

A General Olefin Synthesis

Ernest Wenkert*[†] and Tamis W. Ferreira

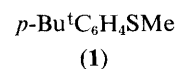
Department of Chemistry, Rice University, Houston, TX 77001, U.S.A.

The reaction between secondary Grignard reagents and alkylthioarenes or alkylthioalkenes in the presence of 1:1 nickel dichloride–triphenylphosphine causing the substitution of alkylthio-groups by hydrogen atoms, the nickel(0)-induced replacement of alkylthio-groups of the aforementioned sulphides by alkyl or aryl functions, and the observation of regiocontrol in the catalysed reactions of Grignard reagents with unsymmetrical 1,1-bis(alkylthio)alkenes have led to a scheme of general, regio-, and stereo-selective olefin synthesis.

A facile substitution of alkoxy-^{1,2} and alkylthio-^{3–5} groups on olefins and arenes by alkyl or aryl functions in reactions with Grignard reagents, under catalysis of low-valent nickel species, with complete stereocontrol (retention of configuration, especially in the reactions of the sulphur-containing compounds)^{3–5} has recently been discovered. This has led to the suggestion that the conversion of alkylthioalkenes into alkyl or aryl olefins might be developed as a general method of olefin synthesis, and the present communication illustrates the use of 1,1-bis(alkylthio)alkenes in such a scheme.

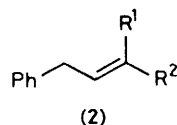
In order to make the new method all-encompassing, a procedure for the replacement of the alkylthio-group by a hydro-

gen atom was sought. The use of a 1:1 mixture of anhydrous nickel dichloride and triphenylphosphine as catalyst and a secondary Grignard reagent as reducing agent accomplished this task.⁶ Thus, for example, treatments of *p*-*t*-butylthioanisole (**1**) with isopropylmagnesium bromide or cyclohexylmagnesium bromide in the presence of the above catalyst in



benzene–ether solvent gave *t*-butylbenzene in 70 and 74% yields, respectively. However, the same reactions under the catalytic influence of (1,3-bisdiphenylphosphino)propane–nickel dichloride [(dppp)NiCl₂] produced a *ca.* 7:1 mixture (80%) of *p*-*t*-butylisopropylbenzene and *p*-*t*-butyl-*n*-

[†] Present address: Department of Chemistry (D-006), University of California-San Diego, La Jolla, CA 92093, U.S.A.



- | | |
|--|---|
| a; R ¹ = R ² = SEt | f; R ¹ = H, R ² = Me |
| b; R ¹ = R ² = Me | g; R ¹ = H, R ² = Et |
| c; R ¹ = SEt, R ² = Me | h; R ¹ = Me, R ² = H |
| d; R ¹ = SEt, R ² = Et | i; R ¹ = Et, R ² = H |
| e; R ¹ = SEt, R ² = H | j; R ¹ = Et, R ² = Me |
| k; R ¹ = Me, R ² = Et | |

propylbenzene, and *p*-*t*-butylphenylcyclohexane (70%), respectively. Thus, manipulation of the ligands surrounding the reactive, low-valent nickel species involved in the substitution process permitted complete control over the otherwise competitive reduction and alkylation pathways. The reduction constitutes a desulphurization process, albeit of thio-units attached only to trigonal carbon centres.⁷ As in the earlier alkylations⁴ reduction of the thio-compound was independent of its substitution or oxidation state, *e.g.* *t*-butylbenzene being the product of the reductions of *p*-*t*-butylbenzenethiol (70%), and of the sulphoxide (75%) and the sulphone (73%) of compound (1).

1,1-Bis(ethylthio)ethylene⁸ reacted with phenylmagnesium bromide in the presence of (Ph₃P)₂NiCl₂ as catalyst yielding α -phenylstyrene (31%) and the (dppp)NiCl₂-induced reaction of 1,1-bis(ethylthio)-2-methylprop-1-ene⁹ with ethylmagnesium bromide led to 3-ethylthio-2-methylpent-2-ene (64%).[‡] Neither early quenching of the reaction nor alteration of the catalyst ligand permitted the first reaction to be stopped after monoarylation and no forcing conditions allowed the second reaction to proceed to the dialkylation product. This experience with an unsubstituted and a fully substituted 1,1-bis(ethylthio)-alkene set the limits of flexibility of the new method of olefin synthesis.

Treatment of 1,1-bis(ethylthio)prop-1-ene⁸ with phenylmagnesium bromide and (Ph₃P)₂NiCl₂ yielded 1,1-diphenylpropene (72%),¹⁰ whereas the use of 1 equiv. of the Grignard reagent in the presence of a 1:1 mixture of triphenylphosphine and nickel dichloride led to 1-phenyl-1-(ethylthio)propene (40%), wherein the phenyl group had replaced the ethylthio-function *cis* to the olefinic hydrogen atom exclusively. Exposure of the latter product to methylmagnesium bromide and (dppp)NiCl₂ afforded (*Z*)-2-phenylbut-2-ene (60%).¹¹ The stereochemistry-dependent difference in rate of alkylthio-group displacement for unsymmetrical 1,1-bis(alkylthio)-alkenes opened a route for the stereoselective synthesis of di- and tri-substituted olefins.

1,1-Bis(ethylthio)-3-phenylprop-1-ene (**2a**)^{‡§} was converted into 3-methyl-1-phenylbut-2-ene (**2b**)¹² (50%) or the ethylthio-alkene (**2c**)[‡] (60%) on treatment with an excess of methylmagnesium bromide and (dppp)NiCl₂ or an equivalent of the Grignard reagent and 1:1 Ph₃P–NiCl₂, respectively. The alkylthioalkenes (**2d**)[‡] (85%) and (**2e**)¹³ (58%) were the products of treatment of (**2a**) with limited amounts of Grignard reagent: ethylmagnesium bromide [(dppp)NiCl₂] and isopropylmagnesium bromide (1:1 Ph₃P–NiCl₂), respectively. Reduction of the compounds (**2c**) and (**2d**) with iso-

propylmagnesium bromide in the presence of a 1:1 mixture of tri-*n*-octylphosphine and nickel dichloride produced the *trans*-olefins (*E*)-1-phenylbut-2-ene (**2f**)¹² (39%) and (*E*)-1-phenylpent-2-ene (**2g**)¹⁴ (39%), respectively. Alternatively, treatment of (**2e**) with methylmagnesium and ethylmagnesium bromides under (dppp)NiCl₂ influence yielded the *cis*-isomers (*Z*)-1-phenylbut-2-ene (**2h**)¹⁵ (64%) and (*Z*)-1-phenylpent-2-ene (**2i**)¹⁴ (50%), respectively. Finally, (dppp)NiCl₂-induced substitution of (**2c**) and (**2d**) with ethylmagnesium and methylmagnesium bromides, respectively, produced the trisubstituted alkene (**2j**)¹⁴ (14%) and its isomer (**2k**)[‡] (66%), respectively.

In view of the ease of transformation of the alkylthio-alkenes of aldehydic nature into those of ketonic nature [*e.g.* (**2e**) → (**2c**) or (**2d**)] by lithiation and alkylation¹⁶ a combination of this two-step process and the above nickel-induced reductions or alkylations adds a different dimension to the new synthesis of di- or tri-substituted olefins. Finally, since the 1,1-bis(alkylthio)alkenes are masked carboxylic acids and their mono(alkylthio)alkene products are aldehyde or ketone derivatives, the substitution of a single alkylthio-group of a 1,1-bis(alkylthio)alkene by hydrogen or an alkyl (or aryl) function constitutes a formal transformation of an organic acid into an aldehyde or ketone, respectively.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Received, 15th February 1982; Com. 165

References

- 1 E. Wenkert, E. L. Michelotti, and C. S. Swindell, *J. Am. Chem. Soc.*, 1979, **101**, 2246.
- 2 T. Hayashi, Y. Katsuro, and M. Kumada, *Tetrahedron Lett.*, 1980, 3915.
- 3 H. Okamura, M. Miura, and H. Takei, *Tetrahedron Lett.*, 1979, 43.
- 4 E. Wenkert, T. W. Ferreira, and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, 1979, 637.
- 5 H. Takei, H. Sugimura, M. Miura, and H. Okamura, *Chem. Lett.*, 1980, 1209.
- 6 This reduction was discovered first by E. L. Michelotti (post-doctoral research associate, Rice University, 1977–1979). For a related study see B. M. Trost and P. L. Ornstein, *Tetrahedron Lett.*, 1981, 3463.
- 7 For earlier transition metal-induced desulphurizations other than the well known Raney nickel reduction procedure, see T. Mukaiyama, M. Hayashi, and K. Narasaka, *Chem. Lett.*, 1973, 291; H. Alper, *J. Org. Chem.*, 1975, **40**, 2694; *Pure Appl. Chem.*, 1980, **52**, 607; J. J. Eisch and K. R. Im, *J. Organomet. Chem.*, 1977, **139**, C51; H. Alper and H. Paik, *J. Org. Chem.*, 1977, **42**, 3522; H. Alper and C. Blais, *J. Chem. Soc., Chem. Commun.*, 1980, 169.
- 8 L. C. Rinzema, J. Stoffelma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas.*, 1959, **78**, 354.
- 9 G. Scherowski and J. Weiland, *Liebigs Ann. Chem.*, 1974, 403.
- 10 R. Boyce, W. S. Murphy, and K. P. Klein, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1292.
- 11 S. A. Theine and J. G. Traynham, *J. Org. Chem.*, 1974, **39**, 153.
- 12 F. J. McEnroe, C.-K. Sha, and S. S. Hall, *J. Org. Chem.*, 1976, **41**, 3465.
- 13 T. Mukaiyama and K. Saigo, *Chem. Lett.*, 1973, 479.
- 14 J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, 1974, **77**, 269.
- 15 H. Morrison and R. Peiffer, *J. Am. Chem. Soc.*, 1968, **90**, 3428.
- 16 K. Oshima, K. Shimozi, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, 1973, **95**, 2694; R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1976, 990; B. Harirshian and P. Magnus, *ibid.*, 1977, 522.

‡ Characterized by full spectroscopy and high-resolution mass measurement.

§ Prepared by the aluminium chloride-induced reaction of hydrocinnamyl chloride with ethanethiol and subsequent toluene-*p*-sulphonic acid-induced ethanethiol elimination from the resultant orthothioester (see footnote ‡).