Electronic Supplementary Information (ESI)

Treasures from the *Free Radical Renaissance Period* – Miscellaneous Hexenyl Radical Kinetic Data

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Procedures for the preparation of **1b-H, 2b-H, 3b-H, 3c-H, 4a-H, 4b-H, 7-H, 8-H, 25-H** and **27**; derivation of equation 6; kinetic data for the cyclization of **1a, 1b, 1c, 6** and **24** under various reaction conditions (10 pages).

Preparation of product standards.

3-Butyltetrahydrofuran (5-H). (*E*)-1-Bromo-2-(2-hexenyl-1-oxy)ethane (**13**) (60 mg, 290 μmol) was dissolved in hexane (1.0 mL), tributyltin hydride (88 mg, 300 μmol) and a few crystals of AIBN added, the mixture sealed in a glass tube and heated at 80° overnight. The mixture was cooled and separated by preparative GC (20% Se-30 on Chromosorb W), the major product was collected and identified as the title compound (22 mg, 59%). ^{1}H NMR δ 3.68 – 3.94 (m, 4H), 3.28 – 3.35 (m, 1H), 1.95 – 2.28 (m, 2H), 0.90 – 1.35 (m, 9H); ^{13}C NMR δ 73.5, 67.9, 39.4, 33.0, 32.5, 30.8, 22.8, 14.0; IR (neat): 1455, 1465 cm^{-1}; MS *m/z* (relative intensity) 127 (5), 81 (53), 56 (100). HRMS calcd. for $C_8H_{16}O$ $[M - H]^+$ 127.1123, found 127.1122.

1-Methoxy-5-hexene (1b-H). 5-Hexen-1-ol (500 mg, 5.0 mmol) was added dropwise to a suspension of sodium hydride (130 mg, 5.5 mmol) in dry DME (5 mL). The mixture was stirred until the evolution of hydrogen had ceased. Methyl iodide (1.0 mL) was added and the mixture heated at reflux overnight. Separation was achieved by fractional distillation and the fraction (Bp = 110 – 120°) collected proved to contain the title ether contaminates with trace amounts of DME. (Bp[S1] = 122°). ^{1}H NMR δ 5.71 – 5.92 (m, 1H), 4.92 – 5.05 (m, 5H), 3.60 – 3.69 (t, J = 6.4 Hz, 2H), 3.33 (s, 3H), 2.06 – 2.17 (m, 2H), 1.44 – 1.68 (m, 4H).

S1. H. C. Brown and G. J. Lynch, *J. Org. Chem.* 1981, **46**, 531.

***Cis*- and *trans*-1-methoxy-2-methylcyclopentane (2b-H, 3b-H)**. Sodium hydride was suspended in dry DMSO and the mixture stirred at 80° until the evolution of hydrogen had ceased. 2-Methylcyclopentanol (20% *cis*, 80% *trans*)[S2] (200 mg, 2.0 mmol) and methyl iodide (1.0 mL) were added and the mixture stirred at 80° for 90 min. and then at r.t. overnight. The reaction mixture was fractionally distilled to give the title compound as a colourless oil and as a 20:80 *cis:trans* mixture. Bp = 95 – 110°; ^{1}H NMR δ 3.30 (m, 4H), 1.51 – 2.00 (m, 7H), 0.98 (d, J = 6.6 Hz, 2.4H), 0.96 (d, J = 6.9 Hz, 0.6H); ^{13}C NMR δ 89.6 (*trans*), 85.2 (*cis*), 56.9 (*cis*), 56.8 (*trans*), 39.7 (*trans*), 38.0 (*cis*), 32.2 (*trans*), 31.2 (*cis*), 30.8 (*trans*), 29.9 (*cis*), 22.3 (*trans*), 21.5 (*cis*), 19.1 (*trans*), 18.1 (*cis*); MS *m/z* (relative intensity) 114 (19), 85 (25), 71 (100). HRMS calcd. for $C_7H_{14}O$ $[M]^+$ 114.1045, found 114.1045.

S2 H. C. Brown and V. Varma, *J. Am. Chem. Soc.* 1966, **88**, 2871; M.-H. Rei, *J. Org. Chem.* 1978, **43**, 2173.

***Trans*-1-trifluoromethyl-2-methylcyclopentane (3c-H)**. *Trans*-2-Methylcyclopentanecarboxylic acid[S3] (2.0 g, 15.6 mmol) (containing 5% *cis* isomer) was added to 50 mL stainless-steel pressure vessel fitted with a pressure regulator and inlet/outlet valve. The vessel was sealed and cooled in liquid nitrogen. Sulfur tetrafluoride (18 g) was introduced and the vessel warmed to r.t. and then heated at 120° for 10 h. After cooling to r.t., the volatile gases were vented and the vessel opened. The residual oil was washed with satd. sodium bicarbonate, dried ($MgSO_4$) and distilled to yield the title compound as a colourless oil containing 5% *cis* isomer as determined by GC analysis. ^{1}H NMR δ 1.45 – 2.16 (m, 8H), 1.10 (d, J = 6.3 Hz, 3H); ^{13}C NMR δ 129.0 (q, J_{CF} = 278.4 Hz), 50.2 (q, J_{CF} = 26.4 Hz), 35.5, 35.3, 26.9, 24.7, 19.6; MS *m/z* (relative intensity) 152 (2), 113 (16), 69 (56), 56 (100). HRMS calcd. for $C_7H_{11}F_3$ $[M]^+$ 152.0813, found 152.0813.

S3 C. D. Nenitzescu and C. N. Ionescu, *Justus Liebigs Ann. Chem.* 1931, **491**, 189.

(*E*)-1-Ethoxy-2-hexene (4a-H). (*E*)-2-Hexen-1-ol (1.0 g, 10.0 mmol) was added to a suspension of sodium hydride (240 mg, 10.0 mmol) in iodoethane (10 mL) and the mixture was sonicated until the evolution of hydrogen has ceased, after which time it was heated under reflux for 4.5 h. The solid was removed by filtration and the solvent removed *in vacuo* to give a pale oil that was separated by flash chromatography (dichloromethane) and distilled by Kügelrohr to afford the title ether as a colourless oil (300 mg, 23%). Bp ~ 140°/100 mm; ^{1}H NMR δ 5.51 – 5.69 (m, 2H), 3.89 – 3.92 (m, 2H), 3.47 (q, J = 7.1 Hz, 2H), 1.95 – 2.10 (m, 2H), 1.35 – 1.46 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 134.3, 126.7, 71.5, 65.4, 34.5, 22.3, 15.2, 13.7; IR (neat): 1455, 1770 cm^{-1}. (Found: C, 74.8; H, 12.3. $C_8H_{16}O$ requires C, 74.9; H, 12.6%).

(*Z*)-1-Ethoxy-2-hexene (4b-H) was prepared in identical fashion to **4a-H**. Bp ~ 140°/100 mm; ^{1}H NMR δ 5.50 – 5.60 (m, 2H), 4.01 – 4.04 (m, 2H), 3.48 (q, J = 7.1 Hz, 2H), 1.99 – 2.16 (m, 2H), 1.31 – 1.51 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 133.1, 126.5, 66.2, 65.5, 29.6, 22.7, 15.2, 13.7; IR (neat): 1455, 1770 cm^{-1}. (Found: C, 74.9; H, 12.6. $C_8H_{16}O$ requires C, 75.3; H, 12.3%).

(*E*)- and (*Z*)-1-Butyl-2-butylidenecyclopentane (27). Sodium hydride (265 mg, 11.0 mmol) was stirred in DMSO (25 mL) at 70° until the evolution of hydrogen had ceased. *n*-Butyltriphenylphosphonium bromide (4.23 g, 10.6 mmol) in DMSO (10 mL) was added and the red solution stirred at 70°C before cooling to r.t. 2-Butylcyclopentanone[S4] (1.0 g, 7.1 mmol) was added and the mixture stirred at r.t. for 3 h. The mixture was poured into water (300 mL), extracted with pentane (4x), the combined extracts washed with water (2 x), dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by flash chromatography (pentane) to give the title olefin as a colourless oil (275 mg, 29%). Bp ~ 80°/0.1 mm (Kügelrohr); ^{1}H NMR δ 5.14 – 5.22 (m, 1H), 0.8 – 2.58 (m, 23H); ^{13}C NMR δ 147.3, 146.9, 120.7, 119.7, 44.4, 40.3, 34.9, 34.6, 33.5, 33.0, 32.1, 31.7, 31.5, 30.3, 30.2, 29.3, 24.7, 24.2, 23.1, 23.0, 14.8, 14.2, 14.0, 13.9 (both isomers); IR (neat): 1465, 1670 cm^{-1}; MS *m/z* (relative intensity) 118 (16), 123 (45), 95 (45), 81 (100). (Found: C, 86.5; H, 13.9. $C_{13}H_{24}$ requires C, 86.6; H, 13.4%).

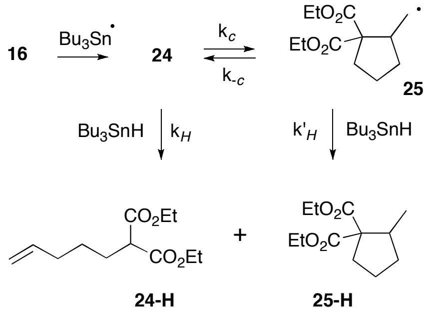
S4 A. Ijima, H. Mizuno and K. Takahashi, *Chem. Pharm. Bull.* 1972, **20**, 197.

***Cis*- and *trans*-1,2-Dibutylcyclopentane (7-H, 8-H)**. The mixture of olefins (**27**) (130 mg, 720 μmol) was dissolved in pentane (1.0 mL), 10% palladium on charcoal (30 mg) added and the mixture stirred under an atmosphere of hydrogen for 2h. Filtration and removal of the solvent *in vacuo* yielded a colourless oil identified as a mixture *cis*-1,2-dibutylcyclopentane (**7-H**, 91%) and *trans*-1,2-dibutylcyclopentane (**8-H**, 9%) by CG (25QC2/BP1) (125 mg, 98%). ^{13}C NMR δ 46.1 (*cis*), 42.6 (*trans*), 35.5 (*trans*), 35.1 (*cis*), 32.5 (*cis*), 32.3 (*trans*), 30.9 (*cis*), 30.2 (*trans*), 29.0 (*trans*), 26.8 (*trans*), 24.0 (*cis*), 23.2 (*cis*), 14.3 (*cis*), 14.1 (*trans*); MS *m/z* (relative intensity) 182 (4), 125 (26), 97 (18), 83 (67), 69 (100). HRMS calcd. for $C_{13}H_{26}$ $[M]^+$ 182.2035, found 182.2034.

Diethyl 2-methylcyclopentane-1,1-dicarboxylate (25-H). Diethyl 1-bromo-5-hexen-1,1-dicarboxylate (100 mg, 325 μmol) was dissolved in benzene (6 mL) and the solvent deoxygenated by bubbling argon through at a moderate rate for 10 min. Tributyltin hydride (90 μL, 330 μmol) and a dew crystals of AIBN were added and the mixture heated at reflux under argon overnight. The mixture was cooled, concentrated at reduced pressure and bromide added until an excess was just evident. The mixture was filtered through a short silica column eluted with dichloromethane and the solvent removed *in vacuo*. The residue was dissolved in pentane (1 mL) and separated by preparative GC (3% OV-17 on GC-Q (80 – 100 mesh) to give the title diester as a colourless oil which was further purified by Kügelrohr distillation. Bp ~ 100°/8 mm (lit[S5]: 120 – 122° / 17.5 mm); ^{1}H NMR δ 4.18 (m, 4H), 2.30 – 2.75 (m, 1H), 1.25 – 2.10 (m, 6H), 1.24 (t, J = 6.6 Hz, 3H), 1.25 (t, J = 6.6 Hz, 3H), 0.99 (d, J = 7.1 Hz, 3H); IR (neat): 1460, 1730 cm^{-1}.

S5 M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.* 1969, 2415.

Derivation of equation 6.



From the scheme above:

$$\frac{d[\mathbf{25}]}{dt} = k_c[\mathbf{24}] - k_{-c}[\mathbf{25}] - k'_H[\mathbf{25}][Bu_3SnH] \quad ...(A)$$

$$\frac{d[\mathbf{24\text{-}H}]}{dt} = k_H[\mathbf{24}][Bu_3SnH] \quad ...(B)$$

$$\frac{d[\mathbf{25\text{-}H}]}{dt} = k'_H[\mathbf{25}][Bu_3SnH] \quad ...(C)$$

Assuming that the equilibrium is steady state, then:

$$\frac{d[\mathbf{25}]}{dt} = 0 = k_c[\mathbf{24}] - k_{-c}[\mathbf{25}] - k'_H[\mathbf{25}][Bu_3SnH]$$

Rearranging:

$$[\mathbf{25}] = \frac{k_c[\mathbf{24}]}{k_{-c} + k'[Bu_3SnH]} \quad ...(D)$$

Combining C and D:

$$\frac{d[\mathbf{25\text{-}H}]}{dt} = \frac{k'_H[Bu_3SnH]\,k_c[\mathbf{24}]}{k_{-c} + k'_H[Bu_3SnH]} \quad ...(E)$$

Combining B and E:

$$\frac{d[\mathbf{24\text{-}H}]}{d[\mathbf{25\text{-}H}]} = \frac{k_H(k_{-c} + k'_H[Bu_3SnH])}{k'_H\,k_c}$$

$$\frac{d[\mathbf{24\text{-}H}]}{d[\mathbf{25\text{-}H}]} = \frac{k_H}{k'_H K_E} + \frac{k_H[Bu_3SnH]}{k_c} \quad ...(F)$$

$(K_E = k_c / k_{-c})$

Integration of F:

$$[\mathbf{24\text{-}H}] = \int_0^{[\mathbf{25\text{-}H}]_f} \frac{k_H}{k'_H K_E} + \frac{k_H[Bu_3SnH]}{k_c}\; d[\mathbf{25\text{-}H}]$$

Solving (integrating by parts):

$$[\mathbf{25\text{-}H}]_f = r\ln\left(\frac{[Bu_3SnH]_o}{r(1 + 1/K_E)} + 1\right) \quad ...(G)$$

$(r = k_c / k_H)$

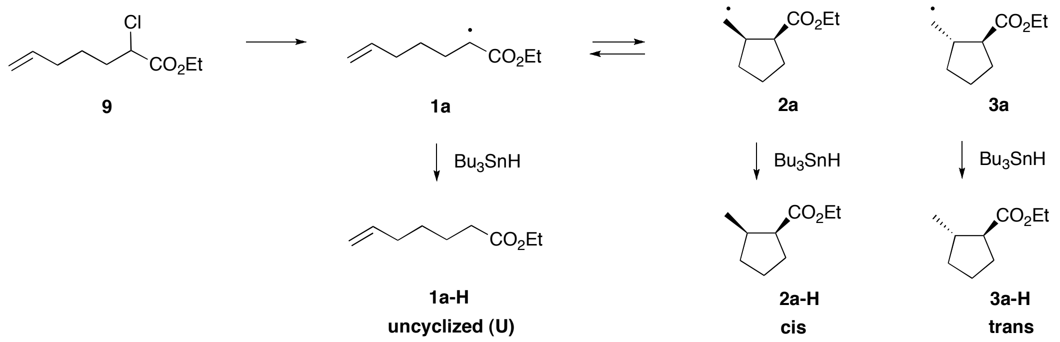
Application of the first two terms of the Taylor series:

$$\ln(x) = \sum_{n=1}^{\infty} \frac{x^n(-1)^{n+x}}{n}$$

Leads to:

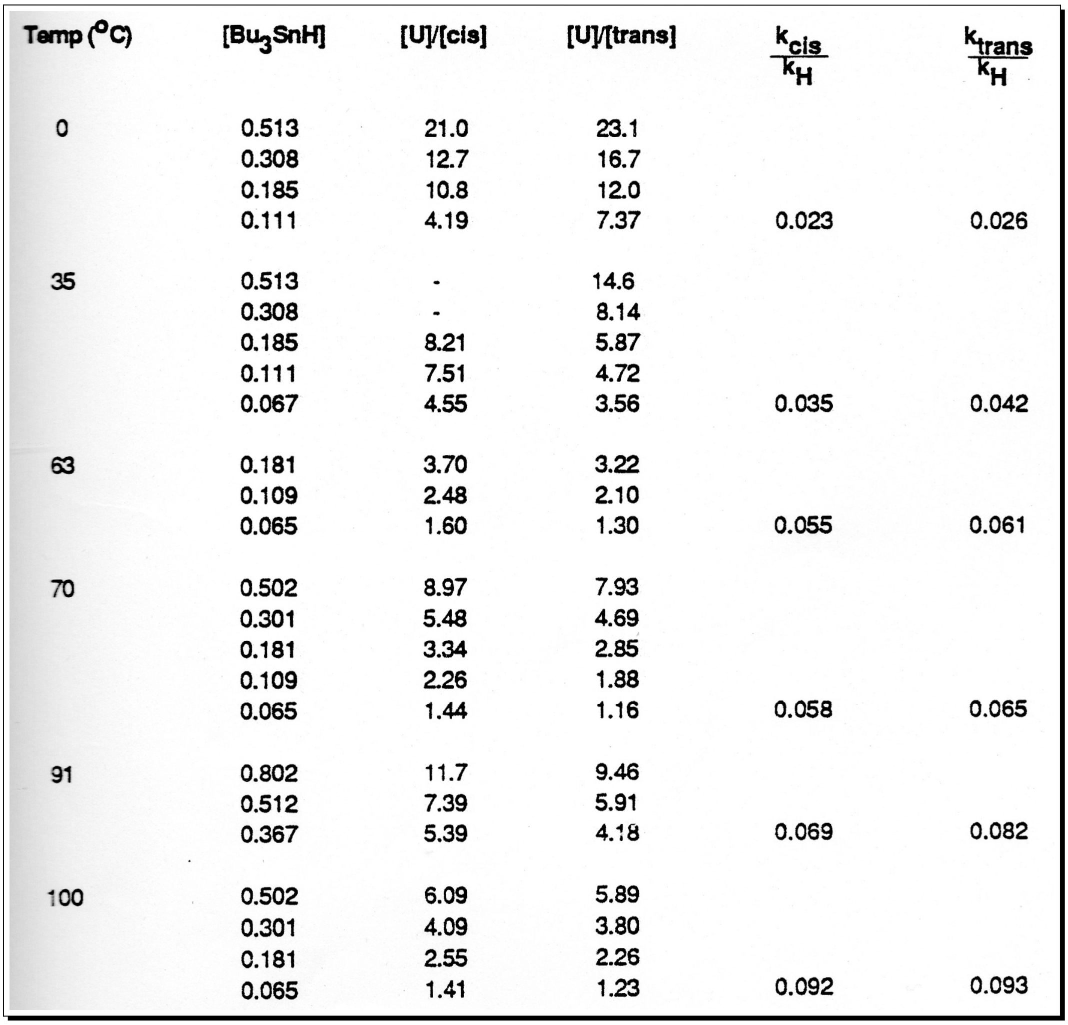
$$\frac{1}{[\mathbf{25\text{-}H}]_f} = \frac{1}{2r} + \frac{1 + 1/K_E}{[Bu_3SnH]_o} \quad \text{... equation (6)}$$

1-(Ethoxycarbonyl)-5-hexen-1-yl radical (1a).



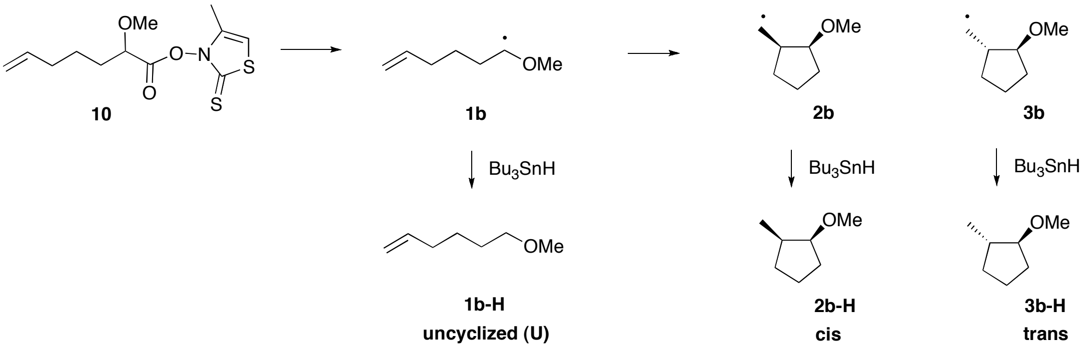
Experimental method: A
Analytical GC performed with: **SGE–SCOT GSC/SF96**
Solvent: **Benzene**
Reaction time: **overnight**

Kinetic analysis: **equation 4**



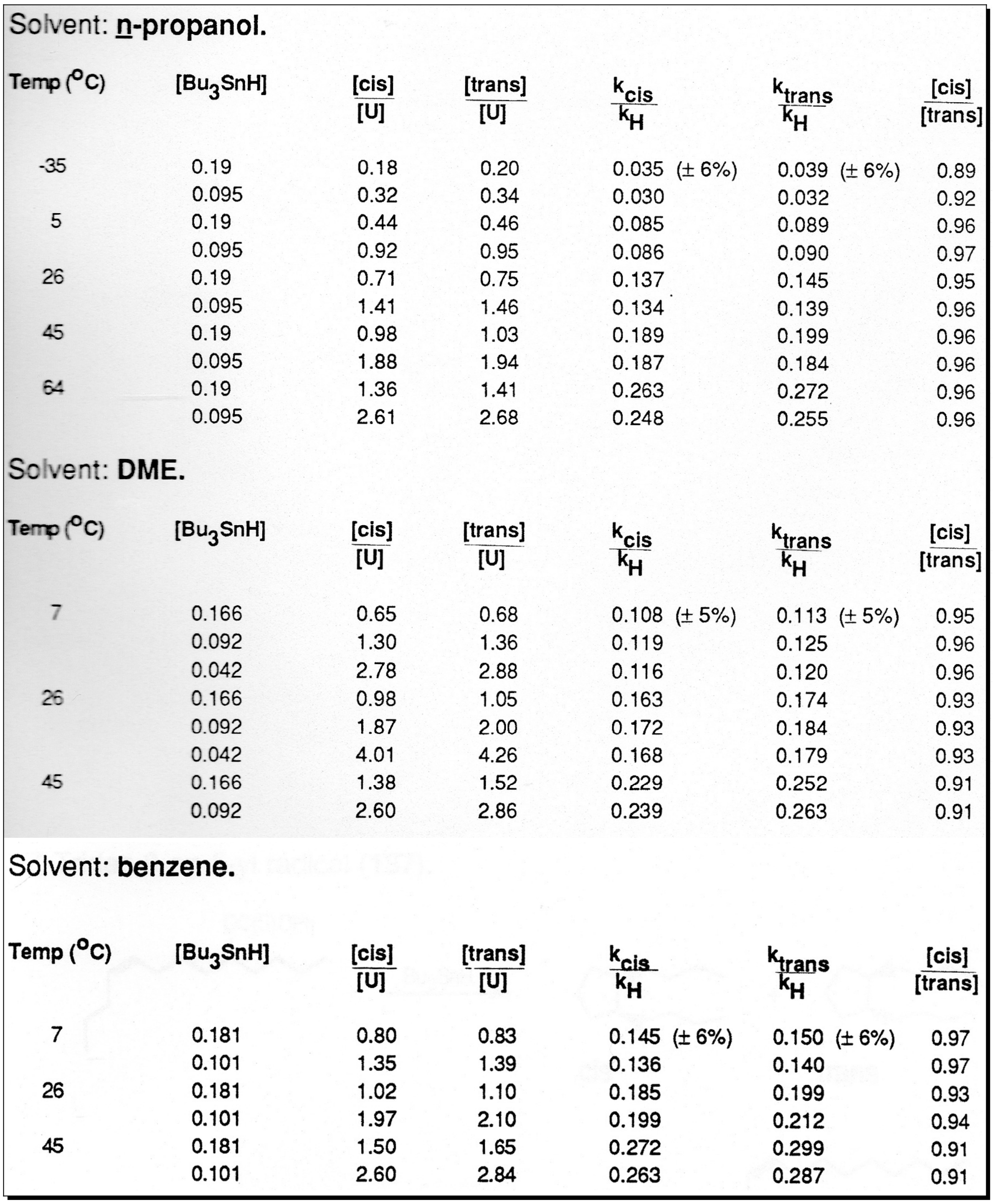
Temp (^oC)	[Bu_3SnH]	[U]/[cis]	[U]/[trans]	$\frac{k_{cis}}{k_H}$	$\frac{k_{trans}}{k_H}$
0	0.513	21.0	23.1		
	0.308	12.7	16.7		
	0.185	10.8	12.0		
	0.111	4.19	7.37	0.023	0.026
35	0.513	-	14.6		
	0.308	-	8.14		
	0.185	8.21	5.87		
	0.111	7.51	4.72		
	0.067	4.55	3.56	0.035	0.042
63	0.181	3.70	3.22		
	0.109	2.48	2.10		
	0.065	1.60	1.30	0.055	0.061
70	0.502	8.97	7.93		
	0.301	5.48	4.69		
	0.181	3.34	2.85		
	0.109	2.26	1.88		
	0.065	1.44	1.16	0.058	0.065
91	0.802	11.7	9.46		
	0.512	7.39	5.91		
	0.367	5.39	4.18	0.069	0.082
100	0.502	6.09	5.89		
	0.301	4.09	3.80		
	0.181	2.55	2.26		
	0.065	1.41	1.23	0.092	0.093

1-Methoxy-5-hexen-1-yl radical (1b).



Experimental method: A
Analytical GC performed with: **SGE–25QC2/BP1 1.0**
Reaction time: **1 – 2 h**

Kinetic analysis: **equation 2**



Solvent: **n-propanol.**

Temp (°C)	$[Bu_3SnH]$	[cis]/[U]	[trans]/[U]	k_{cis}/k_H	k_{trans}/k_H	[cis]/[trans]
-35	0.19	0.18	0.20	0.035 (± 6%)	0.039 (± 6%)	0.89
	0.095	0.32	0.34	0.030	0.032	0.92
5	0.19	0.44	0.46	0.085	0.089	0.96
	0.095	0.92	0.95	0.086	0.090	0.97
26	0.19	0.71	0.75	0.137	0.145	0.95
	0.095	1.41	1.46	0.134	0.139	0.96
45	0.19	0.98	1.03	0.189	0.199	0.96
	0.095	1.88	1.94	0.187	0.184	0.96
64	0.19	1.36	1.41	0.263	0.272	0.96
	0.095	2.61	2.68	0.248	0.255	0.96

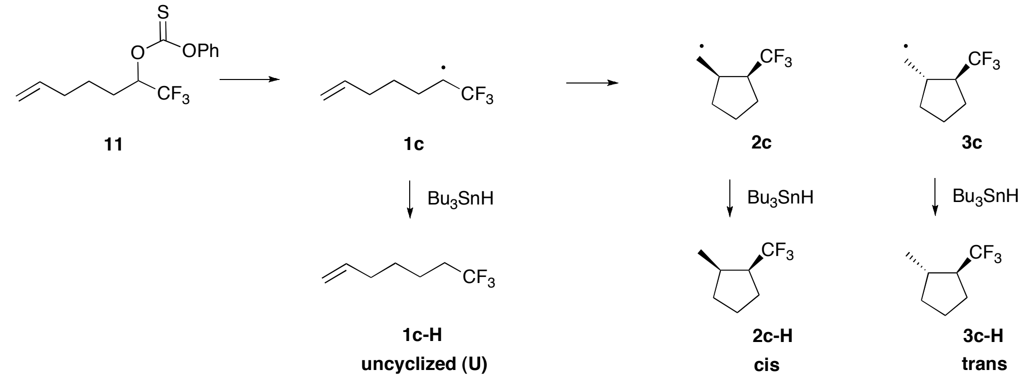
Solvent: **DME.**

Temp (°C)	$[Bu_3SnH]$	[cis]/[U]	[trans]/[U]	k_{cis}/k_H	k_{trans}/k_H	[cis]/[trans]
7	0.166	0.65	0.68	0.108 (± 5%)	0.113 (± 5%)	0.95
	0.092	1.30	1.36	0.119	0.125	0.96
	0.042	2.78	2.88	0.116	0.120	0.96
26	0.166	0.98	1.05	0.163	0.174	0.93
	0.092	1.87	2.00	0.172	0.184	0.93
	0.042	4.01	4.26	0.168	0.179	0.93
45	0.166	1.38	1.52	0.229	0.252	0.91
	0.092	2.60	2.86	0.239	0.263	0.91

Solvent: **benzene.**

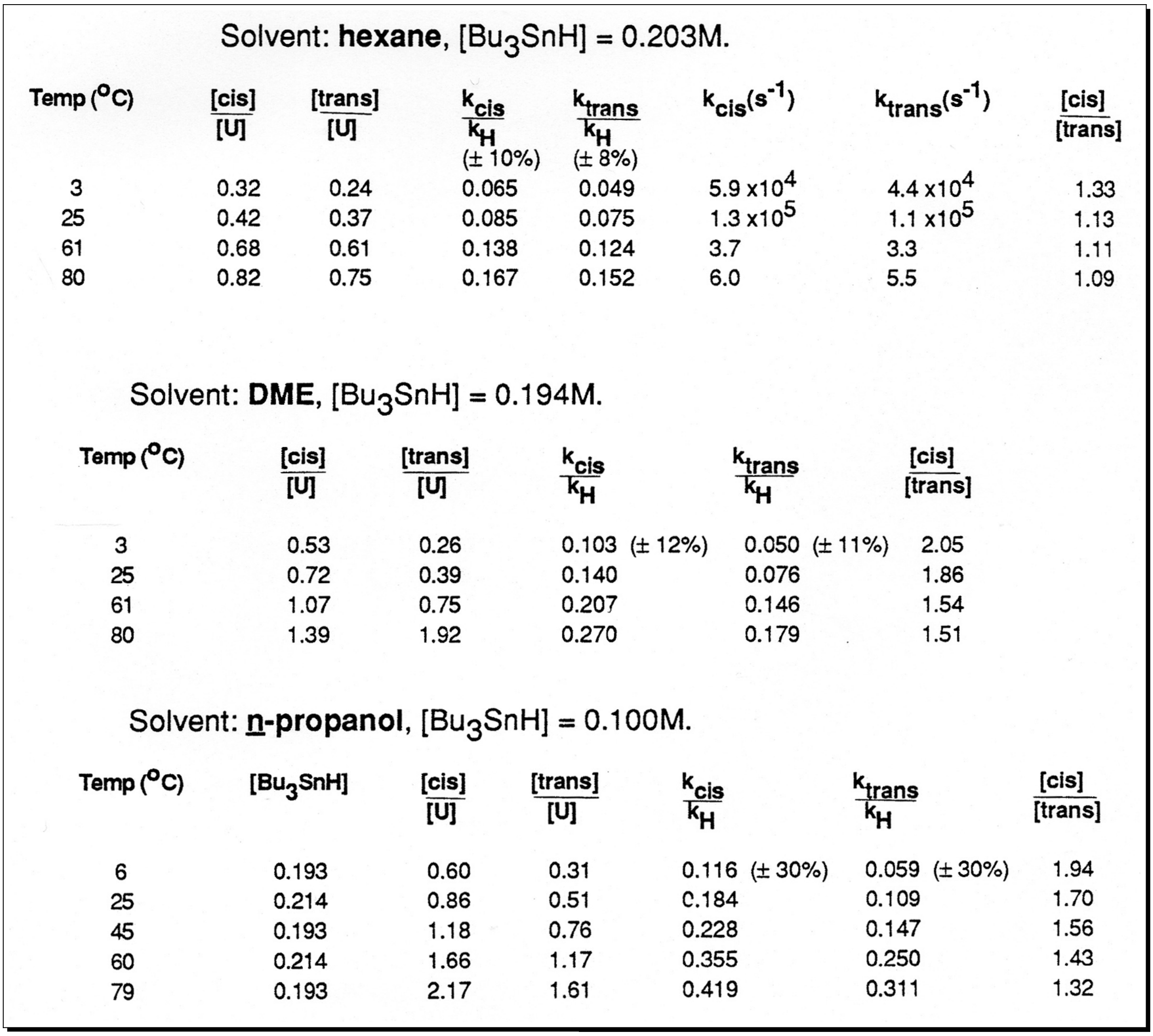
Temp (°C)	$[Bu_3SnH]$	[cis]/[U]	[trans]/[U]	k_{cis}/k_H	k_{trans}/k_H	[cis]/[trans]
7	0.181	0.80	0.83	0.145 (± 6%)	0.150 (± 6%)	0.97
	0.101	1.35	1.39	0.136	0.140	0.97
26	0.181	1.02	1.10	0.185	0.199	0.93
	0.101	1.97	2.10	0.199	0.212	0.94
45	0.181	1.50	1.65	0.272	0.299	0.91
	0.101	2.60	2.84	0.263	0.287	0.91

1-(Trifluoromethyl)-5-hexen-1-yl radical (1c).



Experimental method: A
Analytical GC performed with: **SGE–25QC2/BP1 1.0**
Reaction time: **4 – 6 h**

Kinetic analysis: **equation 2**



Solvent: **hexane**, $[Bu_3SnH] = 0.203M$.

Temp (°C)	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$ (± 10%)	$\frac{k_{trans}}{k_H}$ (± 8%)	$k_{cis}(s^{-1})$	$k_{trans}(s^{-1})$	$\frac{[cis]}{[trans]}$
3	0.32	0.24	0.065	0.049	5.9×10^4	4.4×10^4	1.33
25	0.42	0.37	0.085	0.075	1.3×10^5	1.1×10^5	1.13
61	0.68	0.61	0.138	0.124	3.7	3.3	1.11
80	0.82	0.75	0.167	0.152	6.0	5.5	1.09

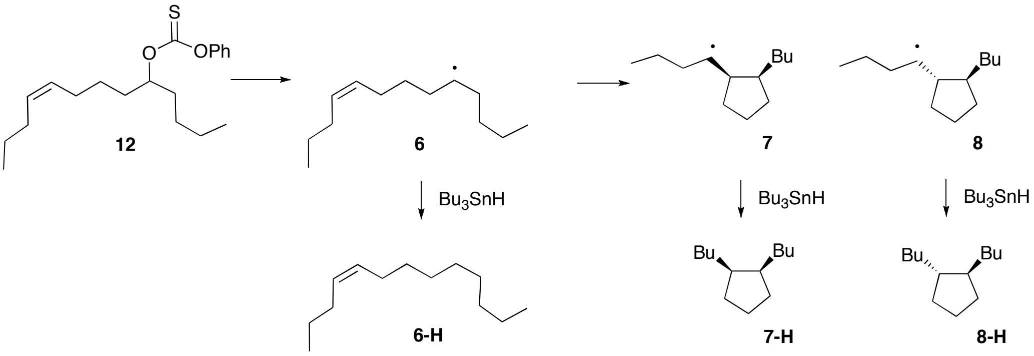
Solvent: **DME**, $[Bu_3SnH] = 0.194M$.

Temp (°C)	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$	$\frac{k_{trans}}{k_H}$	$\frac{[cis]}{[trans]}$
3	0.53	0.26	0.103 (± 12%)	0.050 (± 11%)	2.05
25	0.72	0.39	0.140	0.076	1.86
61	1.07	0.75	0.207	0.146	1.54
80	1.39	1.92	0.270	0.179	1.51

Solvent: **n-propanol**, $[Bu_3SnH] = 0.100M$.

Temp (°C)	$[Bu_3SnH]$	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$	$\frac{k_{trans}}{k_H}$	$\frac{[cis]}{[trans]}$
6	0.193	0.60	0.31	0.116 (± 30%)	0.059 (± 30%)	1.94
25	0.214	0.86	0.51	0.184	0.109	1.70
45	0.193	1.18	0.76	0.228	0.147	1.56
60	0.214	1.66	1.17	0.355	0.250	1.43
79	0.193	2.17	1.61	0.419	0.311	1.32

(*Z*)-9-Tritridecen-5-yl radical (6).



12 **6** **7** **8**

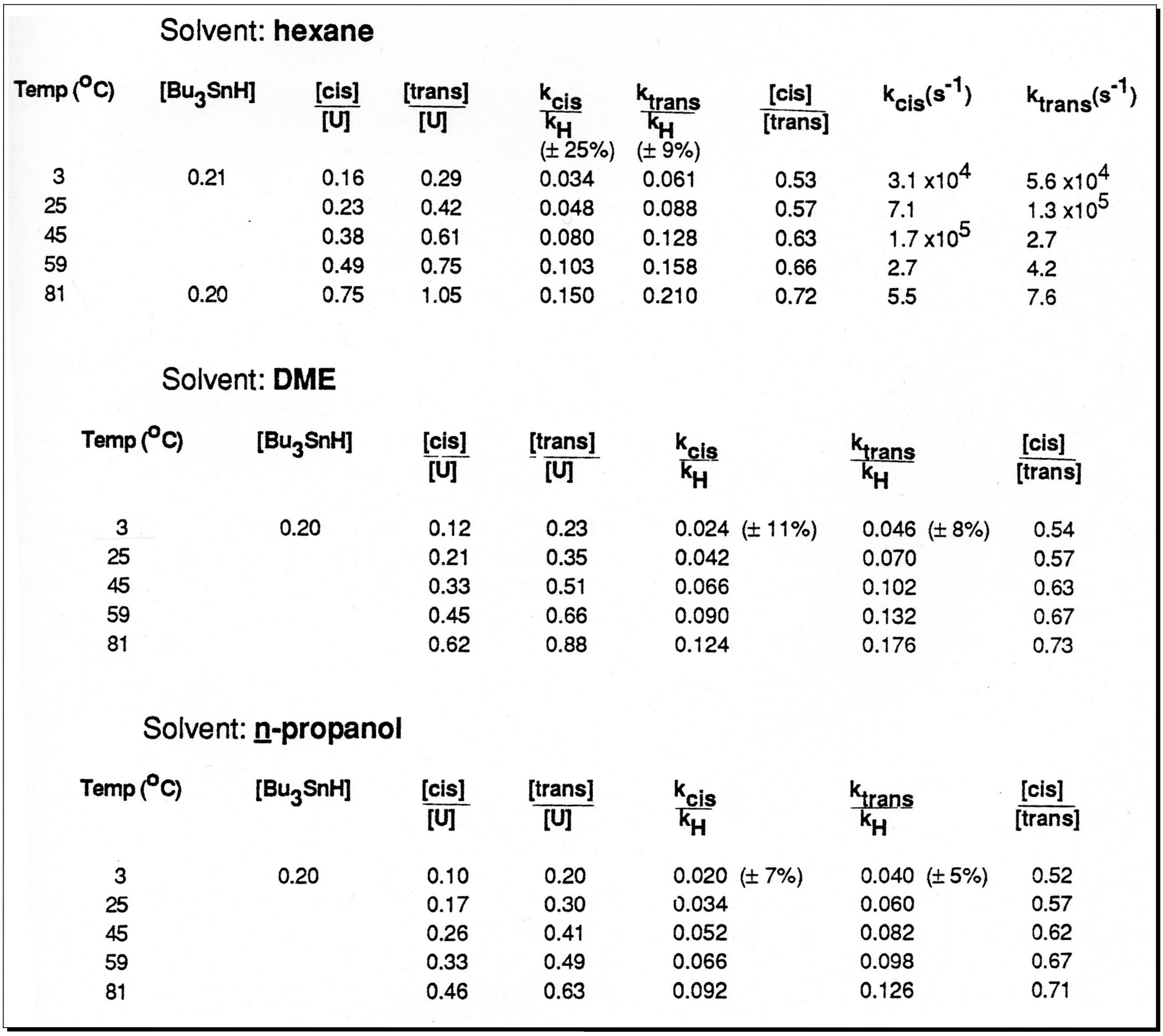
6-H
uncyclized (U)

7-H
cis

8-H
trans

Experimental method: A
Analytical GC performed with: **SGE–25QC2/BP1 1.0**
Reaction time: **4 – 6 h**

Kinetic analysis: **equation 2**



Solvent: **hexane**

Temp (^oC)	[Bu_3SnH]	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$ (± 25%)	$\frac{k_{trans}}{k_H}$ (± 9%)	$\frac{[cis]}{[trans]}$	$k_{cis}(s^{-1})$	$k_{trans}(s^{-1})$
3	0.21	0.16	0.29	0.034	0.061	0.53	3.1×10^4	5.6×10^4
25		0.23	0.42	0.048	0.088	0.57	7.1	1.3×10^5
45		0.38	0.61	0.080	0.128	0.63	1.7×10^5	2.7
59		0.49	0.75	0.103	0.158	0.66	2.7	4.2
81	0.20	0.75	1.05	0.150	0.210	0.72	5.5	7.6

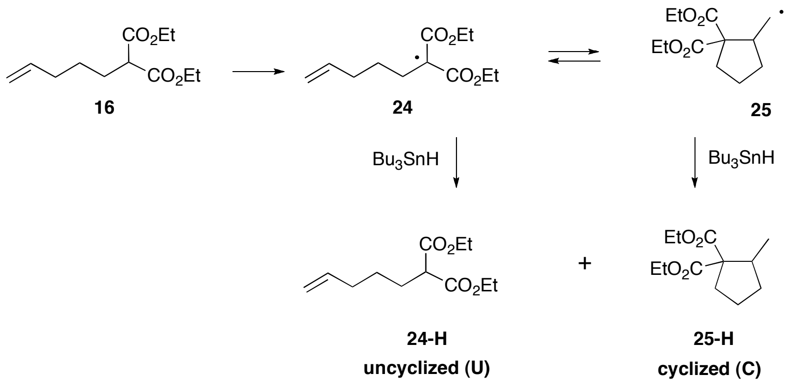
Solvent: **DME**

Temp (^oC)	[Bu_3SnH]	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$	$\frac{k_{trans}}{k_H}$	$\frac{[cis]}{[trans]}$
3	0.20	0.12	0.23	0.024 (± 11%)	0.046 (± 8%)	0.54
25		0.21	0.35	0.042	0.070	0.57
45		0.33	0.51	0.066	0.102	0.63
59		0.45	0.66	0.090	0.132	0.67
81		0.62	0.88	0.124	0.176	0.73

Solvent: n-propanol

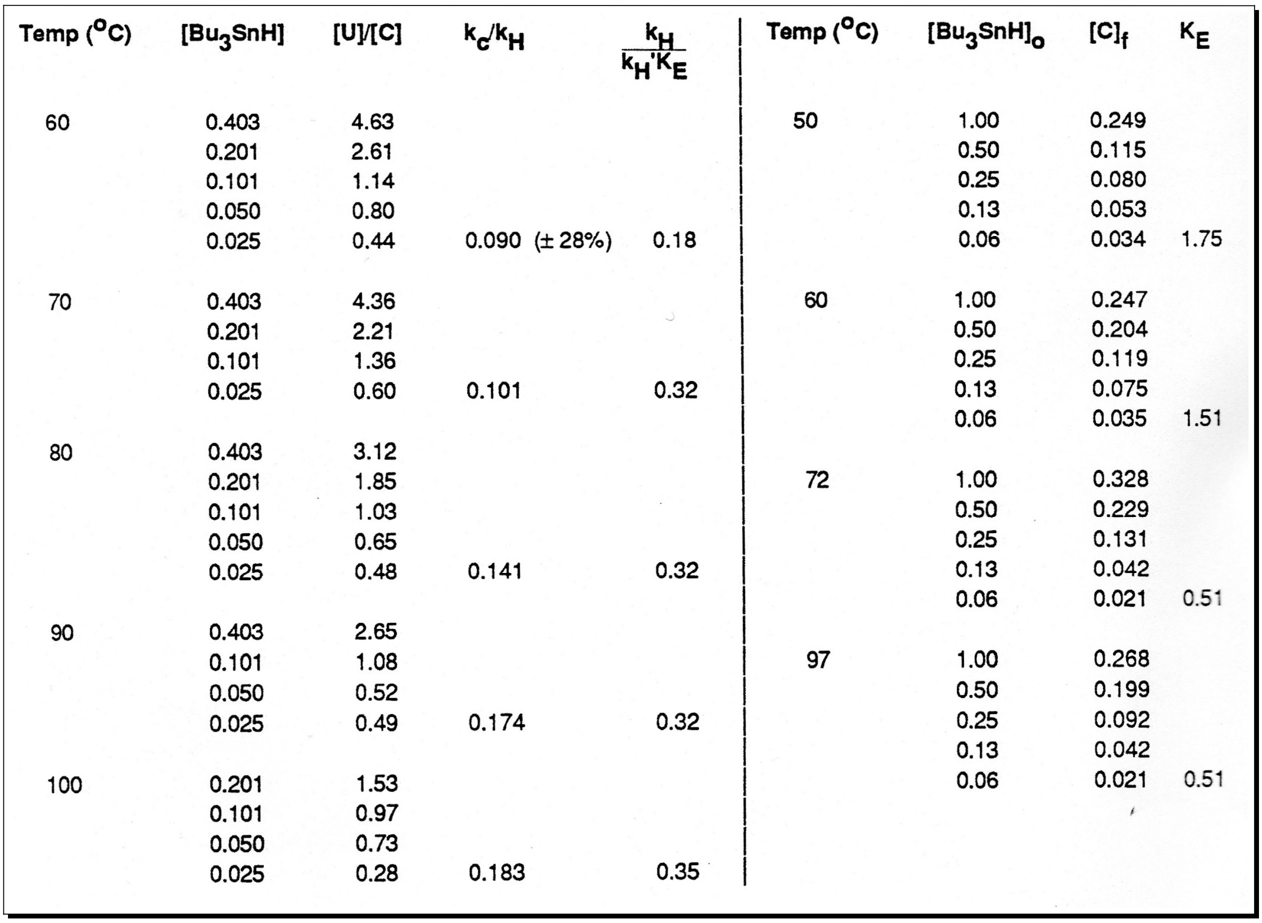
Temp (^oC)	[Bu_3SnH]	$\frac{[cis]}{[U]}$	$\frac{[trans]}{[U]}$	$\frac{k_{cis}}{k_H}$	$\frac{k_{trans}}{k_H}$	$\frac{[cis]}{[trans]}$
3	0.20	0.10	0.20	0.020 (± 7%)	0.040 (± 5%)	0.52
25		0.17	0.30	0.034	0.060	0.57
45		0.26	0.41	0.052	0.082	0.62
59		0.33	0.49	0.066	0.098	0.67
81		0.46	0.63	0.092	0.126	0.71

1,1-(Diethoxycarbonyl)-5-hexen-1-yl radical (24).



Experimental method: A, C
Analytical GC performed with: **SGE–SCOT GSD Apiezon L**
Solvent: **Benzene**
Reaction time: **overnight**

Kinetic analysis: **equations 4 and 6**



Using method A and equation 4

Temp (°C)	[Bu_3SnH]	[U]/[C]	k_c/k_H	$\frac{k_H}{k_H'K_E}$
60	0.403	4.63		
	0.201	2.61		
	0.101	1.14		
	0.050	0.80		
	0.025	0.44	0.090 (± 28%)	0.18
70	0.403	4.36		
	0.201	2.21		
	0.101	1.36		
	0.025	0.60	0.101	0.32
80	0.403	3.12		
	0.201	1.85		
	0.101	1.03		
	0.050	0.65		
	0.025	0.48	0.141	0.32
90	0.403	2.65		
	0.101	1.08		
	0.050	0.52		
	0.025	0.49	0.174	0.32
100	0.201	1.53		
	0.101	0.97		
	0.050	0.73		
	0.025	0.28	0.183	0.35

Using method C and equation 6

Temp (°C)	[Bu_3SnH]$_o$	[C]$_f$	K_E
50	1.00	0.249	
	0.50	0.115	
	0.25	0.080	
	0.13	0.053	
	0.06	0.034	1.75
60	1.00	0.247	
	0.50	0.204	
	0.25	0.119	
	0.13	0.075	
	0.06	0.035	1.51
72	1.00	0.328	
	0.50	0.229	
	0.25	0.131	
	0.13	0.042	
	0.06	0.021	0.51
97	1.00	0.268	
	0.50	0.199	
	0.25	0.092	
	0.13	0.042	
	0.06	0.021	0.51