

HOMOGENEOUS CATALYSIS

III*. HYDROSILYLATION OF α,β -UNSATURATED ALDEHYDES; REGIOSPECIFIC REDUCTION OF C=O USING Ni⁰ CATALYSTS

M.F. LAPPERT* and T.A. NILE

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received July 23rd, 1975)

Summary

The addition of trialkoxysilanes across the carbonyl bond in crotonaldehyde has been demonstrated for a variety of nickel(0) complexes. The carbon-carbon double bond is left intact. This differs from catalysts used previously, such as chloroplatinic acid or Wilkinson's compound, where 1,4-addition is reported for simple α,β -unsaturated aldehydes. The Ziegler system, Ni(acac)₂-Et₃Al, proved ineffective as a catalyst, due to competing polymerisation of the crotonaldehyde. The 1,4-addition of trialkoxysilanes to crotonaldehyde, catalysed by Wilkinson's compound, has been confirmed; the new *cis*- and *trans*-but-1-enoxytriethoxysilanes have been isolated and identified.

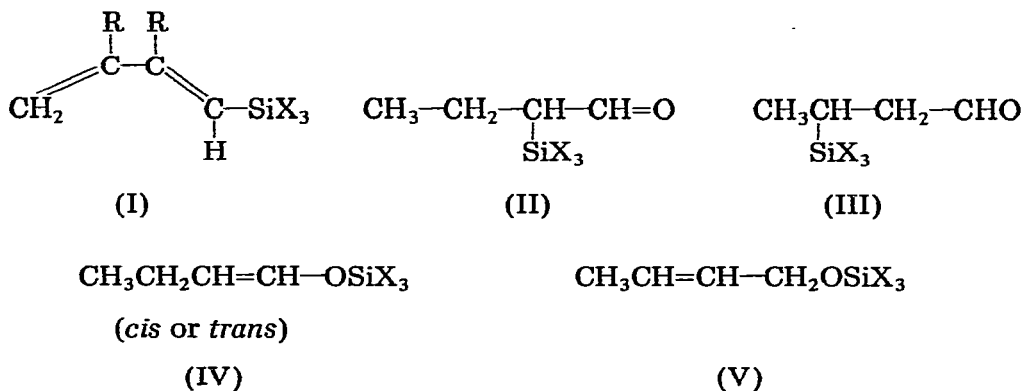
Introduction

In Part II we described the use of Ziegler catalysts for the homogeneous hydrosilylation of terminal acetylenes or 1,3-dienes [1]. Typically we used Ni(acac)₂-AlEt₃ in the hydrocarbon medium to which the silane HSiX₃ was added. It was presumed that a low valent nickel species, probably of Ni⁰, was formed prior to the onset of the catalytic cycle. Interestingly, it was found that this type of catalyst gave products which often differed qualitatively from those obtained by use of conventional reagents, such as H₂PtCl₆. For example, with terminal acetylenes RC≡CH, the major product was I, rather than a simple 1,1-adduct.

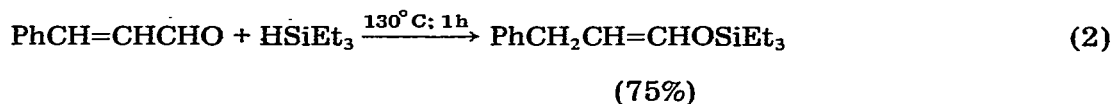
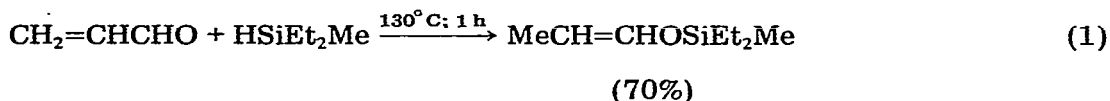
This paper describes extensions of earlier studies to α,β -unsaturated aldehydes as substrates. The use of Ni(acac)₂-AlEt₃ did not prove particularly fruit-

* For Part II, see ref. 1.

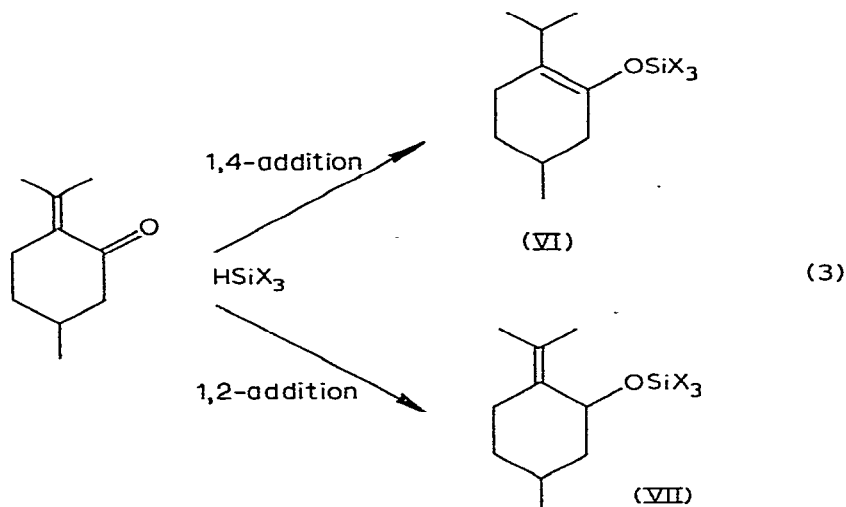
ful for crotonaldehyde, possibly because of the aluminium alkyl-induced polymerisation of the aldehyde. Attention was therefore turned to preformed Ni^0 systems. In principle, one of several 1,1-adducts may be formed, II-V.



The chloroplatinic acid-catalysed hydrosilylation of α,β -unsaturated aldehydes gives the *o*-silyl-enol by 1,4-addition e.g. eqns. 1, 2 [2]. A similar sequence gives $\text{MeCH}_2\text{CH} = \text{CHOSiEt}_3$ (96%) from $\text{Me}_2\text{CH} = \text{CHCHO}$ and HSiEt_3 using $[\text{RhCl}(\text{PPh}_3)_3]$ at 60°C [3]. Chlorosilanes react to give products which polymerise immediately [4].



Addition across $\text{C} = \text{O}$ (1,2-addition) can occur with $[\text{RhCl}(\text{PPh}_3)_3]$ with more complex molecules such as pulegone [eqn. 3]. The ratio of VI/VII is de-



pendent on the silane used, being 75/25 for HSiMe₂Ph, 50/50 for HSiEt₃, and 0/100 for H₂SiPh₂ [5]. These hydrosilylations are of synthetic interest as the siloxy-bonds may be hydrolysed (KOH—MeOH—H₂O); the overall reaction being selective reduction of the carbonyl (from VI) or olefinic (from VII) bonds.

Reduction by NaBH₄ or LiAlH₄ gives large quantities of the completely saturated product, by reduction of both the carbonyl and olefinic bonds [6]. Catalysis by tetracarbonylnickel(0) gives addition across the olefinic double bond (3,4-addition), as in eqn. 4 [7].

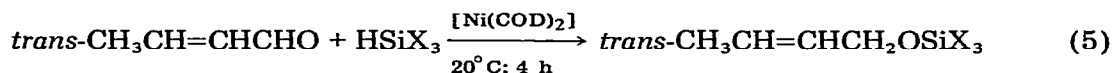


Results and discussion

A number of nickel complexes proved active for the hydrosilylation of crotonaldehyde. The use of chlorotris(triphenylphosphine)rhodium(I) was also re-investigated.

Hydrosilylation of α,β -unsaturated aldehydes catalysed by nickel complexes

The hydrosilylation of crotonaldehyde by alkoxy-silanes was found to be catalysed by [Ni(COD)₂] at 20°C [eqn. 5]. The addition of [Ni(COD)₂] to crotonaldehyde at 0°C, resulted in the formation of a blood-red precipitate. This was exceedingly air-sensitive, and thus its characterisation was not attempted, but it



[VIIIa, X = OEt; VIIIb, X = OMe]

is assumed to be bis(π -crotonaldehyde)nickel(0), analogous to bis(π -acrolein)-nickel(0), [Ni(CH₂=CHCHO)₂], formed from tetracarbonylnickel(0) and acrolein [8], and to bis(π -cinnamaldehyde)nickel(0), [Ni(PhCH=CHCHO)₂], formed from [Ni(COD)₂] and cinnamaldehyde [9]. The blood-red nickel compound was filtered off, and the pale yellow liquid gave the product VIII in high yield (80%). Compounds VIII were identified by microanalyses and from their mass spectra as 1/1 crotonaldehyde/silane adducts; small amounts of an isomer were also formed. The ¹H NMR spectra (Table 1) indicated that the products VIII are but-2-enoxytrialkoxysilanes. The IR spectra showed absorptions at 3010 cm⁻¹,

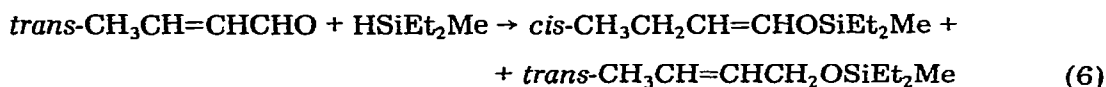
TABLE 1
CHEMICAL SHIFT DATA (τ) FOR BUT-2-ENOXYTRIALKOXYSILANES VIII^a

Compound	$-\underline{\text{CH}}=\underline{\text{CH}}-$ ^b	$-\text{C}=\text{C}-\underline{\text{CH}}_2-\text{O}$ ^c	$\text{C}=\text{C}-\underline{\text{CH}}_3$ ^d
VIIIa ^e	4.4	5.9	8.3
VIIIb ^f	4.3	5.9	8.3

^a 60 MHz spectra, CCl₄ solution; TMS reference. ^b 2H, centre of broad multiplet. ^c 2H, centre of broad multiplet. ^d 3H, centre of broad multiplet. ^e Also signals at τ 6.28, 6H, quartet, $J = 7$ Hz, Si—O—CH₂—C; τ 8.81, 9H, triplet, $J = 7$ Hz, Si—O—C—CH₃. ^f Also signal at τ 6.50, 9H, singlet, Si—O—CH₃.

due to the C—H stretch of the =CH moiety, and at 1650 cm^{-1} due to the C=C double bond stretch. The configuration about the double bond in the products is assigned as that of the *trans*-isomer, as the ^1H NMR signals were similar in line shape and chemical shift to those in crotyl alcohol, *trans*- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$.

When the hydrosilylation of crotonaldehyde was attempted using diethylmethylsilane, there was no reaction at room temperature. Heating at 60°C for 3 h caused decomposition of the bis(π -crotonaldehyde)nickel(0), and a black precipitate was formed, presumably metallic nickel. Crotonaldehyde/silane 1/1-adducts were formed in 40% yield, but GLC showed two isomers in the ratio of 80/20, identified from the ^1H NMR spectra of the mixture as *cis*-but-1-enoxydiethylmethylsilane and *trans*-but-2-enoxydiethylmethylsilane, respectively, [eqn. 6]. Preliminary exploratory experiments showed that similar reactions of cinnamaldehyde or mesityl oxide gave low yields of mixed products.



The reduction of nickel(II) acetylacetonate in crotonaldehyde at 0°C by triethylaluminium resulted in a blood-red precipitate, similar in appearance to that formed from $[\text{Ni}(\text{COD})_2]$ and crotonaldehyde. Subsequent addition of triethoxysilane at 0°C produced a mildly exothermic reaction. After stirring at 20°C for 16 h, distillation at reduced pressure yielded small amounts of VIIIa (~5%) with tetraethoxysilane (~20%). These compounds were identified by their ^1H NMR spectra and GLC characteristics. The residue consisted of a viscous oil which, from its spectra, was identified as a polymer of crotonaldehyde, containing some triethoxysilyl groups. It is known that trialkoxyaluminium compounds polymerise crotonaldehyde to a gelatinous polymer, even at low temperature (~0°C) [10]; and similar IR absorptions at 3500, 1720, and 1630 cm^{-1} were reported for a polymer of crotonaldehyde [11], and assigned to OH, C=O, and C=C, respectively. It seems likely that such a polymer of crotonaldehyde is formed during the attempted hydrosilylation, together with some hydro-silylation of the carbon—oxygen or carbon—carbon double bonds.

The addition of triphenylphosphine (P) to $[\text{Ni}(\text{COD})_2]$ (P/Ni = 2) prevented the formation of the blood-red precipitate, and instead gave a golden-brown solution. This proved to be an active catalyst for the hydrosilylation of crotonaldehyde by triethoxysilane (20°C for 6 h), giving a high yield (85%) of VIIIa.

TABLE 2

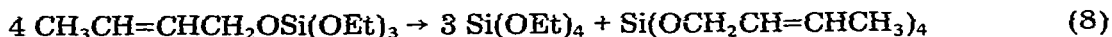
HYDROSILYLATION OF CROTONALDEHYDE BY TRIETHOXYSILANE CATALYSED BY $\text{Ni}[\text{P}(\text{OEt})_3]_4$ ^a

Temperature (°C)	Time (h)	Yield (%) of VIIIa ^b	Yield (%) of $\text{Si}(\text{OEt})_4$ ^b
80 ^c	5	30	39
80	3	50	29
100	2	67	5

^a Crotonaldehyde (25 mmol) and $[\text{NiP}_4]$ (7×10^{-2} mmol) heated together at 80°C for 0.5 h; cooled to 0°C, triethoxysilane (11 mmol) added; heated to stated temperature. ^b Based on silane; calculated by quantitative GLC. ^c Crotonaldehyde and catalyst not heated together before addition of silane.

Complexes such as $[\text{Ni}(\text{CH}_2=\text{CHCHO})_2(\text{PPh}_3)_2]$, which are red-yellow, are known [8,12], and similar compounds are probably involved in our reaction.

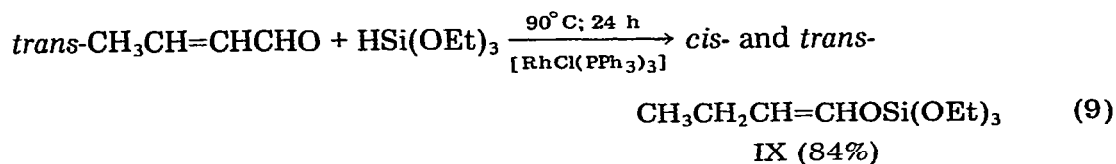
Tetrakis(triethyl phosphite)nickel(0) also proved to be an active catalyst (Table 2). The formation of tetraethoxysilane during these reactions is unusual. It could arise by redistribution either of the silane [eqn. 7], or the product [eqn. 8]. Heating the crotonaldehyde and catalyst together prior to addition of



silane gave a pale-yellow solution, and also increased the yield. This may be due to formation of a species such as $[\text{Ni}(\text{CH}_3\text{CH}=\text{CHCHO})_2\text{P}(\text{OEt})_3]$.

Hydrosilylation of crotonaldehyde catalysed by Wilkinson's compound

Previous work [3] on hydrosilylation of crotonaldehyde, catalysed by chlorotris(triphenylphosphine)rhodium(I), Wilkinson's compound, did not include trialkoxysilanes. We find that hydrosilylation of crotonaldehyde by triethoxysilane [eqn. 9], catalysed by Wilkinson's compound, is slower than that reported for trialkylsilanes, requiring 24 h at 90°C for completion, compared with 15 min at 60°C for triethylsilane.



As further distinction, two isomers IX were formed in the ratio 60/40. These were isolated by preparative GLC and identified as *trans*- and *cis*-but-1-enoxysilanes by their ^1H NMR characteristics (Table 3). The *trans*-isomer was the major component. The slower reaction with triethoxysilane is consistent with the

TABLE 3

^1H NMR DATA FOR BUT-1-ENOXYTRIETHOXYSILANES. a $\text{C}(\text{H}_\text{A})_3-\text{C}(\text{H}_\text{B})_2-\text{C}(\text{H}_\text{C})=\text{C}(\text{H}_\text{D})-\text{OSi}(\text{OCH}_2\text{CH}_3)$

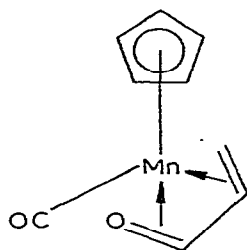
Compound	Chemical shift (τ)	Integration	Description, assignment, coupling constant(s)
<i>trans</i> -IX ^b	3.80	1H	Doublet, H _D , J_{CD} 12 Hz
	4.97	1H	Doublet of triplets (overlapping), H _C , J_{CD} 12 Hz, J_{BC} 7 Hz
	8.08	2H	Quintet (overlapping doublet of triplets), H _B , J_{BC} 7 Hz, J_{AB} 7 Hz
<i>cis</i> -IX ^c	9.00	3H	Triplet, H _A , J_{AB} 7 Hz
	3.85	1H	Doublet, H _D , J_{CD} 6 Hz
	5.82	1H	Overlapping doublet of triplets, J_{CD} 6 Hz, J_{BC} 7 Hz
	7.91	2H	Multiplet, H _C
	9.05	3H	Triplet, H _A , J_{AB} 7 Hz

^a 60 MHz spectrum; CCl₄ solvent; TMS reference. ^b Also signals due to Si—O—CH₂—CH₃ at τ 6.19 (quartet) and 8.79 (triplet), $J = 7$ Hz. ^c Also signals due to Si—O—CH₂—CH₃ at τ 6.18 (quartet) and 8.87 (triplet), $J = 7$ Hz.

observation that the rate of hydrosilylation of hex-1-ene catalysed by $[\text{RhCl}(\text{PPh}_3)_3]$ decreased in the order $\text{Ph}_3\text{SiH} > \text{Et}_3\text{SiH} > (\text{EtO})_3\text{SiH} > \text{Cl}_3\text{SiH}$, which is the inverse order of stability of the adducts formed between the silanes and the rhodium(I) complex [13].

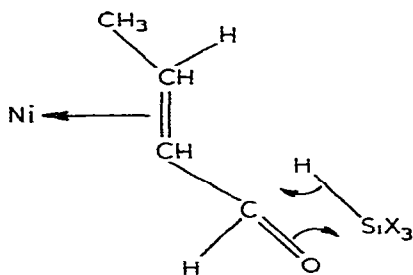
Mechanism

A mechanism has not previously been proposed for the hydrosilylation of α,β -unsaturated compounds, but coordination of the unsaturate to the transition metal must be involved. In the complex X the configuration of acrolein has been assigned as *cis* [14]. This complex gives only 1,4-addition on hydrogenation and hydrosilylation [14]. The structure of bis(acrylonitrile)nickel(0) has been postulated to involve bonding through only the carbon-carbon double



(X)

bond, i.e. a *trans*-configuration. The probable catalytic intermediate in our hydrosilylation, bis(crotonaldehyde)nickel(0), is expected to have a similar structure, and thus a monodentate (C=C only) *trans*-configuration is likely, but this would not be expected to give 1,4-addition, and instead addition across the carbon-carbon double bond. This is not observed. The reaction mixture, from $[\text{Ni}(\text{COD})_2]$, always contains the blood-red precipitate, probably of bis(crotonaldehyde)nickel(0). The unusual reactivity of $[\text{Ni}(\text{COD})_2]$ may be due to the fact that the reaction is heterogeneous. The crotonaldehyde may be bound strongly to the nickel(0) by a π -bond to the carbon-carbon double bond, leaving the carbonyl group free to interact with the silane, the carbonyl bond being activated by the coordination of the carbon-carbon double bond; thus C=C coordination effectively protects the double bonds as in XI.



(XI)

Experimental

Hydrosilylation of crotonaldehyde by triethoxysilane catalysed by bis(π -cyclo-octadiene)nickel(0)

Crotonaldehyde (2.0 g, 27 mmol) was added to bis(π -cyclo-octadiene)-nickel(0) (0.2 g, 0.7 mmol) at 0°C to give a yellow solution and a blood-red precipitate. Triethoxysilane (3.5 g, 22 mmol) was added and the reaction was set aside, with stirring, for 5 h at room temperature. After an induction period of 1 h a very exothermic reaction ensued, necessitating further cooling. The red solid was filtered off and the volatile materials removed under reduced pressure (2 mmHg). Distillation yielded *trans*-but-2-enoxytriethoxysilane (4.0 g, 80%); b.p. 60°C/2 mmHg (Found: C, 51.5; H, 9.49. C₁₀H₂₂O₄Si calcd.: C, 51.3; H, 9.46%); for ¹H NMR data, see Table 1.

Hydrosilylation of crotonaldehyde by trimethoxysilane catalysed by bis(π -cyclo-octadiene)nickel(0)

This reaction was carried out in an analogous fashion using crotonaldehyde (2.1 g, 30 mmol), trimethoxysilane (2.9 g, 24 mmol), and bis(π -cyclo-octadiene)-nickel(0) (0.2 g, 0.7 mmol). Distillation, after removal of the red precipitate and excess volatiles, gave *trans*-but-2-enoxytrimethoxysilane (3.9 g, 84%); b.p. 55°C/10 mmHg (Found: C, 44.2; H, 8.61. C₇H₁₆O₄Si calcd.: C, 43.7; H, 8.39%); for ¹H NMR data, see Table 1.

Hydrosilylation of crotonaldehyde by diethylmethylsilane using bis(π -cyclo-octadiene)nickel(0)

Crotonaldehyde (2.5 g, 35 mmol) was added to bis(π -cyclo-octadiene)-nickel(0) (0.2 g, 0.7 mmol) at 0°C to yield a yellow solution and a blood-red precipitate. Diethylmethylsilane (2.8 g, 27 mmol) was added and the mixture was left stirring at room temperature for 9 h. GLC analysis of the reaction mixture showed that no reaction had occurred. After heating at 60°C for 3 h, product formation was indicated by GLC. The catalyst had decomposed and a black precipitate was observed. Volatile materials were removed under reduced pressure and the black precipitate filtered off, yielding 1.7 g of the adducts; yield 40% (based on silane). GLC analysis showed two isomers in the ratio of 80/20. The major isomer was identified as *cis*-but-1-enoxydiethylmethylsilane and the minor isomer as *trans*-but-2-enoxydiethylmethylsilane upon comparison of an ¹H NMR spectrum of the product mixture with the ¹H NMR spectra of the pure compounds.

The attempted hydrosilylation of crotonaldehyde by triethoxysilane catalysed by the nickel(II) acetylacetonate-triethylaluminium system

The reduction of nickel(II) acetylacetonate (0.13 g, 0.5 mmol) in crotonaldehyde (2.0 g, 27 mmol) with triethylaluminium (1 mmol in 1 ml benzene) was carried out using ice-bath cooling. This afforded a yellow solution and a red precipitate. After addition of triethoxysilane (3.5 g, 22 mmol) the mixture was set aside with stirring at room temperature for 16 h. The reaction was mildly exothermic. GLC analysis indicated that small amounts of *trans*-but-2-enoxytriethoxysilane and tetraethoxysilane were formed. Distillation at reduced pressure

(25°C/0.1 mmHg) yielded small amounts of these compounds which were identified by their ¹H NMR spectra and GLC characteristics. The residue was a viscous oil. The IR spectra indicated the presence of hydroxyl and carbonyl groups, and a carbon-carbon double bond by absorptions at 3400, 1750, and 1650 cm⁻¹, respectively. The ¹H NMR confirmed the presence of a double bond with a signal at τ 4.5 (very broad) and the presence of the triethoxysilyl group by its characteristic signals (τ 6.3, quartet; τ 8.9, triplet; $J = 7$ Hz).

Hydrosilylation of crotonaldehyde by triethoxysilane catalysed by chlorotris(triphenylphosphine)rhodium(I)

Chlorotris(triphenylphosphine)rhodium(I) (0.1 g, 1 mmol) was added to crotonaldehyde (2.0 g, 27 mmol) and triethoxysilane (3.5 g, 22 mmol) and the mixture heated to 90°C for 24 h. The colour of the solution changed from red to yellow within 0.5 h. After removal of volatile materials under reduced pressure, distillation gave the 1/1 adducts (4.2 g, 84%); b.p. 70-72°C/4 mmHg (Found: C, 51.4; H, 9.47. C₁₀H₂₂O₄Si calcd.: C, 51.3; H, 9.46%). GLC analysis showed that the product consisted of two compounds in the ratio of 60/40. The isomers were separated by preparative GLC. The major isomer was identified as *trans*-but-1-enoxytriethoxysilane and the minor isomer as *cis*-but-1-enoxytriethoxysilane by their ¹H NMR spectra (Table 3).

Acknowledgements

We thank Dow Corning Limited (Barry) for their support.

References

- 1 M.F. Lappert, T.A. Nile and S. Takahashi, *J. Organometal. Chem.*, **72** (1974) 425.
- 2 S.I. Sadykh-Zade and A.D. Petrov, *Zh. Obshch. Khim.*, **29** (1959) 3194 [*Chem. Abs.*, **54** (1960) 12978g].
- 3 I. Ojima, T. Kogure, N. Nihonyanagi and Y. Nagai, *Bull. Chem. Soc. Jap.*, **45** (1972) 3506.
- 4 A.D. Petrov and S.I. Sadykh-Zade, *Proc. Acad. Sci. USSR*, (1958) 523.
- 5 I. Ojima, T. Kogure and Y. Nagai, *Tetrahedron Lett.*, (1972) 5035.
- 6 M.R. Johnson and B. Rickborn, *J. Org. Chem.*, **35** (1970) 1041; J.W. Wheeler and R.H. Chung, *ibid.*, **34** (1969) 1149.
- 7 E.Ts. Chukovskaya and R.Kh. Freidlina, *Izv. Sibirsk Otdel. Akad. Nauk, Ser. Khim. Nauk*, (1963) 761 [*Chem. Abs.*, **59** (1963) 7551g].
- 8 G.N. Schrauzer, *J. Amer. Chem. Soc.*, **81** (1959) 5310.
- 9 P. Heimbach, P.W. Jolly and G. Wilke, *Adv. Organometal. Chem.*, **8** (1970) 29.
- 10 T. Ota and S. Masuda, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **86** (1965) 850 [*Chem. Bas.*, **65** (1966) 15523b].
- 11 J.N. Koral, *J. Polymer Sci. Pt. C.*, **61** (1962) S37.
- 12 G.N. Schrauzer, *Chem. Ber.*, **94** (1961) 642.
- 13 R.N. Haszeldine, R.V. Parish and D.J. Parry, *J. Chem. Soc. A*, (1969) 683.
- 14 P. Dixneuf, personal communication.