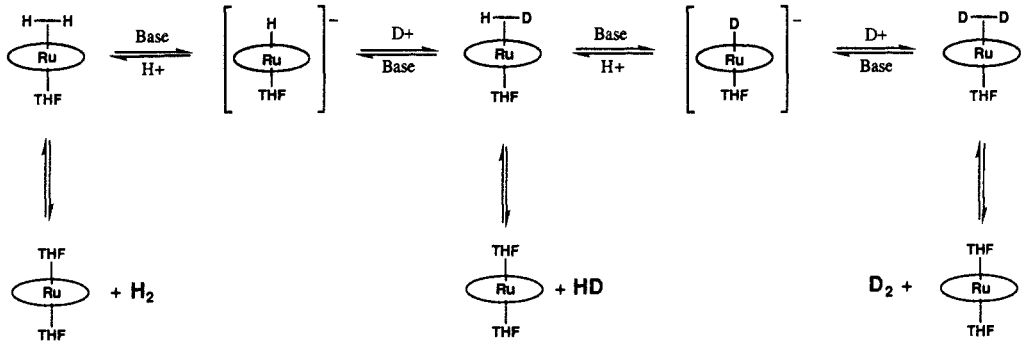
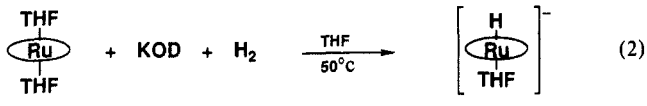
Scheme I



the absence of **Ru(THF)$_2$**, no measurable H/D exchange occurs. H/D exchange also does not occur in the absence of KOD. Additionally, this exchange is slowed by 30% when 120 equiv of KOD is added. Scheme I presents a mechanism we propose for this H/D exchange. The sequential acid–base equilibrium proposed in Scheme I has been independently shown to operate for the osmium analogue: e.g., **OsH$_2$** is formed from protonation of **OsH** and is deprotonated by lithium diisopropylamide.[25] Also, **Ru(THF)$_2$** forms the monohydride, **RuH**, when stirred in THF with KOD at 50 °C under 1 atm of H_2 (eq 2). The proposed



(2)

mechanism suggests that the rate of exchange should go through a maximum with pH since the overall process involves both a protonation and a deprotonation. This behavior is roughly exhibited with the above exchange results for **Ru(THF)$_2$**. Hydrogenase is also known to catalyze such H/D exchange and exhibits a similar pH profile.[26]

Because **RuH** forms from **Ru(THF)$_2$** in the presence of H_2 and base, hydride transfer from **RuH** to a substrate may constitute a catalytic hydrogenation cycle involving **Ru(THF)$_2$** as a catalyst. When a stoichiometric amount of the NAD^+ analogue (1-benzyl-*N*,*N*-diethylnicotinamide)PF_6 is introduced to an NMR solution of **RuH** in THF-d_8, a species with broad ^1H NMR resonances forms. Addition of a drop of pyridine to this mixture yields Ru(OEP)(py)$_2$ and the reduced nicotinamide, 1-benzyl-*N*,*N*-diethyl-1,6-dihydronicotinamide, as shown by the ^1H NMR. To our knowledge, this is the first example of a transition-metal hydride reducing an NAD^+ analogue.[27] This 1,6-addition contrasts with hydrogenase, which reduces NAD^+ at the 1,4-positions of the pyridinium.[4a] Further studies are planned to examine the selectivity of the NAD^+ reduction, to survey possible substrates for catalytic hydrogenation employing the **Ru(THF)$_2$**/H_2 system, and to further characterize dihydrogen complexes of transition-metal porphyrins.

Acknowledgment. P.S.W. acknowledges support as a National Science Foundation Graduate Research Fellow, 1986–1989. R.T.H. acknowledges support as a National Institutes of Health Postdoctoral Fellow, 1987–1989. Support from the National Science Foundation (NSF CHE88-14949), the National Institutes of Health (NIH 5R37-GM17880), and the Gas Research Institute is acknowledged. Helpful discussions with Greg Venburg, Jim Hutchison, Dean Harman, and Scott Bohle are gratefully acknowledged. Contribution No. 8032 from the Division of Chemistry and Chemical Engineering, California Institute of Technology.

(23) H_2, HD, and D_2 were separated and detected by gas chromatography.[24]

(24) (a) Walters, A. B. Ph.D. Dissertation, Stanford University, 1970. (b) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647–657.

(25) Activation of the dihydrogen ligand toward heterolytic cleavage is known. Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824–1826 and ref 2e.

(26) (a) Lespinat, P. A.; Berlier, Y.; Fauque, G.; Czechowski, M.; Dimon, B.; LeGall, J. *Biochimie* **1986**, *68*, 55–61. (b) Arp, D. J.; Burris, R. H. *Biochim. Biophys. Acta* **1982**, *700*, 7–15. (c) Teixeira, M.; Fauque, G.; Moura, I.; Lespinat, P. A.; Berlier, Y.; Prickril, B.; Peck, H. D., Jr.; Xavier, A. V.; LeGall, J.; Moura, J. J. G. *Eur. J. Biochem.* **1987**, *167*, 47–58 and references therein.

(27) Metal hydrides have been suggested in catalytic NAD^+ and NAD^+-model compound reductions.[28,29]

(28) Ruppert, R.; Herrmann, S.; Steckhan, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1150–1151.

(29) Aoyama, Y.; Midorikawa, K.; Toi, H.; Ogoshi, H. *Chem. Lett.* **1987**, 1651.

Free-Radical Carbonylation. Efficient Trapping of Carbon Monoxide by Carbon Radicals

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The reaction of carbon radicals with carbon monoxide to form acyl radicals[1,2] is thought to be an equilibrium process and to be difficult to control due to the ready back reaction.[3] In 1952, the formation of polyketones by peroxide-initiated copolymerization was first disclosed by Coffmann et al., who suggested the intermediacy of acyl radicals for this polymerization.[2a] In 1956, Foster et al. reported that the peroxide-initiated reaction of mercaptans with ethylene and carbon monoxide under 3000 atm at 130 °C gave 3-(alkylthio)propanal in 11–18% yields.[2c] While this reaction was noteworthy as a pioneering effort to effect trapping of acyl radicals by hydrogen abstraction, the results were of limited utility because of the extremely high pressures of CO and the low yields

(1) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 13, p 94.

(2) (a) Coffman, D. D.; Pinkney, P. S.; Wall, F. T.; Wood, W. H.; Young, H. S. *J. Am. Chem. Soc.* **1952**, *74*, 3391. (b) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *Ibid.* **1952**, *74*, 1509. (c) Foster, R. E.; Larchar, A. W.; Lipscomb, R. D.; McKusick, B. C. *Ibid.* **1956**, *78*, 5606. (d) Sauer, J. C. *Ibid.* **1957**, *79*, 5314.

(3) For examples of decarbonylation from acyl radicals, see: (a) Cadman, P.; Dodwell, C.; Trotman-Dickenson, A. F.; White, A. J. *J. Chem. Soc. A* **1970**, 2371. (b) Cadman, P.; Trotman-Dickenson, A. F.; White, A. J. *Ibid.* **1970**, 3190. (c) Lewis, S. N.; Miller, J. J.; Winstein, S. *J. Org. Chem.* **1972**, *37*, 1478. (d) Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 297. (e) Schuh, H.; Hamilton, E. J., Jr.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 2011. (f) Lunazzi, L.; Ingold, K. U.; Scalano, J. C. *J. Phys. Chem.* **1983**, *87*, 529. (g) Turro, N. J.; Gould, I. R.; Baretz, B. H. *Ibid.* **1983**, *87*, 531. (h) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475. (i) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Ingold, K. U. *Ibid.* **1984**, *106*, 2923. (j) Patel, V. F.; Pattenden G. *Tetrahedron Lett.* **1988**, *29*, 707. (k) Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *Ibid.* **1988**, *29*, 955. (l) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1988**, *53*, 1632.

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Scheme I

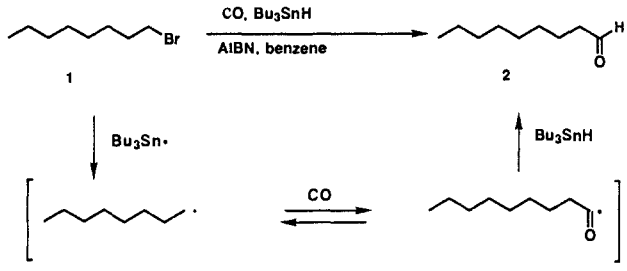


Table I. Product Ratios of Reactions of Octyl Radical with CO under Bu_3SnH Conditions[a]

run	[1], mol/L	CO, atm	Bu_3SnH, equiv	2,[b] %	3,[b] %	2/(2 + 3)
1	0.05	1	1.2	0	90	
2	0.05	15	1.2	38	49	0.44
3	0.05	30	1.2	56	43	0.57
4	0.05	50	1.2	63	36	0.64
5	0.17	50	1.2	42	54	0.44
6	0.05	50	3.0	6	85	0.07
7	0.05	80	1.2	66	26	0.67

[a] Reactions except for run 1 were carried out by using a 50-mL stainless steel autoclave with a glass tube inserted. Conditions: **1** (0.5 mmole *n*-Bu_3SnH (0.6 or 1.5 mmol), AIBN (0.06 mmol), carbon monoxide (15, 30, 50, or 80 atm), benzene (10, 5, or 3 mL), 80 °C, 1.1 h. [b] GC yields.

of carbonylated products. Subsequently, the chemistry of acyl radical has evolved in ways other than the radical/CO reaction.[4] Reasoning that the ineffectiveness shown in the above work primarily stemmed from low efficiency in the generation of starting radical species, we considered that the reinvestigation of the radical/CO reaction using modern free-radical techniques[5] would be promising. We disclose here the first example of the highly efficient trapping of carbon monoxide by free-radical reaction.

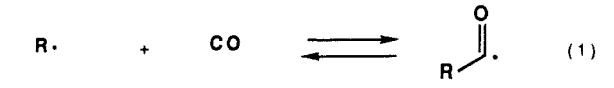


Table II. Conversion of Organo Halides into Aldehyde by Free-Radical Carbonylation[a]

run	RX	yield,[b] %
1	*n*-$C_8H_{17}Br$	61 (66)
2	$PhCH_2CH_2CH_2Br$	58
3	$PhCH_2CH_2Br$	65
4	$PhCH_2Br$	*c*
5[d]	PhI	(60)
6[d]	p-$MeOC_6H_4I$	(70)
7	c-$C_6H_{11}Br$	60
8[e]		46
9	(*E*)-$EtCH{=}CHCH_2CH_2Br$	(70)
10	(*Z*)-$EtCH{=}CHCH_2CH_2Br$	(80)

[a] Reactions were carried out on a 0.5-mmol scale by using a stainless steel autoclave with a glass tube inserted. Conditions: 1.2–1.3 equiv of *n*-Bu_3SnH, 0.1–0.2 equiv of AIBN, carbon monoxide (runs 1, 2, and 8, 80 atm; runs 3–7, 70 atm; runs 9 and 10, 65 atm), benzene (10 mL), 80 °C, 1.1–5 h. See footnote 6. [b] Yields refer to chromatographically purified materials. GC yields are in parentheses. [c] Toluene was formed in 93% yield. [d] Conducted in 15 mL of benzene. [e] Conducted at 100 °C.

We examined the AIBN-induced radical reaction of *n*-octyl bromide (**1**) (Scheme I) with Bu_3SnH under CO pressure in hope of trapping of carbon monoxide by octyl radical followed by hydrogen abstraction from tin hydride. When the reaction on a 0.5-mmol scale was conducted under CO pressure, using an autoclave with an inserted glass tube (5 mol % of AIBN, benzene (10 mL), 80 °C, 3 h), the desired aldehyde **2** was obtained together with *n*-octane (**3**), formed via simple reduction of **1** (Table I). Surprisingly, this radical/CO trapping sequence proceeds even at 15 atm of CO pressure to give **2** in 38% yield (run 2). Generally, higher pressures of CO resulted in the increase of **2**. Thus, the best result was obtained with the reaction at 80 atm of CO, yielding 66% of **2** (run 7). On the other hand, experiments employing a large excess of tin hydride resulted in a remarkable increase of reduction product **3** (run 6). These results demonstrate that the control of the relative concentrations of CO to tin hydride is an important factor to effect the CO trapping leading to aldehyde **2**.

The scope and efficiency of the radical/CO trapping sequence are illustrated by the results summarized in Table II. In general, the reactions were carried out at 80–100 °C for 3–5 h under 65–80 atm of CO.[6] Thus primary, secondary, and tertiary alkyl bromides were carbonylated to give the corresponding aldehydes. The reacton with benzyl bromide gave only toluene (run 4), indicating that benzyl radicals did not trap CO.[7] From *trans*- and *cis*-3-hexenyl bromides, aldehydes that contain double bonds at the C_4–C_5 positions were obtained without loss of stereochemistry (runs 9 and 10).[8] Carbonylation of aromatic iodides also took place, to give good yields of aromatic aldehydes (runs 5 and 6).

(4) For methods of acyl radical generation other than radical carbonylation, see the folllowing. For H abstraction of aldehydes: (a) Kharasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* **1949**, *14*, 248. (b) Harris, E. F. P.; Waters, W. A. *Nature* **1952**, *170*, 212. (c) Patric, T. M., Jr. *J. Org. Chem.* **1952**, *17*, 1009. (d) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, *473*; (e) *J. Chem. Soc., Perkin Trans. 2* **1980**, 819. (f) Chatgilialoglu, C.; Lunazzi, L.; Macciantelli, D.; Placucci, G. *J. Am. Chem. Soc.* **1984**, *106*, 5252. (g) Gottschalk, P.; Neckers, D. C. *J. Org. Chem.* **1985**, *50*, 3498. (h) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674. Also see refs. 3a–d,j. For photochemical degradation with Norrish type I cleavage: (i) Urry, W. H.; Pai, M. H.; Chen, C. Y. *J. Am. Chem. Soc.* **1964**, *86*, 5342. (j) Fraser-Reid, B.; Anderson, R. C.; Hicks, D. R.; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3986. (k) Druliner, J. D.; Wasserman, E. *J. Am. Chem. Soc.* **1988**, *110*, 5270. (l) Querin, B.; Johnston, L. J.; Quach, T. *J. Org. Chem.* **1988**, *53*, 2826. For decomposition of acylmetals: (m) Patel, V. F.; Pattenden, G. *Tetrahedron Lett.* **1988**, *29*, 707. Also see ref 3j. For reaction of acyl chlorides with R_3SnH: (n) van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 356. (o) Kupchik, E. J.; Kiesel, R. J. *J. Org. Chem.* **1964**, *29*, 3690; (p) **1966**, *31*, 456. (q) Kuivila, H. G.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 571. (r) Walsh, E. J., Jr.; Kuivila, H. G. *Ibid.* **1966**, *88*, 576. (s) Cekovic, Z. *Tetrahedron Lett.* **1972**, 749. (t) Walsh, E. J., Jr.; Messinger, J. M., II; Grudoski, D. A.; Allcin, C. A. *Tetrahedron Lett.* **1980**, *21*, 4409. For radical addition to α-diketones and degradation: (u) Urry, W. H.; Huyser, E. S. *J. Am. Chem. Soc.* **1953**, *75*, 4876. (v) Bentrude, W. G.; Darnall, K. R. *J. Am. Chem. Soc.* **1968**, *90*, 3588. Also see ref 3k. For reaction of acyl selenides with R_3SnH: (w) Pfenninger, J.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 1562. (x) Pfenninger, J.; Heuberger, C.; Graf, W. *Ibid.* **1980**, *63*, 2328. (y) Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641. (z) Bachi, M. D.; Bosch, E. *Ibid.* **1988**, *29*, 2581. (aa) Crich, D.; Fortt, S. M. *Ibid.* **1988**, *29*, 2585. (bb) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1988**, *53*, 3377. (cc) Bachi, M. D.; Bosch, E. *J. Org. Chem.* **1989**, *54*, 1234. (dd) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1989**, *54*, 1777.

(5) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. (b) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (c) Hart, D. J. *Science* **1984**, *223*, 883. (d) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(6) Typical experimental procedure: *n*-Octyl bromide (**1**; 96 mg, 0.5 mmol), Bu_3SnH (189.2 mg, 0.65 mmol), AIBN (6 mg, 0.036 mmol), and benzene (10 mL) were placed in a 50-mL stainless steel autoclave with an inserted glass tube. The reaction mixture was stirred under carbon monoxide pressure (80 atm) at 80 °C for 3 h. After the evacuation of excess carbon monoxide at room temperature, benzene was removed under reduced pressure. The residue, after removal of benzene, was stirred rapidly for 1 h with 4 mL of diethyl ether and 4 mL of saturated aqueous potassium fluoride solution. Filtration, extraction with ether, drying (sodium sulfate), and concentration, followed by purification by flash chromatography (SiO_2, pentane/ether = 9/1), gave nonanal (**2**) in 61% yield.

(7) This result is in good agreement with the previous observations that phenylacetyl radical decarbonylates nearly 100 times more rapidly than pivaloyl radical.[3f,g]

(8) Cf.: Takeuchi, R.; Tsuji, Y.; Fujita, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1989**, *54*, 1831.

In summary, we have demonstrated that carbon monoxide can be efficiently trapped by carbon radicals at reasonably low CO pressures, contrary to previous observations. The success of this *free-radical carbonylation* obviously provides a new method for the introduction of carbon monoxide into organic molecules.[9,10] Further studies on the scope and synthetic application are currently under investigtion.

(9) For the preexisting methodologies for carbonylation with CO involving other acyl species (acylmetals, acyl anions, and acyl cations), see recent reviews: (a) Narayama, C.; Periasamy, M. *Synthesis* **1985**, 253. (b) Weil, T. A.; Casser, L.; Foa, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 517. (c) Bahrman, H.; Cornils, B.; Frohling, C. D.; Mullen, A. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer: Berlin, 1980.

(10) The overall transformation as a method for aldehyde synthesis is noteworthy, since the carbonylation of aliphatic substrates is particularly difficult by transition-metal methods. In this context, the radical method reported here complements the method involving Pd catalysis by J. K. Stille; see: Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7175.

Registry No. 1, 111-83-1; **2**, 124-19-6; **3**, 111-65-9; $Ph(CH_2)_3Br$, 637-59-2; $Ph(CH_2)_2Br$, 103-63-9; $PhCH_2Br$, 100-39-0; PhI, 591-50-4; p-$MeOC_6H_4I$, 696-62-8; c-$C_6H_{11}Br$, 108-85-0; (*E*)-EtCH=CH-$(CH_2)_2Br$, 63281-96-9; (*Z*)-EtCH=CH$(CH_2)_2Br$, 5009-31-4; Ph-$(CH_2)_3CHO$, 18328-11-5; $Ph(CH_2)_2CHO$, 104-53-0; $PhCH_3$, 108-88-3; PhCHO, 100-52-7; p-$MeOC_6H_4CHO$, 123-11-5; c-$C_6H_{11}CHO$, 2043-61-0; (*E*)-EtCH=CH$(CH_2)_2CHO$, 929-22-6; (*Z*)-EtCH=CH-$(CH_2)_2CHO$, 6728-31-0; CO, 630-08-0; 1-adamantyl bromide, 768-90-1; 1-adamantanecarboxaldehyde, 2094-74-8.

Supplementary Material Available: ^1H and ^{13}C NMR, IR, and some mass spectral data for products listed in Table I (3 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Thermal Encapsulation and Photochemical Deencapsulation of Ag(I) by $[Ir_2(dimen)_4](PF_6)_2$ (dimen = 1,8-Diisocyanomethane). X-ray Crystal Structure of $[AgIr_2(dimen)_4](PF_6)_3 \cdot 2DMSO$ [*J. Am. Chem. Soc.* **1988**, *110*, 8252]. ANDREW SYKES and KENT R. MANN*

Page 8253: In Figure 2, the formation constant for the thermal encapsulation of Ag^+ in DMSO is misstated as 1.5×10^8 M^{-1}. The correct value is 1.5×10^7 M^{-1}. The calculations in the text (page 8253) should be adjusted to give log K of 7.2 and the corresponding free energy change of −9.8 kcal/mol.

Time-Resolved Raman Detection of ν(Fe–O) in an Early Intermediate in the Reduction of O_2 by Cytochrome Oxidase [*J. Am. Chem. Soc.* **1989**, *111*, 6439–6440]. CONSTANTINOS VAROTSIS, WILLIAM H. WOODRUFF, and GERALD T. BABCOCK*

The spectrometer used in this characterization of the dioxygen adduct of cytochrome a_3^{2+} in the reaction of fully reduced cytochrome oxidase with O_2 was miscalibrated in the 540–660 cm^{-1} region. With proper calibration, the 589- and 565-cm^{-1} lines occur at 571 and 546 cm^{-1}, respectively. Therefore, we assign the $\nu(Fe^{2+}–O)$ frequency at 571 cm^{-1}. This value is very similar to that which we measured for the iron–oxygen stretching frequency in an imidazole–heme $a^{2+}–O_2$ model compound (see ref 7 in the original publication) and identical with that which we measured in the reaction of mixed valence cytochrome oxidase with O_2. (Varotsis, C.; Woodruff, W. H.; Babcock, G. T. *J. Biological Chem.* Submitted).

This indicates, contrary to our earlier conclusion, that the cytochrome $a_3 \cdot O_2$ complex is unperturbed by distal effects in the cytochrome a_3/Cu_B binding pocket. Weakening and rupture of the O=O bond occurs subsequent to formation of the initial dioxygen–a_3^{2+} adduct.

Selenium Coronands: Synthesis and Conformational Analysis [*J. Am. Chem. Soc.* **1989**, *111*, 6582]. RAYMOND J. BATCHELOR, FREDERICK W. B. EINSTEIN, IAN D. GAY, JIAN-HUA GU, BLAIR D. JOHNSTON, and B. MARIO PINTO*

Recent investigations in our laboratory show that the solid-state ^{77}Se chemical shifts reported in ref 1 are incorrect. This arises from an error in the referencing procedure. Our measurements were referred to a solution of aqueous H_2SeO_3 and converted to the $(CH_3)_2Se$ scale with use of the literature value[2,3] of 1282 ppm for the shift of H_2SeO_3. Direct measurement shows this figure to be incorrect, and the shifts reported in Table XI of ref 1 should be corrected by +22 ppm to give shifts relative to $(CH_3)_2Se$ in $CDCl_3$.

Page 6584: In footnotes *i* and *j* to Table II *W* should be *w*.

Page 6588 first column, line 25: "clockwise" should be "counterclockwise".

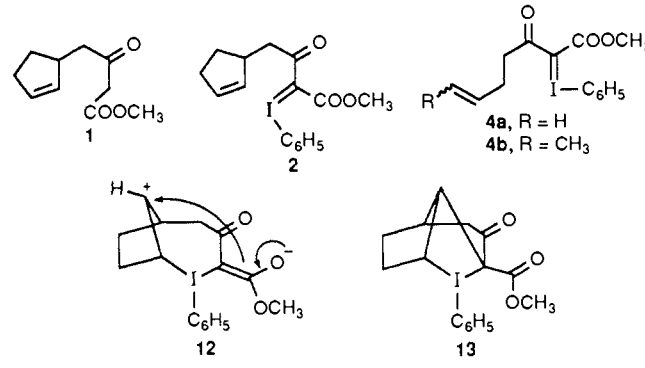
(1) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Johnston, B. D.; Pinto, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6582.

(2) *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978.

(3) Lardon, M. *J. Am. Chem. Soc.* **1970**, *92*, 5063.

A Novel Intramolecular Cyclopropanation Using Iodonium Ylides [*J. Am. Chem. Soc.* **1989**, *111*, 6443]. ROBERT M. MORIARTY,* OM PRAKASH, RADHE K. VAID, and LEI ZHAO

Pages 6443 and 6444: The correct structures for **1**, **2**, **4**, **12**, and **13** follow:



Page 6443: The following should be added to ref 10. **4a**: ^1H NMR ($CDCl_3$) δ 2.50 (t, 2 H, CH_2), 3.20 (m, 2 H, CH_2), 3.75 (s, 3 H, $COOCH_3$), 5.10 (m, 2 H, CH=CH_2), 6.09 (m, 1 H, CH=CH_2), 7.40–7.90 (m, 5 H, aromatic protons). **6**: ^1H NMR ($CDCl_3$) δ 1.30–2.10 (m, 4 H, 2 × CH_2), 2.85 (m, 1 H, CH), 3.20 (m, 1 H, CH), 3.70 (s, 3 H, $COOCH_3$), 4.15 (m, 1 H, CH), 5.80 (m, 2 H, CH=CH), 6.20 (m, 1 H, CH=CH), 7.30–7.90 (m, 5 H, aromatic protons).