probably to the smaller deviation from planarity of the s-trans form. Thus in methanol we observe the temperature-dependent equilibrium between the chiral s-cis forms the calculated value of 2.0 kJ/mol representing the free energy difference between the two conformers involved. In isopentane the s-cis portion of **1** becomes dominant at the cost of s-trans only at lower temperatures, and only then do we observe the development of the prominent CD band at 267 nm.

The spectra of **2** confirm our hypothesis up to a point. The extinction coefficient in isopentane decreases most rapidly between −30 and −60 °C, reaching the low methanol value already at −70 °C. This behavior is reflected in the temperature-dependent CD spectra (Figure 1). The negative band at 269 nm grows much faster than in **1** resulting in a rotational strength of -1.7×10^{-39} cgs already at −60 °C. At lower temperatures there appears another band with opposite sign the intensity of which increases at the expense of the negative band. In methanol the CD spectra of **2** exhibit only this band at 259 nm, with the amplitude slowly increasing upon cooling. At −90 °C $\Delta\epsilon$ is about one-fifth the value in isopentane at −140 °C.

These spectra indicate that in isopentane at temperatures down to −60 °C the same equilibrium between chiral s-cis forms is involved as in **1**. Then a second equilibrium begins to establish itself, which completely takes over from about −140 °C on. The nature of the conformers involved is still unknown to us. Since no absorptivity change in the UV spectrum is observed they should be s-cis conformers with reserved stabilities of the opposite helicities caused perhaps by hydrogen bonding.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

Registry No. 1, 91112-30-0; **2**, 91112-31-1; β-cyclocitral, 432-25-7; (*S*)-$NH_2CH(CH_3)CH_2CH_3$, 513-49-5; (*S*)-$NH_2CH(CH_3)CH_2OH$, 2749-11-3.

Supplementary Material Available: Plot of the dependence of UV extintion on temperature and CD spectra of **1** in methanol and isopentane (1 page). Ordering information is given on any current masthead page.

Alkylation of β-Substituted Styrenes by a Free Radical Addition–Elimination Sequence[1]

Glen A. Russell,* Hasan Tashtoush,[2] and
Preecha Ngoviwatchai

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received April 16, 1984

We have found that the β-styrenyl or β,β-diphenylvinyl derivatives **1** and **2** undergo a free radical chain reaction with al-

(*E*)-$PhCH{=}CHQ$ **1** $Ph_2C{=}CHQ$ **2** $PhCH{=}CHR$ **3**

$Ph_2C{=}CHR$ **4**

a, Q = Bu_3Sn; **b**, Q = HgCl; **c**, Q = HgBr; **d**, Q= I; **e**, Q = $PhSO_2$; **f**, Q = PhSO; **g**, Q = PhS

kylmercury halides (RHgX) to yield alkenes **3** and **4** (Table I). The reaction involves regioselective addition of R· to **1** or **2** followed by the β-elimination of Q·. The chain reaction continues by virtue of the attack of Q· upon RHgX to regenerate the alkyl radical by either S_H2 attack upon Hg for Q· = I·, PhS·, PhSO·, $PhSO_2$· or electron transfer and/or halogen atom transfer from RHgX to Q· in the case of Bu_3Sn· or HgCl (Scheme I).[3,4] The

Table I. **1** or **2** + RHgCl → **3** or **4**

substrate	R (equiv)	conditions[a]	% **3** or **4** (*E*/*Z*)
1a	*i*-Pr (1.2)	PhH, S, 18 h	86 (11.5)
1a	*i*-Pr (1.2)	PhH, AIBN, 80 °C, 16 h	73 (15)
1a	*i*-Pr (1.2)	PhH, dark, 50 °C	0
1a	*i*-Pr (1.2)	PhH, S, DTNO, 16 h	35 (10)
1a	*i*-PrI (5)	PhH, R, 15 h	18
1b	*i*-Pr (5)	Me_2SO, R, 12 h	83
1d	*i*-Pr (2)	Me_2SO, R, 14 h	76 (10)
1d	*i*-Pr (2)	Me_2SO, Bz_2O_2, 100 °C	68 (19)
1d	*i*-Pr (2)	Me_2SO, dark, 25 °C	0
1e	*i*-Pr (2)	Me_2SO, R, 38 h	68 (6)
1f	*i*-Pr (5)	Me_2SO, R	20
1g	*i*-Pr (5)	Me_2SO, R, 18 h	35[b] (6.5)
2a	*i*-Pr (5)	PhH, R, 28 h	73
2c	*i*-Pr (5)	Me_2SO, R, 12 h	96
2c	*i*-PrMgBr (2)	PhH, R	35
2d	*i*-Pr (5)	Me_2SO, R, 8 h	89
2e	*i*-Pr (2)	Me_2SO, R	62
2e	*i*-Pr (5)	Me_2SO, R	87
2g	*i*-Pr (5)	Me_2SO, R, 96 h	55[c]
5	*i*-Pr (5)	Me_2SO, R	55[d]
6	*i*-Pr (5)	Me_2SO, R, 38 h	35[d]
1a	*t*-Bu (1.2)	PhH, S, 14 h	83 (49)
1a	*t*-BuBr (5)	PhH, AIBN, 80 °C	0
1a	*t*-BuBr (5)	PhH, R	0
1b	*t*-Bu (5)	Me_2SO, R, 12 h	40
1e	*t*-Bu (2)	Me_2SO, R, 16 h	43 (81)
1f	*t*-Bu (5)	Me_2SO, R	32
2a	*t*-Bu (2)	PhH, 18 h	78
2a	*t*-BuBr (5)	PhH, R	0
2c	*t*-Bu (5)	Me_2SO, R, 12 h	100
2d	*t*-Bu (5)	Me_2SO, R, 14 h	86
2e	*t*-Bu (5)	Me_2SO, R	88
1a	*n*-Bu (1.2)	PhH, R, 40 h	46 (6)
1a	*n*-BuI (2)	PhH, R, 30 h	62 (7)
1d	*n*-Bu (2)	Me_2SO, R, 48 h	22
5	*n*-Bu (5)	Me_2SO, R, 43 h	38[d]
1a	Δ^5-C_6H_{11} (1.2)	PhH, 32 h	55[e] (7)
1a	*c*-$C_5H_9CH_2$ (1.2)	PhH, R, 48 h	52[e] (6)
1a	Δ^3-C_4H_7 (1.2)	PhH, R, 36 h	45 (7)
1a	Cl_3CCl	CCl_4, R, 38 h	62 (19)
1a	MeO_2CCH_2Br	PhH, R, 44 h	38 (5)
1b	$(EtO)_2PO$ (1)[f]	Me_2SO, R, 8 h	65 (10)
1d	$(EtO)_2PO$ (1)[f]	Me_2SO, R, 8 h	85
2a	$(EtO)_2PO$ (3)	Me_2SO, R	65
2a	$(EtO)_2PO$ (1)[g]	Me_2SO, R	14
2c	$(EtO)_2PO$ (1)[f]	Me_2SO, R, 12 h	85
2c	$(EtO)_2PO$ (3)	Me_2SO, R, 2 h	59
2c	$(EtO)_2PO$ (3)	Me_2SO, R, DTNO, 2h	0
2d	$(EtO)_2PO$ (3)	Me_2SO, R, 2h	84
2d	$(EtO)_2PO$ (1)[g]	Me_2SO, R	86
2d	$(EtO)_2PO$ (1)[g]	Me_2SO, dark	0
2c	*c*-C_6H_{11} (1)[h]	PhH, S, 18	36
2b	*c*-C_6H_{11} (5)[h]	PhH, R, 2 h	37
2e	*c*-C_6C_{11} (5)[h]	PhH, R	23
1f	*c*-C_6H_{11} (5)[h]	PhH, R	33
1d	PhS (1)[i]	Me_2SO, R	97
2d	PhS (1)[i]	Me_2SO, R	100
2c	$PhSO_2$ (5)[j]	Me_2SO, R, 12 h	100
2c	$PhCOCH_2$ (1)[k]	Me_2SO, R, 13 h	64

[a] Typical conditions involved 1 mmol of substrate in 10 mL of nitrogen-purged solvent at 35–40 °C for 24 h unless otherwise specified: S = radiation by a 275-W sunlamp; R, radiation in a Rayonet reactor at 350 nm; DTNO = 10 mol% di-*tert*-butyl nitroxide; AIBN = azobisisobutyronitrile; Bz_2O_2 = benzoyl peroxide. [b] A 50% yield of *i*-PrSPh observed. [c] 26% yield of *i*-PrSPh. [d] 2-Alkylbenzothiazole (7). [e] Only cyclopentylcarbinyl product observed. [f] $(EtO)_2POHgCl$ or $((EtO)_2PO)_2Hg$. [g] $((EtO)_2PO)_2Hg$. [h] $(c\text{-}C_6H_{11})_3B$. [i] $(PhS)_2Hg$. [j] $(PhSO_2)_2Hg$. [k] $(PhCOCH_2)_2Hg$.

---

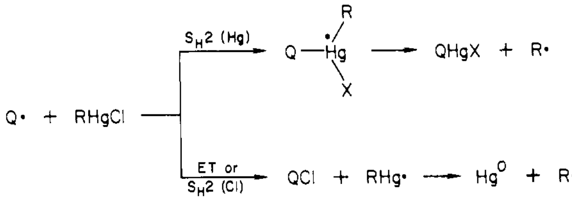
[1] Supported by Grant CHE-8119343 from the National Science Foundation.

[2] Supported by a scholarship from Yarmouk University, Irbid, Jordan, 1980–1983.

[3] Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.

0002-7863/84/1506-4622$01.50/0

Scheme I



coupling products **3** or **4** are formed (R = 1°, 2°, or 3° alkyl) without contamination by the dimers R–R, $(PhCH{=}CH)_2$, or $(Ph_2C{=}CH)_2$.[5]

Evidence for the free radical chain follows from the observed photostimulation and initiation by AIBN or Bz_2O_2, the inhibitory effect of di-*tert*-butyl nitroxide, and the rearrangement of R = Δ^5-hexenyl to cyclopentylcarbinyl. The photostimulated reactions proceed more readily with R = *tert*-butyl than for R = isopropyl and more rapidly with 2° alkylmercurials than with 1° alkylmercurials. This reactivity sequence appears to reflect the efficiencies of the steps in which R· is formed in Scheme I although the rate of the photoinitiation process may also be involved. Mercurials can also provide heterocentered radicals by the reactions of Scheme I. Thus, $((EtO)_2PO)_2Hg$ or $(EtO)_2POHgCl$ forms the vinyl phosphonate in photostimulated chain reactions with **1** or **2** (Q = Bu_3Sn, HgX, I) (Table I) while $(PhSO_2)_2Hg$ or $(PhS)_2Hg$ give chain reactions forming the vinyl sulfones or sulfides.[6]

Tributyl-1-alkenyltins, including **1a**, have been reported to undergo a thermal substitution reaction with Br– or $I{-}CH_2CO_2Et$ to give the β,γ-unsaturated ester in low yield.[7] This reaction can be photostimulated and substitution also occurs with *n*-BuI (Table I). However, reactions of **1a** or **2a** with isopropyl iodide or *tert*-butyl bromide with photostimulation or AIBN initiation are ineffective and only low yields of **3** or **4** can be detected.[8] On the other hand, **3** or **4** with R = CCl_3 are readily formed by the reaction of **1a** or **2a** with CCl_4, $BrCCl_3$, or CCl_3SO_2Cl.

The chain reaction of 1-alkenylmercurials with heterocentered radicals has been previously reported.[9] The 1-alkenyltin derivatives, with or without 2-phenyl substituents, also react by the free radical chain reaction of eq 1 with Q–Y reagents such as

$$(R_1)(R_2)C{=}CHMXn + Q{-}Y \xrightarrow[\text{AIBN}]{h\nu\text{ or}} (R_1)(R_2)C{=}CHQ + YMXn \quad (1)$$

RS–SR, $PhSO_2{-}Cl$, or $p\text{-}MeC_6H_4SO_2{-}SePh$. However, whereas PhSeSePh is reactive when MXn = HgCl, the reaction fails to occur with the corresponding 1-alkenyltins (MXn = $SnBu_3$). Competition studies support the conclusion that the 1-alkenylmercurials are more reactive than the 1-alkenyltins and that PhSe· will add to **1b**,**c** but not to **1a** at 35 °C.

Alkylmercury halides can also be substituted for alkyl halides in the free radical chain S_H2' substitution reaction with alkylstannanes[10] and with stannyl enol ethers. Some aromatic systems such as 2-substituted benzothiazoles (**5** = 2-iodo, **6** = 2-(phenylsulfonyl)) will also react with RHgX by the addition–elimination sequence to form the 2-alkylbenzothiazole (**7**) (Table I). The alkenes **1** or **2** with Q = HgX, $PhSO_2$, or PhSO also react with R_3B to yield **3** or **4** by a chain sequence inhibited by $(t\text{-}Bu)_2NO\cdot$, which most likely involves regioselective addition of R· to the styrenyl system rather than the formation of the β-styrenyl radical as suggested previously.[11]

---

[4] Russell, G. A.; Hershberger, J.; Owens, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312.

[5] Except when R = $PhCH_2\cdot$ where bibenzyl is the major product from the S_H2 substitution reaction, $PhCH_2\cdot + PhCH_2HgCl \rightarrow PhCH_2CH_2Ph + HgCl$.[3]

[6] Reactions of 1-alkenylmercury halides with R_2Hg (R = $(EtO)_2PO$, $PhSO_2$, PhS, $PhCOCH_2$) may form the (1-alkenyl)HgR as an intermediate which decomposes in a photostimulated free radical addition–elimination reaction in which the elimination fragment (RHg) decomposes to form R· and Hg°. Formation of $PhCH{=}CHHgR$ or $Ph_2C{=}CHHgR$ may also be involved in the reaction of **1b** or **2c** with RHgX, RMgX, or R_3B (Table I).

[7] Saihi, M. L.; Pereyre, M. *Bull. Soc. Chem. Fr.* **1973**, 1251.

[8] The reaction of ethyl β-tributylstannylacrylate with a dihydrooxazole derivative of bromocyclopentane (86 °C, $PhCH_3$, in the presence of hexabutylditin) has been recently reported to give an excellent yield of the substitution product: Baldwin, J. E.; Kelly, D. R.; Ziegler, C. B. *J. Chem. Soc., Chem. Commun.* **1984**, 133.

[9] Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.

[10] Kosugi, M.; Kurino, K.; Takayama, K.; Migita, T. *J. Organomet. Chem.* **1973**, *56*, C11. Grignon, J.; Pereyre, M. *Ibid.* **1973**, *61*, C33. Grignon, J.; Servens, C.; Pereyre, M. *Ibid.* **1975**, *96*, 225. Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829.

[11] Miyamoto, N.; Fukuoda, D.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 503.

Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase. The Bond Energy of $FeCo^+$

D. B. Jacobson and B. S. Freiser*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received March 30, 1984

Transition-metal clusters[1] have been the focus of intense experimental[2,3] and theoretical[4] investigations due to their important role in catalysis. Gas-phase ion techniques are ideally suited for studying size-selected metal cluster ions. To date these cluster ions have been generated by either electron impact or multiphoton ionization,[5] typically on multinuclear carbonyl complexes. The former method has been employed, for example, to generate and study the gas-phase chemistry of Co_2^+ and Mn_2^+ by ion cyclotron resonance spectrometry[6] and ion beam techniques.[7]

In this report we describe a general technique for in situ synthesis and subsequent study of metal cluster ions using Fourier transform mass spectrometry–collision induced dissociation (FTMS–CID). This technique promises to greatly extend the variety and size of metal clusters now accessible by electron impact and multiphoton ionization. The methodology is demonstrated for $FeCo^+$ with use of a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer[8,9] equipped with laser ionization.[10]

Transition-metal ions and metal–carbonyl fragment ions react rapidly with the parent metal carbonyl in the gas phase generating cluster ions.[11-13] Laser-desorbed cobalt and iron cations react

---

[1] For a recent review of metal clusters, see: Faraday Discussions of the Royal Society of Chemistry, Faraday Symposium No. 14. 1980 "Diatomic Metals and Metallic Clusters".

[2] (a) Ford, T. A.; Huber, H.; Klotzbucher, W.; Kundig, E. P.; Moskovits, M.; Ozin, G. A. *J. Chem. Phys.* **1977**, *66*, 524. (b) Moskovits, M.; Hulse, J. E. *J. Chem. Phys.* **1977**, *66*, 3988.

[3] (a) Miedema, A. R.; Gingerich, K. A. *J. Phys. B* **1979**, *12*, 2081. (b) Miedema, A. R.; Gingerich, K. A. *Ibid.* **1979**, *12*, 2255.

[4] (a) Shim, I.; Dahl, J. P.; Johansen, H. *Int. J. Quantum Chem.* **1979**, *15*, 311. (b) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1982**, *77*, 2490. (c) Shim, I. *Theor. Chim. Acta* **1981**, *59*, 413. (d) Goodgame, M. M.; Goddard, W. A., III *Phys. Rev. Lett.* **1982**, *48*, 135.

[5] Leopold, D. G.; Vaida, V. *J. Am. Chem. Soc.* **1983**, *105*, 6809.

[6] (a) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (b) Ridge, D. P. "Lecture Notes in Chemistry"; Springer-Verlag: New York, 1982; Vol. 31, p 140.

[7] (a) Ervin, K.; Loh, S. K.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593. (b) Armentrout, P. B.; Loh, S. K.; Ervin, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 1161.

[8] (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

[9] (a) Comisarow, M. B.; Marshall, A. G. *J. Chem. Phys.* **1976**, *64*, 110. (b) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

[10] Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

[11] (a) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 4924. (b) Foster, M. S.; Beauchamp, J. L. *Ibid.* **1975**, *97*, 4808.

[12] Kappes, M. M.; Staley, R. H. *J. Phys. Chem.* **1982**, *86*, 1332.

0002-7863/84/1506-4623$01.50/0