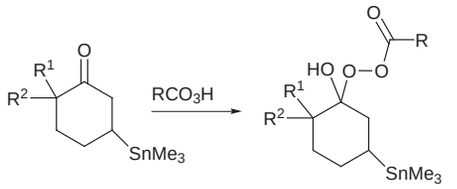
3 R^1, R^2 = H
4 R^1 = Me, R^2 = H
5 R^1 = Me, R^2 =Me



6 R^1, R^2 = H
7 R^1 = Me, R^2 = H
8 R^1 = Me, R^2 =Me

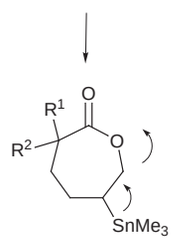
methylcyclohex-2-enone **7** was prepared by the method of Stotter[31] and 6,6-dimethylcyclohex-2-enone **8** was prepared in three steps from 2-methylcyclohexanone by modified literature procedures.[32–34] Treatment of all three β-stannylcyclohexanones (Scheme 3) with buffered peracids (mcpba for **3** and **4**, and *in situ* generated peracetic acid for **5**) gave rise to a single type of product, the acyclic alkene acids **9**–**11**.

One rationale for the formation of these acids is outlined in Scheme 3 and involves the stannyl assisted heterolysis of the initially formed stannyl-lactones **12**–**14**. The formation of the lactones **12–14** from the Baeyer–Villiger reaction of the ketones **3–5** implies that the 1° carbon activated by the β-stannyl substituent migrates preferentially during the breakdown of the tetrahedral intermediates **15**–**17** in all three substrates. In the case of **5** this result demonstrates that the β-trimethylstannyl substituent raises the migratory ability of the 1° carbon to be above that of a not otherwise activated 3° carbon. It is plausible that the stannyl lactones **12–14** are not involved in the formation of the alkene acids **9–11** but rather they might have arisen by a concerted breakdown (Grob fragmentation)[35] of the tetrahedral intermediates **15–17** (Scheme 4).

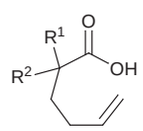


3 R^1, R^2 = H
4 R^1 = H, R^2 = Me
5 R^1, R^2 = Me

15 R^1, R^2 = H
16 R^1 = H, R^2 = Me
17 R^1, R^2 = Me

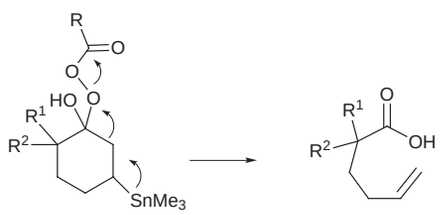


12 R^1, R^2 = H
13 R^1 = H, R^2 = Me
14 R^1, R^2 = Me



9 R^1, R^2 = H
10 R^1 = H, R^2 = Me
11 R^1, R^2 = Me

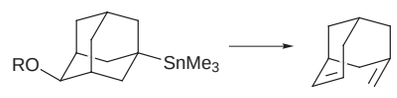
Scheme 3



15-17 **9-11**

Scheme 4

The tetrahedral intermediates **15**–**17** can readily achieve the correct geometry for the concerted breakdown shown in Scheme 3; similar types of fragmented products are formed in high yield in the solvolysis of the δ-trimethylstannyl esters **18**[36] and **19**[37] (Schemes 5 and 6). Whether the alkene products



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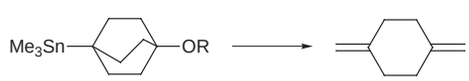
Scheme 5



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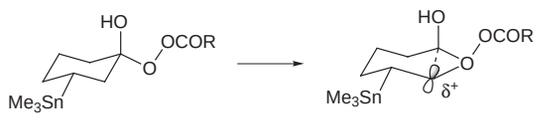
Scheme 6

9–**11** arise from a stepwise breakdown *via* the lactones **12**–**14** or concerted breakdown of the tetrahedral intermediates, either of these two mechanisms requires the preferential participation of the C–C bond activated by the β-stannyl substituent in all cases.

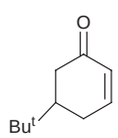
We were interested to see whether the ability of the trimethylstannyl substituent to promote the migration of the β-carbon in the Baeyer–Villiger reaction is dependent upon stereochemistry. The migrating carbon which develops partial carbenium ion character during the migration will benefit from stabilisation by hyperconjugation from the β-trimethylstannyl substituent, provided the Sn substituent is antiperiplanar to it (Scheme 7).



Scheme 7

This requires that the Sn substituent is in the equatorial position; the three substrates **3**, **4** and **5** all satisfy this requirement in their most stable conformations.

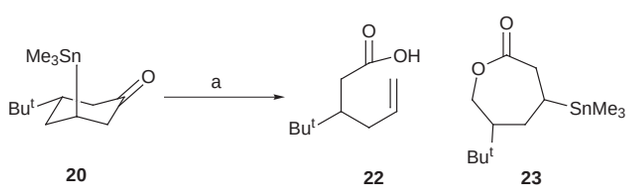
We therefore chose to prepare the β-stannylcyclohexanone derivative **20** in which the trimethylstannyl substituent is fixed into the axial conformation;† if the trimethylstannyl substituent remains axially oriented throughout the Baeyer–Villiger reaction then the C_β-carbon would not be expected to be activated towards migration, and perhaps a mixture of products might result from competing migration of either of the two C–C bonds. The cyclohexanone **20** was prepared by conjugate addition of trimethylstannyllithium to 5-*tert*-butylcyclohex-2-enone **21** which was prepared according to



21

literature procedures.[38] The *trans* stereochemistry of **20** was predicted from the expected axial attack on the cyclohexenone **21** by the trimethylstannyl anion,[39] and is supported by the ^{13}C NMR spectrum. The relevant signal in the ^{13}C NMR spectrum of **20** is the δ value for trimethylstannyl methyl carbons. For an equatorial cyclohexyl trimethylstannyl substituent these resonate in the range −11 to −12 ppm,[39] whereas an axial trimethylstannyl substituent has a resonance in the range −9 to −10 ppm. The ^{13}C NMR spectrum showed a single resonance at −9.98 which is consistent with the assigned structure.

The axial β-stannyl ketone **20** was then subjected to the Baeyer–Villiger reaction by treatment with *in situ* generated peracetic acid for 1 week; this resulted in the exclusive formation of 3-*tert*-butylhex-5-enoic acid **22** with no evidence for the lactone **23** (Scheme 8), suggesting that the axial trimethylstan-



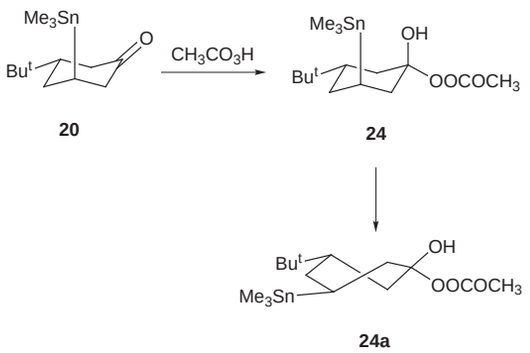
20 **22** **23**

Scheme 8 *Reagents and conditions*: a, CH_3CO_2H, CH_3CO_2K, H_2O_2

† The relative conformational *A* values for a *tert*-butyl substituent and a trimethylstannyl substituent are *ca*. 4.9 and 1.0 kcal mol^{-1} respectively.[42] This ensures a strong preference for the conformation having the trimethylstannyl substituent axial.

nyl substituent in **20** also raises the migratory aptitude of the β-carbon in this reaction.

This result was contrary to our predictions stated above but can be rationalised according to Scheme 9. Addition



Scheme 9

of peracetic acid from the least hindered face of **20** would give the tetrahedral intermediate **24** which suffers from a severe *syn*-1,3-diaxial interaction between the trimethylstannyl substituent and the hydroxy substituent; this steric interaction, however, can be relieved by a conformational change into the twist boat conformation **24a**. Importantly, in the twist boat conformation **24a** the trimethylstannyl substituent is now antiperiplanar to the C–C bond and hence, according to the above analysis, can activate it towards migration in the following ring expansion, or alternatively Grob fragmentation. Thus it appears that this derivative is too flexible to demonstrate the stereoelectronic requirements (if any) for the stannyl-directed Baeyer–Villiger rearrangement.

The observation that the trimethylstannyl substituent directs the course of the Baeyer–Villiger reaction raises the question as to whether it also accelerates this reaction. To answer this question the progress of the Baeyer–Villiger reaction of the simple β-stannylcyclohexanone **3** was monitored using ^{1}H and ^{13}C NMR and compared with cyclohexanone under identical reaction conditions. It was found that the β-stannylcyclohexanone **3** reacted faster than cyclohexanone, but only by a factor of *ca.* 2.5:1. If the reaction rate is simply determined by the rate of breakdown of the tetrahedral intermediate **15** then these relative rates are not large enough (even allowing for a statistical factor of 2 in cyclohexanone) to explain the exclusive migration of the carbon β to the stannyl substituent in the breakdown of the tetrahedral intermediate **15**. It seems plausible to suggest that although the trimethylstannyl substituent accelerates the breakdown of the tetrahedral intermediate **15**, it may actually hinder its formation from the ketone **3**, by stabilising the ketone **3**. We make this suggestion based on evidence in the literature which suggests that β-trimethylstannyl substituents interact with the carbonyl group in **3** and other related cyclohexanones, perhaps by a percaudel interaction between the σ_{Sn-C} bonding orbital with the π^*_{C-O} orbital.[39–41] Such an interaction would decrease the electrophilicity of the ketone carbonyl in **3** and therefore hinder the formation of the tetrahedral intermediate **15** in Scheme 3; this appears to partially offset any accelerative effects that the trimethylstannyl substituent has on the breakdown of this intermediate. Qualitative evidence that the ketone carbonyl in **3** is less reactive than cyclohexanone towards nucleophilic addition is provided by the observation that the β-stannylcyclohexanone **3** is completely inert to the weakly nucleophilic reagent diazomethane in diethyl ether at room temperature for a week, whereas under the same conditions cyclohexanone readily reacts to give a mixture of epoxide and ring expanded ketones.

Experimental

General experimental details are described elsewhere.[40] 6-Methylcyclohex-2-enone,[31] 5-*tert*-butylcyclohex-2-enone **21**,[38] 3-trimethylstannylcyclohexanone **3**,[30] and a *ca.* 4:1 mixture of 2,2-dimethyl- and 2,6-dimethylcyclohexanone were prepared by a literature procedure.[32] 6,6-Dimethylcyclohex-2-enone **8** was prepared from 2,2-dimethylcyclohexanone by bromination with bromine in chloroform followed by dehydrobromination as reported.[34] Chemical shifts are given in ppm and *J* values in Hz.

Separation of 2,2-dimethyl- and 2,6-dimethylcyclohexanone, preparation of pure 2,2-dimethylcyclohex-2-enone and conversion to 6,6-dimethylcyclohex-2-enone

A mixture of 2,2-dimethyl- and 2,6-dimethylcyclohexanone (35.6 g, 0.28 mol) was stirred in methanol (70 ml) and treated with a solution of semicarbazide hydrochloride trihydrate (48.5 g, 0.29 mol) in water (70 ml). The solution was stirred vigorously for 30 min and the resulting white precipitate filtered and washed with water. Recrystallisation from methanol gave the semicarbazone derivative of 2,2-dimethylcyclohexanone (34.0 g, 71%), mp 189–191 °C. $\delta_C(CDCl_3)$ 159.04, 158.50, 41.05, 38.65, 26.92, 26.22, 22.62, 21.47. The semicarbazone (34.0 g, 0.20 mol) and phthalic anhydride (28.3 g, 0.19 mol) were added to water (200 ml) and methanol (60 ml). The resulting mixture was heated and the steam distillate collected and extracted with ether (3 × 100 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated down to pure 2,2-dimethylcyclohexanone as a clear oil (20.8 g, 82%). $\delta_H(CDCl_3)$ 2.18 (2H, t, *J* 7.5), 1.73–1.49 (6H, m), 0.96 (6H, s). $\delta_C(CDCl_3)$ 205.6, 44.94, 40.86, 38.04, 27.35, 24.93, 21.18.

General procedure for preparation of 4, 5 and 20 by conjugate addition of trimethylstannyllithium to 6-methylcyclohex-2-enone 7, 6,6-dimethylcyclohex-2-enone 8 and 5-*tert*-butylcyclohex-2-enone 21

A solution of trimethyltin chloride (58 mmol) in anhydrous tetrahydrofuran (50 ml) was treated with excess lithium metal. After stirring overnight at room temperature the green solution was cannulated into a dry flask under nitrogen and then treated with a solution of the enone (52 mmol) in anhydrous tetrahydrofuran (20 ml). The resulting mixture was stirred for 4 h, then diluted with water (20 ml), and extracted with ether (3 × 50 ml). The combined ether extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the β-stannyl ketone as a crude oil which was purified by short path distillation under vacuum.

cis- and *trans*-2-Methyl-5-trimethylstannylcyclohexanone (*ca.* 1:1) 4

From 6-methylcyclohex-2-enone (78%). $\delta_C(CDCl_3)$ (aliphatic) 45.68, 45.34, 44.79, 44.15, 40.63, 36.05, 29.85, 27.38, 26.25, 25.38, 15.22, 14.56, −10.01 (Me_3Sn *cis* isomer), −11.91 (Me_3Sn *trans* isomer). $\delta_H(CDCl_3)$ 2.5–2.0 (3H, m), 2.0–1.4 (5H, m), 0.94 (d, *J* 8.6, Me), 0.86 (d, *J* 8, Me), −0.05 (9H).

2,2-Dimethyl-5-trimethylstannylcyclohexanone 5

From 6,6-dimethylcyclohex-2-enone (90%). $\delta_C(CDCl_3)$ 216.3, 45.3, 44.6, 42.0, 25.83, 25.81, 25.5, 24.8, −11.7. $\delta_H(CDCl_3)$ 2.5–2.1 (2H, m), 1.8–1.4 (4H, m), 1.03 (3H, s), 0.96 (3H, s), −0.01 (9H, s).

trans-5-*tert*-Butyl-3-trimethylstannylcyclohexanone 20

From 5-*tert*-butylcyclohex-2-enone (50%). $\delta_C(CDCl_3)$ 213, 48.6, 44.8, 43.2, 32.8, 29.8, 27.3, 27.2, 22.6, −10.05. $\delta_H(CDCl_3)$ 2.65–2.4 (4H, m), 1.95–1.8 (1H, m), 1.6–1.4 (3H, m), 0.65 (9H, s), 0.05 (9H, s).

Baeyer–Villiger reaction of 3-trimethylstannylcyclohexanone 3

A mixture of ketone **3** (3 g, 17 mmol), dichloromethane (60 ml) and saturated sodium bicarbonate (60 ml) was stirred vigorously on an ice bath and treated with *m*-chloroperoxybenzoic acid (70%) (5.5 g). The resulting mixture was stirred at room temperature for 4 h. The solution was diluted with water (200 ml) and the organic layer separated off, dried ($MgSO_4$) and evaporated down to an oily solid which consisted of starting ketone **3** (*ca*. 6 g), unreacted *m*-chloroperoxybenzoic acid and hexamethylditin oxide, $\delta_C(CDCl_3)$ −6.0, δ_H 0.6. The bicarbonate layer was neutralised with HCl and extracted with dichloromethane (2 × 50 ml), the combined organic extracts were dried ($MgSO_4$) and evaporated down to give a mixture of *m*-chlorobenzoic acid and hex-5-enoic acid **9** in the ratio *ca*. 2.5:1 (4 g). For **9** $\delta_C(CDCl_3)$ 179.3, 137.5, 115.2, 33.5, 32.9, 24.01. $\delta_H(CDCl_3)$ 5.8 (1H, m), 5.1–5.0 (2H, m), 2.41 (2H, t, *J* 8), 2.12 (2H, t, *J* 8), 1.77 (2H, tt, *J* 8, 8).

Baeyer–Villiger reaction of *cis*- and *trans*-2-methyl-5-trimethylstannylcyclohexanone (*ca*. 1:1) 4

Subjection of the isomeric mixture **4** to the same reaction conditions as for **3** above similarly gave starting material **4** and hexamethylditin oxide in the neutral layer, and 2-methylhex-5-enoic acid **10**. $\delta_H(CDCl_3)$ 5.75 (1H, m), 5.05 (1H, d, *J* 15), 4.95 (1H, d, *J* 9), 2.44 (1H, m), 2.08 (2H, m), 1.8 (2H, m), 1.5 (2H, m), 1.17 (3H, d, *J* 7.8).

Baeyer–Villiger reaction of 2,2-dimethyl-5-trimethylstannylcyclohexanone 5

A solution of ketone **5** (0.5 g, 1.7 mmol) was stirred in acetic acid (2.0 ml) saturated with potassium acetate (resulting pH 8.5–9.0). The mixture was treated with 30% aqueous H_2O_2 (1.87 mmol) and stirred at room temperature for a week. The resulting mixture was extracted with ether (2 × 30 ml), the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The resulting oil was shown to be a mixture of starting material **5** (*ca*. 40%) and 2,2-dimethylhex-5-enoic acid (*ca*. 60%) **11** and hexamethylditin oxide; these were separated by a base extraction followed by neutralisation giving pure **11** (115 mg), $\delta_C(CDCl_3)$ 182.45, 138.18, 114.23, 41.65, 39.51, 29.15, 24.79. $\delta_H(CDCl_3)$ 5.7 (1H, m), 4.92 (1H, d, *J* 15), 4.82 (1H, d, *J* 9 Hz), 1.97 (2H, m), 1.55 (2H, m), 1.13 (6H, s).

Baeyer–Villiger reaction of *trans*-5-*tert*-butyl-3-trimethylstannylcyclohexanone 20

A solution of **20** (0.3 g, 0.94 mmol) was stirred in acetic acid (2.0 ml) saturated with potassium acetate (resulting pH 8.5–9.0). The mixture was treated with 30% aqueous H_2O_2 (1.32 mmol) and stirred at room temperature for a week. The resulting mixture was extracted with ether (3 × 20 ml), the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield 3-*tert*-butylhex-5-enoic acid (80%). $\delta_C(CDCl_3)$ 180.0, 146.55, 124.99, 44.10, 43.46, 42.07, 36.05. $\delta_H(CDCl_3)$ 5.77 (1H, m), 5.10–4.9 (2H, m), 2.4–2.3 (2H, m), 2.2–2.0 (2H, m), 0.85 (9H, s).

Baeyer–Villiger reactions of 3-stannylcyclohexanone 3 and cyclohexanone, monitored by NMR spectroscopy

Solutions of the ketones (0.18 mmol) were prepared in deuterated chloroform (0.5 ml) and treated with one equivalent of *m*-chloroperoxybenzoic acid (98%) and maintained at room temperature; progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy. After 3.5 h the compositions of the solutions were determined. The 3-trimethylstannylcyclohexanone **3** reaction mixture consisted of hex-5-enoic acid **9** (78%) and starting ketone **3** (22%) while the cyclohexanone reaction mixture consisted of 30% of caprolactone in addition to unchanged cyclohexanone (70%).

Acknowledgements

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References

1 E. Colvin, in *Silicon in Organic Synthesis*, Butterworth's Monographs in Chemistry, Butterworth, Boston, 1981.
2 J. M. White, *Aust. J. Chem.*, 1995, **48**, 1227.
3 J. B. Lambert, *Tetrahedron*, 1990, **46**, 2677.
4 A. N. Egorochkin, *Russ. Chem. Rev.*, 1984, **53**, 445.
5 J. B. Lambert, G. Wang, R. B. Finzel and D. H. Teramura, *J. Am. Chem. Soc.*, 1987, **109**, 7838.
6 J. B. Lambert, G. Wang and D. H. Teramura, *J. Org. Chem.*, 1988, **53**, 5422.
7 J. B. Lambert, R. W. Embledge and S. Malany, *J. Am. Chem. Soc.*, 1993, **115**, 1317.
8 J. B. Lambert and E. C. Chelius, *J. Am. Chem. Soc.*, 1990, **112**, 8120.
9 J. B. Lambert and X. Zhao, *J. Organomet. Chem.*, 1996, **521**, 203.
10 S. G. Wierschke, J. Chandrasekhai and W. L. Jorgensen, *J. Am. Chem. Soc*., 1985, **107**, 1496.
11 M. R. Ibrahim and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1989, **111**, 819.
12 P. S. Furth and J. R. Hwu, *J. Org. Chem.*, 1989, **54**, 3404.
13 I. Fleming and A. Pearce, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 251.
14 I. Fleming and J. P. Michael, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 1549.
15 K. Tanino, Y. Hatanaka and I. Kuwajima, *Chem. Lett.*, 1987, 385.
16 R. T. Taylor and L. A. Paquette, *J. Org. Chem.*, 1978, **43**, 242.
17 J. R. Hwu and J. M. Wetzel, *J. Org. Chem.*, 1992, **57**, 922.
18 I. Fleming and J. P. Michael, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 245.
19 I. Fleming and S. K. Patel, *Tetrahedron Lett.*, 1981, **22**, 2321.
20 A. J. Green, Y. L. Kuan and J. M. White, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2023.
21 A. Hosomi, *Acc. Chem. Res.*, 1988, **21**, 200.
22 T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.
23 S. E. Denmark and R.-C. Klix, *Tetrahedron*, 1988, **44**, 4043.
24 S. E. Denmark and T. K. Jones, *J. Am. Chem. Soc.*, 1982, **104**, 2642.
25 D. A. Smith and C. W. Ulmer, *J. Org. Chem.*, 1993, **58**, 4118.
26 P. F. Hudrlik, M. A. Waugh and A. M. Hudrlik, *J. Organomet. Chem.*, 1984, **271**, 69.
27 T. K. Sarkar and B. K. Ghorai, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1184.
28 P. F. Hudrlik, A. M. Hudrlik, G. Nagendrappa, T. Yimena, E. T. Zellers and E. Chin, *J. Am. Chem. Soc.*, 1980, **102**, 6894.
29 T. Aida, M. Asaoka, S. Sonoda and H. Takei, *Heterocycles*, 1993, **36**, 427.
30 J. B. Lambert, L. A. Salvador and J.-H. So, *Organometallics*, 1993, **12**, 697.
31 R. L. Stotter and K. A. Hill, *J. Org. Chem.*, 1973, **38**, 2576.
32 W. J. Bailey and M. Madoff, *J. Am. Chem. Soc.*, 1954, **76**, 2707.
33 A. E. Gillam and T. F. West, *J. Chem. Soc.*, 1945, 95.
34 E. N. Marvell and E. Magoon, *J. Am. Chem. Soc.*, 1955, **77**, 2542.
35 R. Hofmann, *Acc. Chem. Res.*, 1971, **4**, 1.
36 W. Adcock, J. Coope, V. J. Shiner, Jr. and N. A. Trout, *J. Org. Chem.*, 1990, **55**, 1411.
37 W. Adcock, A. Krystic, P. J. Duggan, V. J. Shiner, J. Coope and M. W. Ensinger, *J. Am. Chem. Soc.*, 1990, **112**, 3140.
38 K. N. Campbell, *J. Am. Chem. Soc.*, 1937, **59**, 1980.
39 G. Wickham, H. A. Olszowy and W. Kitching, *J. Org. Chem.*, 1982, **47**, 3788.
40 A. J. Green, T. Pigdon, J. M. White and J. Yamen, *J. Org. Chem.*, 1998, in the press.
41 J. J. Hudec, *J. Chem. Soc.*, *Perkin Trans. 1*, 1975, 1020.
42 E. L. Eliel and S. H. Wilen, in *Stereochemistry of Carbon Compounds*, Wiley-Interscience, New York, 1993.

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