

Table 2. IR Bands of $\nu(\text{Sn-C})$ and $\nu(\text{Sn-S})$ Modes

Compounds	$\nu(\text{Sn-C})$	$\nu(\text{Sn-S})$
$(t\text{-Bu})_2\text{Sn} \cdot \text{ebdtc}^{22}$	507(m), 545(m)	345(m), 390(s)
$\text{Me}_2\text{SnCl}_2^{20}$	524(s), 563(s)	—
$\text{Me}_2\text{Sn} \cdot (\text{dtc})_2^{22}$	559(m)	367(s)
$\text{Me}_2\text{Sn} \cdot \text{p-pbdtc}$	510(s), 543(s)	340(s), 360(sh)
$\text{Me}_2\text{Sn} \cdot \text{m-pbdtc}$	510(sh), 540(s)	310(sh), 325(s)

The spectral data in the table indicate that the methyl groups in both of $\text{Me}_2\text{Sn} \cdot \text{pbdtc}$ complexes are in *cis*-configuration. Furthermore, it is very interesting to compare the $\nu(\text{Sn-S})$ modes of the pbdtc complexes with those of other known compounds in the table. For instance, $\text{Me}_2\text{Sn}(\text{dtc})_2^{22}$ which is known to have an octahedral coordination with the methyl groups in trans configuration exhibits only one $\nu(\text{Sn-S})$ band whereas two $\nu(\text{Sn-S})$ bands are observed for the ebdtc compound in which the tin atom in a trigonal bipyramidal coordination with one chelated and one monodentate dithiocarbamate groups.

It is suggested from such spectral comparisons that the local geometry of the tin metal in the $\text{Me}_2\text{Sn} \cdot \text{pbdtc}$ complexes is probably not an octahedral but trigonal bipyramidal or tetrahedral structure. For more decisive conclusion, extensive study on the IR spectra of these compounds is necessary.

The H-NMR spectra of organotin(IV)·pbdtc complexes exhibit three kinds of proton resonances: N-H proton resonance appears as a singlet at $\delta = 9.7 - 9.9$ ppm, phenyl protons as a multiplet at round $\delta = 6.5 - 7.7$ ppm and aliphatic C-H in the range of $\delta = 0.8 - 2.1$ ppm. Their integrations are consistent with the proposed compositions of the complexes, but none of the NMR data could be correlated with their structural aspects.

References

1. E.J. Kupchik and P.J. Calabretta, *Inorg. Chem.*, **4**, 975

- (1965).
2. T. Kimura, N. Yashoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **45**, 1649 (1972).
3. J.C. May, D. Detridis, and C. Curran, *Inorg. Chim. Acta*, **5**, 551 (1971).
4. G.M. Sheldrick and W.S. Sheldrick, *J. Chem. Soc. (A)*, 490 (1970).
5. G.M. Sheldrick and W.S. Sheldrick, *J. Chem. Soc. (A)*, 493 (1970).
6. K. Furue, T. Kimura, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **43**, 1661 (1970).
7. O.S. Jung, Y.S. Sohn, and J.A. Ibers, *Inorg. Chem.*, **25**, 2273 (1986).
8. N. Kobayashi, A. Osawa, H. Kimoto, Y. Hayashi, K. Shimizu, and T. Fujisawa, *J. Polymer Sci.*, **15**, 39 (1977).
9. G.J. M. Van der Kerk, C.W. Pluygers, and G. de Vries, *Rec. Trav. Chim.*, **74**, 1262 (1955).
10. C.B. Luginbuhl, U.S. Pat. 2,690,448 (Sept. 28, 1954).
11. C.B. Lyon, J.W. Nemec, and V.H. Unger, U.S. Pat. 3,379,610 (Apr. 23, 1968).
12. J. Lehurean, U.S. Pat. 3,523,960 (Aug. 11, 1970).
13. K. Van den Boogaart and M.N. Louis, U.S. Pat. 3,869,486 (Mar. 4, 1975).
14. F. Bonati and R. Ugo, *J. Organomet. Chem.*, **10**, 257 (1967).
15. M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).
16. T.N. Srivastava, V. Kumar, and R.B. Rastogi, *J. Inorg. Nucl. Chem.*, **40**, 399 (1978).
17. C.P. Sharma, N. Kumar, M.C. Khandpal, S. Chandra, and V.G. Bhide, *J. Inorg. Nucl. Chem.*, **43**, 923 (1981).
18. C.P. Sharma, N. Kumar, and S. Chandra, *J. Indian Chem. Soc.*, 434 (1983).
19. R. Kellner, G. St. Nikolov, and N. Trendafilova, *Inorg. Chim. Acta*, **84**, 233 (1984).
20. W.F. Edgell and C.H. Ward, *J. Mol. Spect.*, **8**, 343 (1962).
21. R. Okawara and M. Wada, *Adv. Organomet. Chem.*, **5**, 137C (1967).
22. O.S. Jung and Y.S. Sohn, Unpublished results.

Reaction of Lithium 2-Pyridyloxyalkylcuprates Having Improved Thermal Stability with Acid Chlorides and α,β -Unsaturated Ketones

Phil Ho Lee, Sang Chul Shim, and Sunggak Kim*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received July 10, 1986

A new heterocuprate containing 2-pyridyloxy ligand, lithium 2-pyridyloxy-n-butylcuprate, has shown improved thermal stability and it reacts with acid chlorides to afford the corresponding ketones in high yields. Similarly, it can be effectively utilized in conjugate addition reactions of α,β -unsaturated ketones. Of synthetic significance is that the complete utilization of n-butyl group in lithium 2-pyridyloxy-n-butylcuprate has been observed.

Introduction

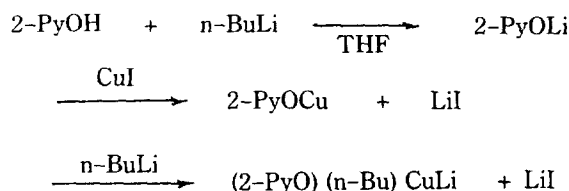
Since organocuprates are capable of effecting transforma-

tions difficult to accomplish effectively with other conventional methods, they have become very popular among synthetic organic chemists for carbon-carbon bond formation reactions

via conjugate addition reactions and substitution reactions.^{1,2} Moreover, of synthetic importance is that organocuprates often react with various substrates in a highly stereoselective, regioselective, and chemoselective manner. However, two major limitations involving the use of organocuprates in synthetic applications have been thermal instability and the need of a large excess of the reagent. In order to circumvent two major limitations of organocuprates, several new types of organocuprates with greatly improved thermal stability and reactivity have been recently developed.³⁻⁶ We wish to report thermal stability of a new heterocuprate containing 2-pyridyloxy ligand and the reaction with acid chlorides and α,β -unsaturated ketones.

Results and Discussion

Preparation of Lithium 2-Pyridyloxy-*n*-butylcuprate and its Stability. We have chosen lithium 2-pyridyloxy-*n*-butylcuprate as a model compound among lithium 2-pyridyloxyalkylcuprates in our study and its preparation is shown in Scheme 1. Treatment of 2-hydroxypyridine (2-PyOH) in tetrahydrofuran with 1 equiv of *n*-butyllithium in hexane at 0°C followed by the addition of 1 equiv of cuprous iodide produced 2-pyridyloxycopper species which were cooled to -30°C and then treated with 1 equiv of *n*-butyllithium in hexane. After being stirred at -30°C for 10 min, lithium 2-pyridyloxy-*n*-butylcuprate was obtained as a black suspended solution.



Scheme 1.

For the purpose of comparing the thermal stability of lithium 2-pyridyloxy-*n*-butylcuprate with other previously known organocuprates, we have chosen the previously known procedure.^{3,7} Thus, lithium 2-pyridyloxy-*n*-butylcuprate prepared as described as above was kept at -50°C, 0°C, and 25°C and then after 30 min at each temperature was quenched with an excess amount (3 equiv) of highly reactive benzoyl chloride. The isolated yields of *n*-butyl phenyl ketone were 87%, 86%, and 54%, after being kept for 30 min at -50°C, 0°C and 25°C, respectively, indicating our reagent might be slowly decomposed to some extent at 25°C. Bertz studied relative thermal stability of a variety of structurally different organocuprates and developed several new heterocuprates such as diphenylphosphidocopper and dicyclohexylamidocopper with greater thermal stability than previously known heterocuprates.⁷ For instance, reaction of lithium diphenylphosphido-*n*-butylcuprate with a large excess of benzoyl chloride after 30 min at -50°C, 0°C, and 25°C affords *n*-butyl phenyl ketone in 90%, 99%, and 95%, respectively, whereas the yields of *n*-butyl phenyl ketone using lithium phenylthio-*n*-butylcuprate⁸ under the same reaction condition is 100%, 19%, and 0%, respectively.⁷ Therefore, lithium

Table 1. Preparation of Ketones from Acid Chlorides with (2-PyO)(*n*-Bu)CuLi^a

acid chloride	temp, °C	yield, % ^b
CH ₃ (CH ₂) ₆ COCl	0	76
c-C ₆ H ₁₁ COCl ^c	-78	84
	0	83
(CH ₃) ₂ CHCOCl	0	73
adamantanecarbonyl chloride	0	93
mesitoyl chloride	0	98
Br(CH ₂) ₅ COCl	-78	84
	0	87
CH ₂ =CH(CH ₂) ₆ COCl	0	98
CH ₃ OOCH(CH ₂) ₆ COCl	0	84

^a The reaction was carried out with 1.2 equiv of (2-PyO)(*n*-Bu)CuLi in THF for 5 min. ^b Isolated yields. ^c c-C₆H₁₁ indicates cyclohexyl group.

2-pyridyloxy-*n*-butylcuprate is thermally less stable than Bertz's new heterocuprates but it has much greater thermal stability than lithium phenylthio-*n*-butylcuprate.

Reaction with Acid Chlorides. Although many methods on the synthesis of ketones from organometallic reagents and carboxylic acid derivatives are available,⁹ the use of organocuprates is the most convenient and efficient in terms of high yield, the mildness of the reaction conditions, and functional group selectivity. However, convenient ketone synthesis from lithium dialkylcuprates and acid chlorides requires the use of a large excess of lithium dialkylcuprates to obtain optimum yields.¹⁰ Therefore, several improved procedures for complete utilization of alkyl groups of organocuprates have been developed by modifying carboxylic acid derivatives such as thiol esters¹¹ and 2-pyridyl esters¹² or organocuprates such as heterocuprates and mixed homocuprates.³⁻⁵

Reaction of acid chlorides with 1.2 equiv of lithium 2-pyridyloxy-*n*-butylcuprate in tetrahydrofuran proceeded almost instantly and cleanly under argon at 0°C. As shown in Table 1, the ketones were generally obtained in high yields without formation of side products. Similarly, this reaction could be carried out at -78°C and was complete within 5 min. Furthermore, it is of interest that sterically hindered acid chlorides such as adamantanecarbonyl chloride and mesitoyl chloride or acid chlorides having other functional groups such as bromo and ester were cleanly converted into the corresponding ketones in high yields.

Reaction with α,β -Unsaturated Ketones. Although conjugate addition reactions of homocuprates to α,β -unsaturated ketones are common,¹ heterocuprates have been less commonly utilized in several occasions due to their reduced reactivity.⁸ Recently, new heterocuprates based on diphenylphosphidocopper³ and higher order, mixed cuprates¹³ have been developed for this purpose. We have studied the effectiveness of our organocuprates containing 2-pyridyloxy ligand using lithium 2-pyridyloxy-*n*-butylcuprate in conjugate addition of α,β -unsaturated ketones. Addition of chalcone to a cold tetrahydrofuran solution of lithium 2-pyridyloxy-*n*-butylcuprate led cleanly to the conjugate addition product. Some experimental results obtained in this study are summarized in Table 2 and the reaction occurred readily at 0°C. Sterically unhindered α,β -unsaturated ketones such as

Table 2. Reaction of α,β -Unsaturated Ketones with (2-PyO) (n-Bu)CuLi^a

enone	temp, °C	time, min	product	yield, ^b %
	0	5		78
	0	60		74
	0	5		99
	0	5		84
	0	10		98
	0	60		22(75)
	-78	40		88 ^c
	-78	50		70 ^c

^a The reaction was carried out with 1.2 equiv of the reagent in THF.

^b The yields refer to isolated yields. The number in parentheses indicates the recovery of the starting material. ^c 1.2 equiv of BF₃·Et₂O was added.

2-cyclohexen-1-one and carvone reacted with lithium 2-pyridyloxy-n-butylcuprate to afford the corresponding ketones in high yields. However, in the case of β -disubstituted α,β -unsaturated ketones, low yields were obtained due to steric inhibition of the reaction. Thus, reaction with isophorone at 0°C for 1 h afforded the 1,4 addition product in 22% yield along with the recovery of the starting material in 75% yield. However, the use of boron trifluoride etherate as an additive¹⁴ led to dramatic enhancements in the reaction rate and product yields, yielding the 1,4 addition product in 88% yield after the reaction was carried out -78°C for 40 min. The similar behaviour has been observed with pulegone.

In conclusion, we believe that new heterocuprates containing 2-pyridyloxy ligand offer several advantages over other previously reported organocuprates with respect to improved thermal stability, complete utilization of alkyl groups, the functional group selectivity, the mildness, and easy workup.

Experimental

Preparation of (2-PyO) (n-Bu)CuLi and Determination of its Stability. To a solution of 2-hydroxypyridine (152mg,

1.6mmol) in tetrahydrofuran (3ml) at 0°C under argon was added n-butyllithium in hexane (1.60M, 1ml, 1.6mmol), the resulting orange suspended solution was stirred at 0°C for 30 min and then transferred into a suspension of cuprous iodide (305mg, 1.6mmol) in tetrahydrofuran (3ml). After being stirred at room temperature for 45 min, the reaction was cooled to -30°C and n-butyllithium in hexane (1.60M, 1ml, 1.6mmol) was added. For the purpose of comparing thermal stability, the cuprate was stirred at -30°C for an additional 10 min, cooled to -50°C, kept at -50°C for 30 min, quenched with an excess amount of benzoyl chloride (675mg, 4.8mmol). The reaction mixture was stirred for an additional 20 min and excess benzoyl chloride was quenched with aqueous NH₄Cl (30%, 3ml). The reaction mixture was stirred at room temperature for 30 min, diluted with diethyl ether (40ml), and washed with aqueous NH₄Cl (20ml) and brine (20ml). The organic layer was dried over anhydrous MgSO₄ and evaporated to dryness. The residue was subjected to silica gel column chromatography with ethyl acetate-hexane (1:30) as an eluant to yield n-butyl phenyl ketone (226mg, 87%). Similarly, the freshly prepared (2-PyO) (n-Bu)CuLi (1.6mmol) as described above was warmed to 0°C and 25°C, kept at 0°C and 25°C for 30 min, quenched with excess benzoyl chloride (670mg, 4.8mmol), respectively. n-Butyl phenyl ketone (222mg, 86% at 0°C and 140mg, 54% at 25°C) was isolated after usual workup. NMR(CDCl₃) δ 0.72–1.92 (m, 7H), 2.96 (t, 2H, J=7 Hz), 7.20–8.00 (m, 5H); IR(film) 1685 cm⁻¹.

Reaction of 6-Bromohexanoyl Chloride with (2-PyO) (n-Bu)CuLi. To a freshly prepared solution of (2-PyO) (n-Bu)CuLi (1.6mmol) in tetrahydrofuran at 0°C under argon was added 6-bromohexanoyl chloride (284mg, 1.3mmol). After being stirred at 0°C for 5 min, the reaction mixture was quenched with aqueous NH₄OH (30%, 3ml), stirred at room temperature for 30 min, diluted with diethyl ether (40ml), washed with aqueous NH₄OH (20ml) and brine (20ml). The organic layer was dried over anhydrous MgSO₄ and evaporated to dryness under reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate-hexane (1:20) as an eluant to yield 10-bromo-5-dodecanone (273mg, 87%). NMR(CDCl₃) δ 0.76–2.20 (m, 13H), 2.26–2.62 (t, 4H), 3.42 (t, 2H, J=6 Hz); IR(film) 1715 cm⁻¹.

Reaction of 2-Cyclohexen-1-one with (2-PyO) (n-Bu)CuLi. To a freshly prepared solution of (2-PyO) (n-Bu)CuLi in tetrahydrofuran (1.6mmol) was added 2-cyclohexen-1-one (128mg, 1.3mmol). After 5 min of being stirred at 0°C, the reaction mixture was quenched with aqueous NH₄OH (3ml). The reaction mixture was stirred at room temperature for 30 min, diluted with diethyl ether (40ml), washed with aqueous NH₄OH (20ml), and brine (20ml). The organic layer was dried over anhydrous MgSO₄ and evaporated to dryness under reduced pressure. The residue was subjected to silica gel column chromatography with ethyl acetate-hexane (1:5) as an eluant to yield 3-n-butyl-1-cyclohexanone (244mg, 99%) as a colorless oil. NMR(CDCl₃) δ 0.80–1.30 (m, 3H), 1.30–2.80 (m, 15H); IR(film) 1715 cm⁻¹.

Spectral Data of the Products. 5-Dodecanone: NMR(CDCl₃) δ 0.65–1.20 (m, 6H), 1.20–2.20 (m, 14H), 2.45 (t, 4H, J=7 Hz); IR(film) 1715 cm⁻¹. n-Butyl cyclohexyl ketone: NMR(CDCl₃) δ 0.80–1.17 (t, 3H), 1.17–2.62 (m, 17H); IR(film) 1710 cm⁻¹. n-Butyl isobutyl ketone: NMR(CDCl₃) δ 0.80–1.80 (m, 7H), 0.97–1.17 (d, 6H, J=6 Hz), 2.20–

2.60 (m, 3H); IR(film) 1710 cm^{-1} . 1-Adamantyl n-butyl ketone: NMR(CDCl_3) δ 0.70–2.20 (m, 22H), 2.40 (d, 2H, $J=6$ Hz); IR(film) 1710 cm^{-1} . n-Butyl mesitoyl ketone: NMR(CDCl_3) δ 0.70–2.20 (m, 7H), 2.17 (s, 6H), 2.25 (s, 3H), 2.65 (t, 3H, $J=6$ Hz), 6.83 (s, 2H); IR(film) 1695 cm^{-1} . 11-Oxo-1-pentadecene: NMR(CDCl_3) δ 0.76–1.10 (m, 1H), 1.10–2.60 (m, 22H), 4.80–6.20 (m, 3H); IR(film) 1715 cm^{-1} . Methyl 6-oxododecanoate: NMR(CDCl_3) δ 0.70–1.10 (m, 3H), 1.10–2.10 (m, 8H), 2.10–2.80 (m, 6H), 3.70 (s, 3H); IR(film) 1740, 1720 cm^{-1} . β -Phenyl heptanophenone: NMR(CDCl_3) δ 0.80–1.30 (m, 3H), 1.30–2.80 (m, 15H); IR(film) 1715 cm^{-1} . 4-Phenyl-2-octanone: NMR(CDCl_3) δ 0.65–1.95 (m, 9H), 2.00 (s, 3H), 2.65–2.80 (d, 2H, $J=7$ Hz), 2.80–3.40 (m, 1H), 7.30 (s, 5H); IR(film) 1715 cm^{-1} . 3-n-Butyl-1-cyclohexanone: NMR(CDCl_3) δ 0.80–1.30 (m, 3H), 1.30–2.80 (m, 15H); IR(film) 1715 cm^{-1} . 4,4-Dimethyl-3-n-butyl-1-cyclohexanone: NMR(CDCl_3) δ 0.70–1.05 (m, 3H), 1.05–1.18 (d, 6H), 1.18–2.15 (m, 9H), 2.15–2.70 (m, 4H); IR(film) 1715 cm^{-1} . 2,3-Dihydro-3-n-butylcarvone: NMR(CDCl_3) δ 0.60–1.60 (m, 9H), 1.70 (s, 3H), 1.80–2.80 (m, 6H), 4.70 (m, 2H); IR(film) 1715 cm^{-1} . 3-n-Butyl-3-methyl-5,5-dimethyl-1-cyclohexanone: NMR(CDCl_3) δ 0.90–1.10 (m, 3H), 1.22 (s, 9H), 1.30–1.62 (m, 6H), 1.70 (s, 2H), 2.35 (s, 4H); IR(film) 1715 cm^{-1} . 2-(1',1'-dimethylpentyl)-5-methyl-1-cyclohexanone: NMR(CDCl_3) δ 0.70–1.50 (m, 18H), 1.50–2.66 (m, 8H); IR(film) 1715 cm^{-1} .

References

- (a) G.H. Posner, *Org. React. (N. Y.)*, **19**, 1 (1972); (b) G.H. Posner, *ibid.*, **22**, 253 (1975).
- G.H. Posner, "An Introduction to Synthesis Using Organocopper Reagent", John Wiley & Sons, 1980.
- (a) S.H. Bertz, G. Dabbagh, and G.M. Villacorta, *J. Am. Chem. Soc.*, **104**, 5824 (1982); (b) S.H. Bertz and G. Dabbagh, *J. Org. Chem.*, **49**, 1119 (1984).
- C.R. Johnson and D.S. Dhanoa, *J. Chem. Soc., Chem. Commun.*, 358 (1982).
- B.H. Lipshutz, D. Parker, J.A. Kozlowski, and R.D. Miller, *J. Org. Chem.*, **48**, 3334 (1983).
- T. Tsudo, T. Yazawa, K. Watanabe, T. Fujii, and T. Saegusa, *J. Org. Chem.*, **46**, 192 (1981).
- S.H. Bertz and G. Dabbagh, *J. Chem. Soc., Chem. Commun.*, 1030 (1982).
- G.H. Posner, C.E. Whitten, and J.J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).
- (a) D.A. Shirley, *Org. React. (N. Y.)*, **8**, 28 (1954); (b) M.J. Jorgenson, *ibid.*, **18**, 1 (1970).
- (a) G.H. Posner and C.E. Whitten, *Tetrahedron Lett.*, 4647 (1970); (b) G.H. Posner, C.E. Whitten, and P.E. McFarland, *J. Am. Chem. Soc.*, **94**, 5106 (1972).
- (a) R.J. Anderson, C.A. Henrick, and L.D. Rosenblum, *J. Am. Chem. Soc.*, **96**, 3654 (1974); (b) S. Kim, J.I. Lee, and B.Y. Chung, *J. Chem. Soc., Chem. Commun.*, 1231 (1981).
- S. Kim and J.I. Lee, *J. Org. Chem.*, **48**, 2608 (1983).
- B.H. Lipshutz, R.S. Wilhelm, and J. Kozlowski, *Tetrahedron Lett.*, 3755 (1982).
- (a) Y. Yamamoto, S. Yamamoto, H. Yatagai, Y. Ishihara, and K. Maruyama, *J. Org. Chem.*, **47**, 119 (1982). (b) B.H. Lipshutz, D.A. Parker, J. Kozlowski, and S.L. Nguyen, *Tetrahedron Lett.*, 5959 (1984).

Basis Set Requirement for Small Components Besides Kinetic Balance in Relativistic Self-Consistent-Field Calculations of Many Electron Systems

Yoon Sup Lee* and Kyoung Koo Baeck

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131

Received September 16, 1986

It is demonstrated by using a highly positive uranium ion as a test case that the exact relation between the small and the large components of a Dirac spinor in relativistic self-consistent-field (RSCF) calculations is not fully satisfied by the kinetic balance condition only even for two electron systems. For a fixed number of large component basis functions, total energies are sensitive to the change of the size of the small component basis sets even after the kinetic balance condition is fully satisfied. However, the kinetic balance condition appears to be a reasonable guideline in generating reliable and practical basis sets for most applications of RSCF calculations. With a complete small component basis set, energies from RSCF calculations exhibit a variational behavior, implying the stability of the present RSCF procedure.

Introduction

The primary mechanism for variational failure in relativistic self-consistent-field (RSCF) calculation for one electron problems has been identified and practical and theoretical ways of obtaining variationally safe solutions have been derived

recently by many workers. Schwarz and Wallmerer¹ have shown that an inadequate representation of the small component of the four-component Dirac spinor produces a shortfall in the computed kinetic energy, and that this persists even in the nonrelativistic limit ($c = 10^8$) where the small components might be expected to have negligible influence. This leads to