

resulting reddish-brown residue was dissolved in ethyl ether/petroleum ether (1:9, 2 mL) and chromatographed on alumina (activity 3, 5 g) using ethyl ether/petroleum ether (1:9) as eluent. Two distinct orange bands were observed. The faster moving, more intense band yielded a fraction containing the exo compound 46 (0.0023 g, 42%), while the slower band contained the endo complex 47 (0.0009 g, 16%).

Complex 46: red crystals; mp 210–212 °C;  $R_f$  0.47, ethyl ether/methanol/hexane (3:1:6) as eluent; IR (thin film) 2967, 1609, 1574, 1502, 1244, 1063, 808  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.06 (s, 3 H), 1.08 (dd,  $J = 15.0, 3.1$ , 1 H), 1.40 (m, 1 H), 1.83 (ddd,  $J = 15.6, 10.8, 6.3$ , 1 H), 2.10 (m, 2 H), 2.53 (dd,  $J = 15.0, 3.4$ , 1 H), 3.40 (s, 3 H), 3.44 (m, 3 H), 3.69 (t,  $J = 6.1$ , 2 H), 4.51 (s, 5 H), 4.57 (d,  $J = 11.7$ , 1 H), 4.80 (d,  $J = 11.7$ , 1 H), 4.98 (d,  $J = 11.9$ , 1 H), 5.02 (d,  $J = 11.6$ , 1 H), 6.84 (d,  $J = 2.7$ , 1 H), 6.89 (dd,  $J = 8.4, 2.7$ , 1 H), 7.15 (d,  $J = 8.4$ , 1 H); MS (30 eV),  $m/e$  464 (100%), 339 (11), 322 (23), 294 (88), 225 (13), 124 (73); HRMS calcd for  $\text{C}_{26}\text{H}_{29}\text{O}_4\text{Co}$ , 464.1400; found, 464.1392.

Complex 47: orange oil;  $R_f$  0.37, ethyl ether/methanol/hexane (3:1:6) as eluent; IR (thin film) 2966, 1609, 1570, 1502, 1261, 1046, 813  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.56 (dd,  $J = 12.5, 1$ , 1 H), 0.95 (dd,  $J = 12.5, 5.3$ , 1 H), 1.39 (m, 2 H), 1.64 (s, 3 H), 1.89 (ddd,  $J = 12.2, 4.9, 4.9$ , 1 H), 2.16 (m, 2 H), 3.39 (m, 4 H), 3.40 (s, 3 H), 4.41 (d,  $J = 13.8$ , 1 H), 4.44 (s, 5 H), 4.45 (d,  $J = 13.5$ , 1 H), 4.80 (d,  $J = 11.6$ , 1 H), 5.16 (d,  $J = 11.6$ , 1 H), 6.84 (d,  $J = 2.9$ , 1 H), 6.92 (dd,  $J = 8.6, 2.6$ , 1 H), 7.27 (d,  $J = 8.6$ , 1 H); MS (30 eV),  $m/e$  464 (100%), 339 (12), 322 (25), 294 (96), 223 (22), 124 (71); HRMS calcd for  $\text{C}_{26}\text{H}_{29}\text{O}_4\text{Co}$ , 464.1400; found, 464.1392.

(8,9,11,14- $\eta^4$ -B-(6a-Oxa)-homo-11-(trimethylsilyl)-13-exo-3-methoxyestra-1,3,5,8(14),9(11)-pentaen-17-one ethylene ketal)( $\eta^5$ -cyclopentadienyl)cobalt (48). To 44 (0.008 g, 0.0194 mmol) in degassed isooctane (5 mL) was added  $\text{CpCo}(\text{CO})_2$  (0.020 mL, 0.16 mmol). The reaction mixture was then heated for 21 h until starting material had disappeared. After evaporation of the solvent the resulting brown-red residue was dissolved in ethyl ether/petroleum ether (1:9). Chromatography with this solvent system on alumina (activity 2.5) provided a single red-orange fraction leaving a red-orange powder (0.063 g, 61%) which was recrystallized from  $\text{MeOH}/\text{H}_2\text{O}$ : red crystals; mp 172–175 °C;

$R_f$  0.32, THF/hexane (1:9) as eluent; IR (thin film) 2961, 1609, 1573, 1497, 1312, 1249, 809, 682  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (200 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.28 (s, 9 H), 0.83 (s, 3 H), 0.84 (d,  $J = 14.6$ , 1 H), 1.43 (m, 2 H), 2.11 (m, 2 H), 2.57 (d,  $J = 14.6$ , 1 H), 3.38 (s, 3 H), 3.49 (t,  $J = 6.4$ , 2 H), 3.73 (t,  $J = 6.4$ , 2 H), 4.29 (d,  $J = 12.8$ , 1 H), 4.38 (d,  $J = 12.8$ , 1 H), 4.82 (d,  $J = 11.5$ , 1 H), 4.84 (s, 5 H), 6.08 (d,  $J = 11.5$ , 1 H), 6.85 (dd,  $J = 8.5, 2.7$ , 1 H), 6.97 (d,  $J = 2.7$ , 1 H), 7.53 (d,  $J = 8.5$ , 1 H); MS (30 eV),  $m/e$  536 (48%), 463 (17), 325 (35), 339 (14), 325 (35), 124 (42), 73 (100); HRMS calcd for  $\text{C}_{29}\text{H}_{37}\text{O}_4\text{SiCo}$ , 536.1818; found, 536.1805.

(8,9,11,14- $\eta^4$ -B-(6a-Oxa)-homo-13-endo-3-methoxyestra-1,3,5,8(14),9(11)-pentaen-17-one)( $\eta^5$ -cyclopentadienyl)cobalt (49). To 45 (0.007 g, 0.024 mmol) in degassed isooctane (5 mL) was added  $\text{CpCo}(\text{CO})_2$  (0.014 mL, 0.112 mmol). The reaction mixture was heated to reflux for 24 h until all starting material had been consumed. Column chromatography on alumina (activity 3, 5 g) eluting with ethyl ether/petroleum ether (1:9) yielded an orange fraction.  $^1\text{H NMR}$  spectroscopy of the crude material (0.0034 g, 34%) showed it to be a mixture of endo and exo isomers in a ratio of 2.5:1 (Cp endo at  $\delta$  4.36, Cp exo at  $\delta$  4.21; Me endo  $\delta$  1.33, Me exo  $\delta$  0.76). Crystallization of the major isomer from petroleum ether at  $-70$  °C gave compound 49: yellow crystals; mp 139–142 °C;  $R_f$  0.10, THF/hexane (1:9) as eluent; IR (thin film) 2960, 1733, 1610, 1572, 1503, 1248, 1047  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.69 (dd,  $J = 13.5, 1.2, 1$  H), 1.03 (dd,  $J = 13.6, 5.5, 1$  H), 1.33 (s, 3 H), 1.88 (m, 2 H), 2.21 (m, 2 H), 3.20 (dd,  $J = 5.6, 1.4, 1$  H), 3.38 (s, 3 H), 4.31 (d,  $J = 12.6, 1$  H), 4.36 (s, 5 H), 5.43 (d,  $J = 12.6, 1$  H), 4.62 (s, 2 H), 6.72 (d,  $J = 2.6, 1$  H), 6.86 (dd,  $J = 8.5, 2.5, 1$  H), 7.13 (d,  $J = 8.6, 1$  H); MS (30 eV),  $m/e$  420 (13%), 392 (3), 364 (3), 339 (4), 296 (5), 69 (15), 44 (100); HRMS calcd for  $\text{C}_{24}\text{H}_{25}\text{O}_3\text{Co}$ , 420.1128; found, 420.1118.

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## Photochemistry of Alkyl Halides. 11. Competing Reaction via Carbene and Carbocationic Intermediates<sup>1</sup>

Paul J. Kropp,\* Joy A. Sawyer, and John J. Snyder

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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Isotopic analysis of the unsaturated products 6 and 15 resulting from irradiation of the labeled iodides 1-1,1- $d_2$ , 1-2,2- $d_2$ , and 13-1- $d$  has revealed that they are formed substantially, but not exclusively, via  $\alpha$  elimination. The unsaturated products thus arise via competing pathways involving carbene intermediates as well as the previously recognized radical and carbocationic intermediates. Irradiation of iodide 22 in methanol- $d$  afforded ether 23 with partial incorporation of deuterium, but the accompanying ether 24 was formed with no detectable incorporation. Thus, ether 23 is formed via competing pathways involving the carbene 28 and the carbocation 25, whereas ether 24 is formed exclusively via the carbocationic pathway. A mechanism involving formation of the carbene intermediates via either  $\alpha$ -hydrogen atom or  $\alpha$ -proton transfer within the previously proposed intervening radical and ion pairs is suggested. One iodide studied, 17-2- $d$ , exhibited no detectable  $\alpha$  elimination.

Previous studies in these laboratories have shown that irradiation of alkyl iodides in solution is a powerful and convenient method for the generation of carbocations, via a process thought to involve light-induced homolytic cleavage of the carbon-iodine bond followed by electron transfer within the initially formed caged radical pair (Scheme I).<sup>2,3</sup> In bridgehead systems structurally inca-

pable of readily undergoing elimination, the resulting carbocationic intermediate undergoes efficient nucleophilic trapping. However, iodides more capable of undergoing

(2) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* 1976, 98, 8135–8144. Kropp, P. J.; Davidson, R. I.; Worsham, P. R. *J. Am. Chem. Soc.* 1982, 104, 3972–3980.

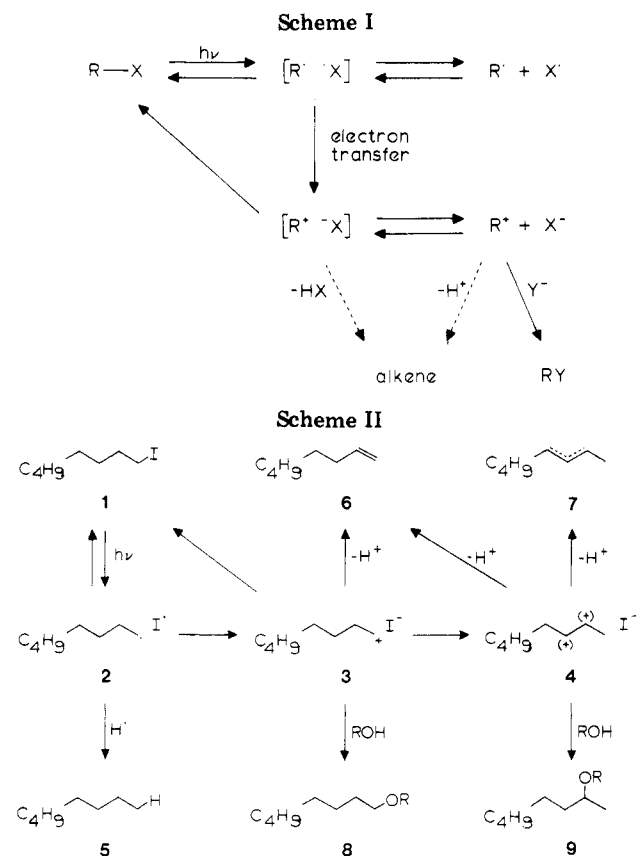
(3) The solution-phase photobehavior of alkyl halides was previously explained only in terms of radical intermediates. See: Sammes, P. G. In "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(1) Part 10: Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* 1983, 105, 6907.

Table I. Irradiation of 1-Iodoctane (1)<sup>a</sup>

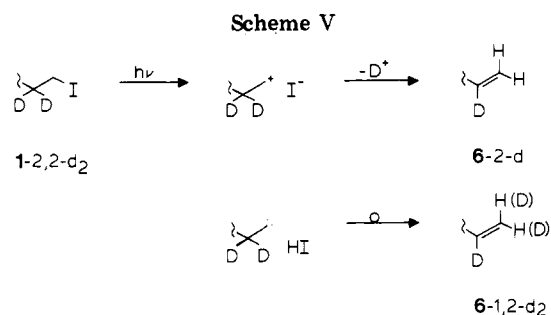
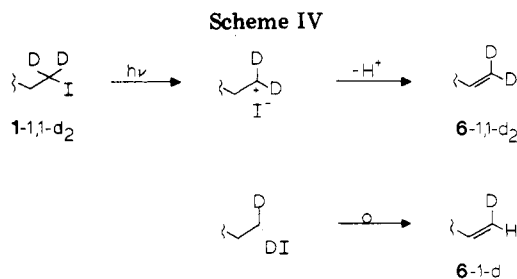
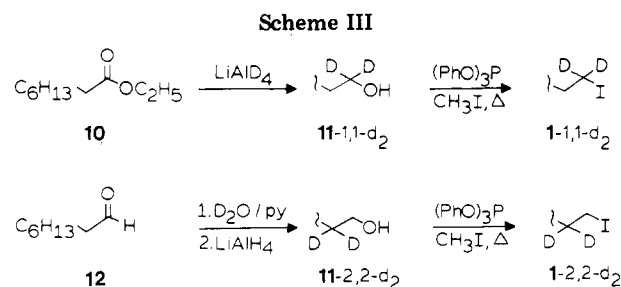
solvent	time, h	yield, <sup>b</sup> %						R
		1	5	6	7	8	9	
CH <sub>3</sub> OH	2	2	6	71	7	3	3 <sup>c</sup>	CH <sub>3</sub>
CH <sub>3</sub> OH <sup>d</sup>	6	1	2	52	2	2	2 <sup>e</sup>	CH <sub>3</sub>
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>f</sup>	2	g	24	69	7			
CH <sub>2</sub> Cl <sub>2</sub> <sup>f</sup>	3	16	14	65	5			
(CH <sub>2</sub> OH) <sub>2</sub> <sup>h</sup>	4	17	5	62	3	2	2 <sup>c</sup>	(CH <sub>2</sub> ) <sub>2</sub> OH
C <sub>5</sub> H <sub>12</sub> <sup>f</sup>	4	3	19	72	6			

<sup>a</sup> Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> 2-Iodoctane was also obtained in 2% yield. <sup>d</sup> Solution saturated with oxygen; irradiation mixture treated with sodium borohydride prior to work up. <sup>e</sup> 1-Octanol (8, R = H), 2-iodooctane, and 1-iodo-2-methoxyoctane were obtained in yields of 28%, 3%, and 5%, respectively. <sup>f</sup> Contained 1 molar equiv of triethylamine. <sup>g</sup> Trace. <sup>h</sup> Contained 2 mL of diglyme.



elimination afford principally unsaturated products, even in nucleophilic media. For example, irradiation of 1-iodooctane (1) in a variety of solvents affords mainly 1-octene (6) accompanied by small amounts of the rearranged alkenes 2- and 3-octene 7 (Scheme II and Table I); even in the nucleophilic solvent methanol the ether 8 is formed only in minor amount.<sup>2</sup>

The predominance of elimination over nucleophilic trapping in these systems has been explained previously on the basis that such behavior is characteristic of carbocationic intermediates formed via a high energy process that involves little or no solvent participation.<sup>2,4</sup> However, the involvement of a carbene intermediate—formed via loss of an  $\alpha$ , rather than  $\beta$ , hydrogen—would afford an alternative explanation not excluded by previous data since alkylcarbenes usually undergo intramolecular insertion more rapidly than intermolecular trapping.<sup>5,6</sup> We report



here that  $\alpha$  elimination of primary and secondary alkyl iodides on irradiation is, in fact, a significant reaction pathway not previously detected.<sup>7,8</sup> It does not, however, dominate over the previously proposed  $\beta$ -elimination pathway.<sup>2</sup>

## Results

**1-Iodoctane (1).** 1,1- and 2,2-Dideuterio-1-iodooctane (1-1,1-*d*<sub>2</sub> and 1-2,2-*d*<sub>2</sub>) were prepared as outlined in Scheme III. As depicted in Scheme IV for 1-1,1-*d*<sub>2</sub>,  $\beta$  elimination would afford 6-1,1-*d*<sub>2</sub> with no loss of deuterium, whereas  $\alpha$  elimination would afford 6-1-*d* with the loss of one deuterium atom. However, as shown in Table II, 6 was

(4) See: Keating, T. J.; Skell, P. S. *Carbonium Ions* 1970, 2, 573.

(5) Baron, W. J.; De Camp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In "Carbenes"; Jones, M., Jr.; Moss, R. H., Ed.; Wiley: New York, 1973; Vol. I, pp 19-63.

(6) Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* 1981, 3749-3752 and references cited therein.

(7) The formation of methylene in low yield on irradiation of methyl iodide in aqueous solution has been proposed but not demonstrated. See: Rama Rao, K. V. S.; Prasad, D.; Shankar, J. *Ind. J. Chem.* 1973, 11, 1045-1047.

(8) For similar report in the gas phase, with more compelling evidence, see: Chou, C. C.; Angelberger, P.; Rowland, F. S. *J. Phys. Chem.* 1971, 75, 2536-2538.

Table II. Irradiation of 1-Iodoctane-1,1- $d_2$  (1-1,1- $d_2$ )<sup>a</sup>

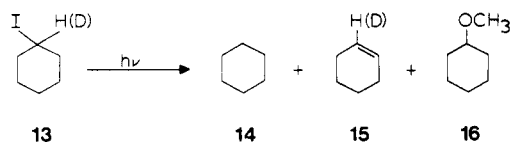
solvent	time, h	yield, <sup>b</sup> %		comp of 6, <sup>c</sup> %			$\alpha$ elim, <sup>d</sup> %
		1	6	$d_0$	$d_1$	$d_2$	
CH <sub>3</sub> OH	1	5	73	3	18	79	19, 19 <sup>e,f</sup>
CH <sub>3</sub> OH <sup>g</sup>	1	57	30	3	17	80	18
CH <sub>3</sub> OH <sup>h</sup>	1	66	16	1	17	82	17
CH <sub>3</sub> OH <sup>i</sup>	6	3	58	<i>j</i>	14	86	14
CH <sub>3</sub> OH <sup>k</sup>	3	3	61	5	24	71	25
(CH <sub>2</sub> OH) <sub>2</sub> <sup>l</sup>	4	19	61	3	20	66 <sup>m</sup>	23
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>n</sup>	1.5	7	72	2	19	79	19, 18 <sup>e,o</sup>
CH <sub>2</sub> Cl <sub>2</sub> <sup>n</sup>	3	3	70	2	18	80	18
C <sub>5</sub> H <sub>12</sub> <sup>n,p</sup>	4	<i>j</i>	68	1	16	83	16

<sup>a</sup> Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section using iodide 1-1,1- $d_2$  having the following composition:  $d_2$ , 97%;  $d_1$ , 2%;  $d_0$ , 1%. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> Determined by mass spectral analysis. <sup>d</sup> Calculated from the isotopic composition of 6 unless otherwise indicated. <sup>e</sup> Determined by <sup>1</sup>H NMR analysis of 6. <sup>f</sup> Relative integration: CH<sub>2</sub>-1, 0.18; CH-2, 0.96. <sup>g</sup> Irradiated at 1/2 relative intensity. <sup>h</sup> Irradiated at 1/4 relative intensity. <sup>i</sup> Solution saturated with oxygen; reductive workup using sodium borohydride. <sup>j</sup> Trace. <sup>k</sup> The broad emission of a 450-W medium-pressure mercury arc was employed. <sup>l</sup> Contained 2 mL of bis(2-methoxyethyl) ether as a co-solvent. <sup>m</sup> 11%  $d_3$ . <sup>n</sup> Contained 1 molar equiv of triethylamine. <sup>o</sup> Relative integration: CH<sub>2</sub>-1, 0.17; CH-2, 0.93. <sup>p</sup> Irradiated by using RPR 1849/2557-A lamps and Supracil glassware.

formed in a variety of solvents with partial, but not complete, loss of one deuterium atom. The ratio of  $\alpha$ - to  $\beta$ -elimination pathways ranged from 0.14 to 0.25, as determined by analysis of the product by both mass and proton NMR spectroscopy.

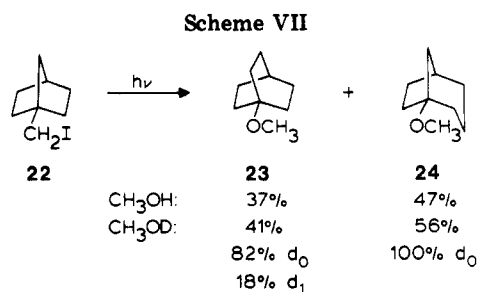
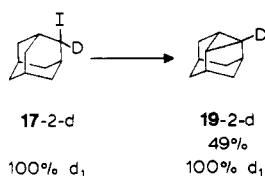
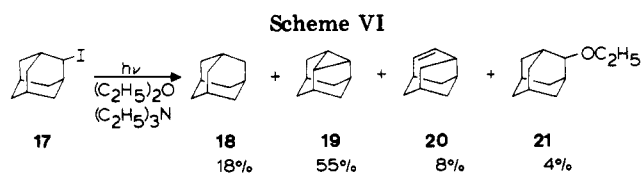
Similar results were obtained with the 2,2-dideuterated derivative of 1. As shown in Scheme V, 1-2,2- $d_2$  would be expected to afford 6-2- $d$  by  $\beta$  elimination (loss of one deuterium atom) and 6-1,2- $d_2$  by  $\alpha$  elimination (migration but no net loss of deuterium). The latter process was once again found to occur to a significant, but not predominant, extent (Table III).

**Iodocyclohexane (13).** Another iodide that undergoes a substantial amount of elimination on irradiation, even in the nucleophilic solvent methanol, is iodocyclohexane (13)

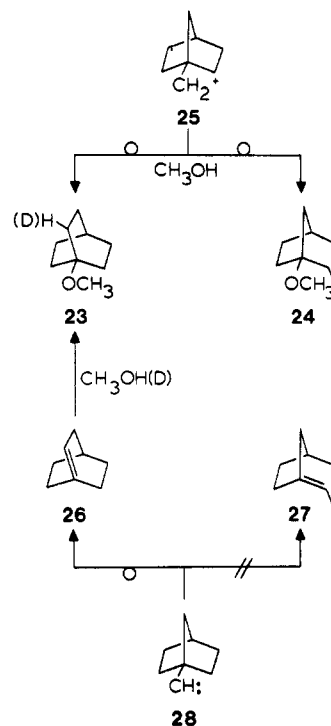


(Table IV). Irradiation of the labeled derivative 13-1- $d$  afforded cyclohexene (15) with substantial loss of deuterium (Table V). Although still not predominant,  $\alpha$  elimination occurred to a greater extent here than in the formation of 1-octene (6).

**2-Iodoadamantane (17).** Previous studies in these laboratories had shown that irradiation of iodide 17 in ether solution containing an equivalent of triethylamine to neutralize the byproduct HI affords principally the 2,4-dehydro derivative 19, accompanied by small amounts of the reduction product 18, the rearranged elimination product 20, and the ether 21 (Scheme VI).<sup>9</sup> In contrast



Scheme VIII



with iodides 1 and 13, irradiation of the  $\alpha$ -deutero derivative 17-2- $d$  afforded the principal product 19 with no detectable loss of deuterium.<sup>10</sup> Thus  $\alpha$  elimination is not involved in this case.

(9) Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* 1978, 201-210.

(10) Isotopic compositions were not determined for the minor products 18, 20, and 21—which were obtained in yields of 17%, 11%, and 3%, respectively.

Table III. Irradiation of 1-Iodooctane-2,2- $d_2$  (1-2,2- $d_2$ )<sup>a</sup>

solvent	time, h	yield, <sup>b</sup> %		comp of 6, <sup>c</sup> %			$\alpha$ elim, <sup>d</sup> %
		1	6	$d_0$	$d_1$	$d_2$	
CH <sub>3</sub> OH	1	8	70	9	71	20	22, 22 <sup>e,f</sup>
CH <sub>3</sub> OH <sup>g</sup>	1	51	30	15	67	18	21
CH <sub>3</sub> OH <sup>h</sup>	1	73	16	13	69	18	21
CH <sub>3</sub> OH <sup>i</sup>	6	1	65	1	84	15	15
CH <sub>3</sub> OH <sup>j</sup>	110	58	29	17	67	16	17
CH <sub>3</sub> OH <sup>k,l</sup>	2	<i>m</i>	60	18	64	18	22
(CH <sub>2</sub> OH) <sub>2</sub>	4	11	65	1	76	23	23
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>n</sup>	1.5	8	67	9	69	22	24, 29 <sup>e,o</sup>
C <sub>5</sub> H <sub>12</sub> <sup>n</sup>	9	10	67	21	58	21	24
C <sub>5</sub> H <sub>12</sub> <sup>n,p</sup>	6	9	62	24	60	16	18

<sup>a</sup> Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section by using iodide 1-2,2- $d_2$  having the following composition:  $d_3$ , 1%;  $d_2$ , 87%;  $d_1$ , 4%;  $d_0$ , 8%. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> Isotopic compositions were determined by mass spectral analysis. <sup>d</sup> Calculated from the isotopic composition of 6 unless otherwise indicated. <sup>e</sup> Determined by <sup>1</sup>H NMR analysis of 6. <sup>f</sup> Relative integration: C<sub>1</sub>, 1.8; C<sub>2</sub>, 0.10. <sup>g</sup> Irradiated at 1/2 relative intensity. <sup>h</sup> Irradiated at 1/4 relative intensity. <sup>i</sup> Solution saturated with oxygen; reductive workup using sodium borohydride. <sup>j</sup> Irradiated using RPR 3000-A lamps and a Corex filter. <sup>k</sup> The broad emission of a 450-W medium-pressure mercury arc was employed. <sup>l</sup> The starting iodide had the following composition:  $d_2$ , 83%;  $d_1$ , 13%;  $d_0$ , 4%. <sup>m</sup> Trace. <sup>n</sup> Contained 1 molar equiv of triethylamine. <sup>o</sup> Relative integration: C<sub>1</sub>, 1.8; C<sub>2</sub>, 0.14. <sup>p</sup> Irradiated by using RPR 1849/2537-A lamps and Suprasil glassware.

Table IV. Irradiation of Iodocyclohexane (13)<sup>a</sup>

solvent	time, h	yield, <sup>b</sup> %			
		13	14	15	16
CH <sub>3</sub> OH	1	<i>c</i>	2	92	6
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	2	<i>c</i>	9	91	
CH <sub>2</sub> Cl <sub>2</sub>	2	<i>c</i>	3	97	
C <sub>5</sub> H <sub>12</sub>	2	<i>c</i>	3	94	

<sup>a</sup> Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> Trace. <sup>d</sup> Contained 1 molar equiv of triethylamine.

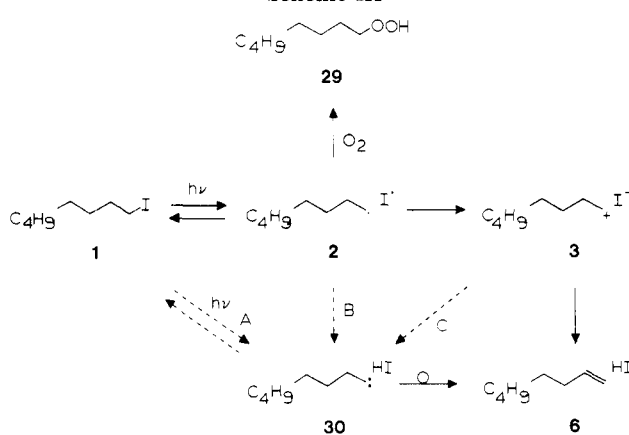
**1-(Iodomethyl)norbornane (22).** Our previous studies had shown that irradiation of iodide 22 in methanol affords a mixture of the ring-expanded ethers 23 and 24 (Scheme VII), which had been assumed to be formed exclusively via nucleophilic trapping of the corresponding bridgehead cations arising from rearrangement of cation 25 (Scheme VIII).<sup>2</sup> In view of the preceding results with iodides 1 and 13, it seemed possible that the bicyclo[2.2.2]octyl ether 23 arises instead, at least in part, via  $\alpha$  elimination. The resulting carbene 28 is known to undergo rearrangement to 1-bicyclo[2.2.2]octene (26) but not to the bicyclo[3.2.1]octenyl analogue 27.<sup>11</sup> The highly strained bridgehead alkene 26 would readily undergo addition of methanol to afford ether 28.<sup>12</sup> Indeed, when iodide 22 was irradiated in methanol-*d*, the bicyclo[2.2.2]octyl ether 23, but not the bicyclo[3.2.1]octyl ether 24, was formed with some incorporation of deuterium.

**Quantum Yields.** The quantum yields for disappearance of 1-iodooctane (1) and iodocyclohexane (13) in methanol were determined by using the disappearance of 1-iodonorbornane for actinometry<sup>2</sup> (Table VI).

### Discussion

The preceding results show quite clearly that some, but not all, primary and secondary alkyl iodides afford unsaturated products via  $\alpha$  elimination on irradiation in solution. In none of the cases was  $\alpha$  elimination observed to predominate over  $\beta$  elimination, the previously proposed route to unsaturated products.<sup>2</sup> However, it should be

Scheme IX



noted that, as shown in Scheme IX for the case of 1-iodooctane (1), the caged carbene-hydrogen iodide pair 30 may undergo undetected insertion to regenerate iodide 1 in competition with rearrangement of the carbene to 1-octene (6). Thus,  $\alpha$  elimination may occur more extensively than reflected by the present deuterium-labeling studies, which measure only the extent to which  $\alpha$  elimination leads to unsaturated product.

The relative involvement of  $\alpha$  and  $\beta$  elimination in 1-iodooctane (1) and iodocyclohexane (13) showed no significant dependence on solvent, wavelength, light intensity, or the presence of oxygen. Likewise, comparison of the behavior of the 1,1- and 2,2-dideuterated derivatives of 1 reveals no significant isotope effect. With the 1-iodooctane (1) system as a model, three conceivable routes to the carbene intermediate 30 are outlined in Scheme IX: (A) direct formation from iodide 1 via concerted loss of HI; (B)  $\alpha$ -hydrogen atom transfer within the radical pair 2; and (C)  $\alpha$ -proton transfer within the ion pair 3. Path A is inconsistent with the lack of effect of oxygen on the relative involvement of  $\alpha$  and  $\beta$  elimination in the formation of 1-octene (6). Previous studies showed that the formation of 6 is partially quenched in the presence of oxygen with the concomitant formation of the hydroperoxide 29, which on reductive workup affords 1-octanol (8, R = H).<sup>2</sup> Since path A should not be affected by the presence of oxygen, partial quenching of the formation of 1-octene (6) via  $\beta$  elimination should result in an increased predominance of  $\alpha$  elimination if path A were involved.<sup>13,14</sup>

(11) Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* 1973, 95, 8209-8210.(12) See: Becker, K. B. *Helv. Chim. Acta* 1977, 60, 94-102.

Table V. Irradiation of Iodocyclohexane-1-d (13-1-d)<sup>a</sup>

solvent	time, h	yield, <sup>b</sup> %		comp of 15, <sup>c</sup> %		$\alpha$ elim, <sup>d</sup> %
		13	15	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	
CH <sub>3</sub> OH	1	2	89	29	71	29
CH <sub>3</sub> OH <sup>e</sup>	24	<i>f</i>	85	27	73	27
CH <sub>3</sub> OH <sup>g</sup>	1	9	80	30	70	30
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>h</sup>	1	20	74	28	72	28
CH <sub>2</sub> Cl <sup>h</sup>	2	11	80	30	70	30
C <sub>5</sub> H <sub>12</sub> <sup>i</sup>	2	12	84	29	71	29

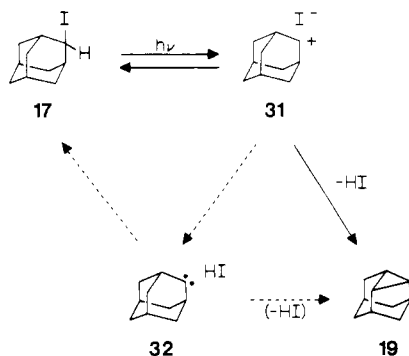
<sup>a</sup> Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section by using iodide 13-1-d that was 100% *d*<sub>1</sub>. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> Isotopic composition was determined by mass spectral analysis. <sup>d</sup> Calculated from isotopic composition of 15. <sup>e</sup> Irradiated by using RPR 3000-A lamps and a Corex filter. <sup>f</sup> Trace. <sup>g</sup> The broad emission of a 450-W medium-pressure mercury arc was employed. <sup>h</sup> Contained 1 molar equiv of triethylamine. <sup>i</sup> Irradiated by using RPR 1849/2537-A lamps and Suprasil glassware.

Table VI. Quantum Yields

iodide	$\Phi$		
	disappearance	$\alpha$ elim	$\beta$ elim
1	0.092	0.018	0.074
13	0.080	0.023	0.057

The parallel quenching by oxygen of both the  $\alpha$ - and  $\beta$ -elimination pathways thus suggests that either the radical pair 2 or the subsequent ion pair 3 serves as a precursor to the carbene intermediate. However, a choice between  $\alpha$ -hydrogen atom transfer within the radical pair 2 (path B) or an  $\alpha$ -proton transfer within the ion pair 3 (path C) is difficult to make based on the available data. Also, it is not clear whether the highly surprising occurrence of  $\alpha$  elimination is an inherent property of such a radical or ion pair or whether it is associated with the high-energy process by which the pair is generated in this case.<sup>15,16</sup>

The one iodide studied that failed to exhibit any detectable  $\alpha$  elimination is 2-iodoadamantane (17). The corresponding carbene intermediate, adamantylidene, is known to undergo internal insertion to the observed photoproduct, 2,4-dehydroadamantane (19).<sup>17</sup> However,



(13) The lack of an observable isotope effect in 1-1,1-d<sub>2</sub> on the relative involvement of  $\alpha$  elimination also argues against path A.

(14) Path A, may, however, be involved in the proposed formation of methylene from methyl iodide in the gas phase.<sup>8</sup>

(15) For a precedent to path C involving generation of carbene intermediates via transfer of  $\alpha$  protons from carbocations to lithium amides, see: Olofson, R. A.; Walinsky, S. W.; Marino, J. P.; Jernow, J. L. *J. Am. Chem. Soc.* 1968, 90, 6554-6555. See also: Curtin, D. Y.; Kampmeier, J. A.; O'Connor, B. R. *Ibid.* 1965, 87, 863-873.

(16) The multiplicity of the initially formed radical pair is unknown. Ketone-sensitized decomposition of alkyl halides has been observed but has been attributed to both the singlet and the triplet excited state of the ketone as the sensitizing species. See: Golub, M. A. *J. Am. Chem. Soc.* 1969, 91, 4925-4926; 1970, 92, 2615-2619; *J. Phys. Chem.* 1971, 75, 1168-1170. Harriman, A.; Rockett, B. W.; Poyner, W. R. *J. Chem. Soc., Perkin Trans. 2* 1974, 485-489. On the other hand, the tendency of the subsequent carbene intermediate to undergo 1,2 insertion indicates that it is singlet. See: Pomerantz, M.; Witherup, T. H. *J. Am. Chem. Soc.* 1973, 95, 5977-5988. Chang, K. T.; Schechter, H. *Ibid.* 1979, 101, 5082-5084.

in contrast with most dialkylcarbenes, internal insertion is sufficiently slow in this case that adamantylidene can be trapped intermolecularly under appropriate conditions.<sup>8</sup> Hence it is not clear whether  $\alpha$ -hydrogen transfer does not occur in this case or whether the resulting adamantylidene-hydrogen iodide pair 32 simply undergoes reversion to iodide 17 more rapidly than internal insertion to afford 19 occurs.

In the case of iodide 22,  $\alpha$  elimination competes not with  $\beta$  or  $\gamma$  elimination but rather rearrangement and nucleophilic trapping of the cationic intermediate 25. From the deuterium incorporation results, it can be calculated that cation 25 rearranges to the 1-bicyclo[2.2.2]octyl and 1-bicyclo[3.2.1]octyl cations in a ratio of 1.7:1, which is close to the statistical ratio of 2:1. Thus when formed photochemically, the cation 25 undergoes rearrangement predominately via kinetic control. By contrast, when formed solvolytically in methanol it affords principally the thermodynamically more stable 1-bicyclo[2.2.2]octyl cation.<sup>2</sup>

### Summary

The photobehavior of alkyl iodides in solution is thus substantially more complex than originally envisioned. In addition to the radical intermediates originally proposed<sup>3</sup> and the ionic intermediates demonstrated in our more recent studies,<sup>2</sup> many primary and secondary systems undergo  $\alpha$  elimination to afford carbene intermediates. The occurrence of this pathway contributes to, but does not totally account for, the usual predominance of elimination over nucleophilic substitution. It is hoped that further studies in progress will provide further insight into this intriguing pathway.

### Experimental Section

**General Procedures.** Infrared spectra were obtained in carbon tetrachloride solution with a Beckman 4250 spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument using 10 ft  $\times$  0.125 in. stainless steel columns packed with either (A) 20% Carbowax 20M or (B) SF-96 on 60-80 mesh Chromosorb W. Preparative gas chromatographic separations were effected on a Varian Aerograph 90-P instrument employing 5 or 10 ft  $\times$  0.25 in. stainless steel columns packed as described above. Melting points were determined on a Thomas-Hoover instrument and are uncorrected and uncalibrated. Nuclear magnetic resonance spectra were obtained in chloroform-*d* solution with a Varian XL-100 or Bruker WM 250 spectrometer. Isotopic compositions were calculated from mass spectra obtained by using a DuPont 21-490B or Hewlett-Packard 5992 spectrometer.

**Irradiations.** A 10-mL, 0.05 M solution of the iodide containing an internal hydrocarbon standard was placed in a 200  $\times$  9 mm quartz tube equipped with a condenser and a nitrogen inlet

(17) Udiding, A. C.; Strating, J.; Wynberg, H.; Schlattmann, J. L. M. A. *J. Chem. Soc., Chem. Commun.* 1966, 657.

tube and suspended in either a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 (254 nm) lamps or a quartz water-cooled immersion well positioned 6 cm from a 450-W mercury arc and reflector. Unless otherwise indicated, the solution was purged with nitrogen 10 min prior to irradiation and maintained under a nitrogen atmosphere. At the completion of the irradiation, the usually yellow solution was poured into 50 mL of water and extracted with three 25-mL portions of ether. The organic layer was washed successively with 40-mL portions each of 10% aqueous sodium thiosulfate solution, saturated aqueous sodium bicarbonate solution, and water. The combined aqueous portions were back-extracted with a 25-mL portion of ether. The combined ether fractions were washed with a 40-mL portion of saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by distillation of the solvent through a 25-cm Vigreux column.

Methanol used in irradiations was distilled from magnesium methoxide.<sup>18</sup> Dichloromethane was washed with concentrated sulfuric acid, water, and then 10% sodium carbonate solution, dried over calcium chloride, and distilled from phosphorus pentoxide. Pentane was purified as described previously.<sup>19</sup> 1,2-Ethandiol was distilled from barium oxide and bis(2-methoxyethyl) ether (diglyme) from lithium aluminum hydride.

**1-Iodoctane (1). A. Purification.** Commercial material was purified prior to use by washing with 10% aqueous sodium thiosulfate solution, water, and saturated aqueous sodium chloride solution followed by drying over anhydrous sodium sulfate and subsequent distillation at reduced pressure.

**B. Irradiation.** The products from the irradiations outlined in Table I were isolated by preparative gas chromatography (column B) and characterized as previously described.<sup>2</sup>

**1-Iodoctane-1,1-*d*<sub>2</sub> (1-1,1-*d*<sub>2</sub>). A. Synthesis.** A solution of 4.3 g (25 mmol) of ethyl octanoate (10) in 20 mL of anhydrous ether was added dropwise to a vigorously stirred mixture of 25 mL of anhydrous ether and 700 mg (17 mmol) of lithium aluminum deuteride. The mixture was stirred at room temperature for 30 min and then heated under reflux for 2 h. Excess lithium aluminum deuteride was quenched and the mixture filtered.<sup>20</sup> The ether solution was dried over anhydrous sodium sulfate and the ether removed by rotary evaporation to afford 3.2 g (98%) of 1-octanol-1,1-*d*<sub>2</sub> (11-1,1-*d*<sub>2</sub>) as a colorless oil.

A mixture of 7.5 g (24 mmol) of triphenyl phosphite and 5.3 g (37 mmol) of iodomethane was heated under gentle reflux to 120 °C according to the procedure outlined for the preparation of iodocyclohexane.<sup>21</sup> The dark, viscous solution was cooled to room temperature, and 3.2 g (24 mmol) of 11-1,1-*d*<sub>2</sub> was added with gentle shaking. The mixture was allowed to stand overnight and then distilled under reduced pressure affording an azeotrope consisting of alcohol 11-1,1-*d*<sub>2</sub>, phenol, and iodide 1-1,1-*d*<sub>2</sub>: bp 38–40 °C (0.05 mm). The resulting mixture was taken up in 100 mL of ether, washed with two 25-mL portions each of 10% aqueous sodium hydroxide and saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. Removal of the ether by rotary evaporation followed by preparative gas chromatographic isolation (column B) gave 1.73 g (30%) of 1-1,1-*d*<sub>2</sub> as a colorless liquid: 97% *d*<sub>2</sub>, 2% *d*<sub>1</sub>, 1% *d*<sub>0</sub>.

**B. Irradiation.** From the irradiations outlined in Table II the major product was isolated by preparative gas chromatography (column B) and its isotopic composition determined by mass spectroscopy or <sup>1</sup>H NMR spectrometry.

**1-Iodoctane-2,2-*d*<sub>2</sub> (1-2,2-*d*<sub>2</sub>). A. Synthesis.** The general procedure of Baldwin and Puduserry was utilized.<sup>22</sup> A mixture of 6.3 g (0.05 mol) of freshly distilled octanal (12), 0.38 g (4.8 mmol) of pyridine, and 12 g (0.6 mol) of deuterium oxide was heated to 100 °C with vigorous stirring for 24 h under a nitrogen atmosphere. The mixture was cooled to room temperature and the aqueous layer was removed, saturated with sodium chloride, and extracted

with three 15-mL portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The recovered octanal (12) was retreated as described above. The yellow oil resulting from four cycles of the exchange procedure was used in the next step without purification.

A solution of the resulting aldehyde in 20 mL of anhydrous ether was added dropwise into a vigorously stirred mixture of 25 mL of anhydrous ether and 1.2 g (30 mmol) of lithium aluminum hydride. The mixture was stirred at room temperature for 30 min and then heated under reflux for 1 h. Excess lithium aluminum hydride was quenched and the mixture filtered.<sup>20</sup> The ether solution was dried over anhydrous sodium sulfate and concentrated by rotary evaporation to give 5.6 g of alcohol 11-2,2-*d*<sub>2</sub> as a yellow oil, which was used without further purification.

A 5.1-g sample of crude alcohol 11-2,2-*d*<sub>2</sub> was treated in a manner identical with that described above for alcohol 11-1,1-*d*<sub>2</sub>. Distillation under reduced pressure afforded an azeotrope consisting of phenol and iodide 1-2,2-*d*<sub>2</sub>: bp 37–40 °C (0.05 mm). The mixture was taken up in 100 mL of ether, washed with two 25-mL portions of 10% sodium hydroxide solution followed by 25 mL of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Removal of the ether by rotary evaporation followed by preparative gas chromatographic isolation (column B) afforded 2.4 g (20% from 12) of iodide 1-2,2-*d*<sub>2</sub> as a colorless liquid: 1% *d*<sub>3</sub>, 87% *d*<sub>2</sub>, 4% *d*<sub>1</sub>, 8% *d*<sub>0</sub>.

**B. Irradiation.** From the irradiations outlined in Table III the major product was isolated by preparative gas chromatography (column B) and its isotopic composition determined by mass spectroscopy and <sup>1</sup>H NMR spectroscopy.

**Iodocyclohexane (13). A. Synthesis.** A 10-g (0.10 mol) sample of cyclohexanol was treated in a manner identical with that described above for alcohol 11-1,1-*d*<sub>2</sub> to afford 6.9 g (33%) of iodide 13 as a colorless liquid: bp 62–64 °C (12 mm).

**B. Irradiation.** The products from the irradiations outlined in Table IV were isolated by preparative gas chromatography (column B). **Cyclohexane (14)** and **cyclohexene (15)** were obtained as colorless liquids whose spectral properties agreed with those of commercial specimens. Methoxycyclohexane (16) was obtained as a colorless liquid whose spectral properties agreed with those of an authentic specimen.<sup>23</sup>

**Iodocyclohexane-1-*d* (13-1-*d*). A. Synthesis.** A solution prepared from 5.88 g (60.0 mmol) of cyclohexanone in 20 mL of anhydrous ether was added dropwise into a stirred mixture of 25 mL of anhydrous ether and 740 mg (18.0 mmol) of lithium aluminum deuteride. The mixture was stirred at room temperature for 15 min and then heated under reflux for 1 h. Excess lithium aluminum deuteride was quenched and the mixture filtered.<sup>20</sup> The ether solution was dried over anhydrous sodium sulfate and concentrated by rotary evaporation to afford 3.6 g (65%) of cyclohexanol-1-*d* as a clear oil, which was treated in a manner identical with that described above for alcohol 11-1,1-*d*<sub>2</sub> to give 1.11 g (15%) of iodide 13-1-*d* as a colorless liquid: 0% *d*<sub>0</sub>, 100% *d*<sub>1</sub>.

**B. Irradiation.** From the irradiations outlined in Table V the major product was isolated by preparative gas chromatography (column B) and its isotopic composition determined by mass spectroscopy.

**2-Iodoadamantane-2-*d* (17-2-*d*). A. Synthesis.** A 1.0-g (6.7-mmol) sample of 2-adamantanone was treated with lithium aluminum deuteride in a manner identical with that described above for cyclohexanone to afford 980 mg (96%) of 2-adamantanol-2-*d* as colorless crystals: mp 291–292 °C dec.

The general procedure of Jung<sup>24</sup> was utilized in the preparation of iodide 17-2-*d*. Nitrogen was bubbled through a solution of 500 mg (3.30 mmol) of 2-adamantanol-2-*d* in 20 mL of dichloromethane contained in a 25-mL round-bottomed flask equipped with magnetic stirring bar. After 10 min, a septum cap was placed over the top of the flask and 1.0 mL (2.0 g, 10 mmol) of trimethylsilyl iodide<sup>25</sup> was added via syringe. The resulting mixture was stirred for 24 h and then quenched by addition of 1 mL of water. This solution was extracted with three 25-mL portions of ether and then washed with consecutive 20-mL

(18) Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Wiley: New York, 1970; Vol. II, p 640.

(19) Kropp, P. J.; Tise, F. P. *J. Am. Chem. Soc.* 1981, 103, 7293–7298.

(20) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 584.

(21) Rydon, H. N. *Org. Synth.* 1971, 51, 44.

(22) Baldwin, J. E.; Puduserry, R. G. *J. Chem. Soc., Chem. Commun.* 1968, 408.

(23) Kropp, P. J. *J. Am. Chem. Soc.* 1969, 91, 5783–5791.

(24) Jung, M. E.; Ornstein, P. L. *Tetrahedron Lett.* 1977, 2659–2662.

(25) Jung, M. E.; Lyster, M. A. *Org. Synth.* 1979, 59, 35–41.

portions of water, 10% sodium thiosulfate solution, saturated sodium bicarbonate solution, and saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation to afford 1.11 g of a yellow oil. The oil was eluted through a silica column with dichloromethane, and the solvent was removed by rotary evaporation. Recrystallization from hot methanol afforded 480 mg (55%) of iodide 17-2-*d* as colorless needles: mp 47-48 °C; 0% *d*<sub>0</sub>, 100% *d*<sub>1</sub>.

**B. Irradiation.** A 10-mL ethereal solution containing 130 mg (0.500 mmol) of iodide 17-2-*d* and 50 mg (0.50 mmol) of triethylamine was irradiated at 254 nm as described above for 1.5 h. The principal product was isolated by preparative gas chromatography (column A) and its isotopic composition determined by mass spectroscopy: 100% *d*<sub>1</sub>.

**Irradiation of 1-(Iodomethyl)norbornane (22).** A 10-mL solution of 236 mg (1.00 mmol) of iodide 22<sup>26</sup> in methanol-*d* was irradiated at 254 nm as described above for 4.5 h. The products were isolated by preparative gas chromatography (column A) and characterized as described previously.<sup>2</sup> Their isotopic compositions were determined by mass spectroscopy (Scheme VII).

(26) Tipson, R. S.; Clapp, M. A.; Cretcher, L. H. *J. Org. Chem.* 1947, 12, 133.

**Quantum Yields.** Solutions containing 1 mmol each of iodides 1 and 13 and 1-iodonorbornane (actinometer<sup>2</sup>) in 20 mL of methanol containing a hydrocarbon internal standard were placed in 11-mm i.d. (13-mm o.d.) × 140-mm quartz tubes and deaired for 15 min with nitrogen bubbling. The tubes were sealed, placed in a merry-go-round apparatus in a RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 G8T5 lamps, and irradiated for 15 min. The progress of the photolyses was monitored by gas chromatographic analysis, and the quantum yields for the disappearance of iodide were calculated (Table VI).

**Acknowledgment.** Generous financial assistance by the National Science Foundation is gratefully acknowledged.

**Registry No.** 1-1,1-*d*<sub>2</sub>, 89232-08-6; 1-2,2-*d*<sub>2</sub>, 89232-09-7; 6, 111-66-0; 6-1-*d*, 72084-42-5; 6-2-*d*, 72084-45-8; 6-1,1-*d*<sub>2</sub>, 54439-94-0; 6-1,2-*d*<sub>2</sub>, 89232-14-4; 10, 106-32-1; 11-1,1-*d*<sub>2</sub>, 78510-02-8; 11-2,2-*d*<sub>2</sub>, 89232-16-6; 12, 124-13-0; 12-2,2-*d*<sub>2</sub>, 89232-15-5; 13, 626-62-0; 13-1-*d*, 89232-10-0; 15, 110-83-8; 15-1-*d*, 42843-17-4; 16, 931-56-6; 17-2-*d*, 89232-13-3; 19-2-*d*, 89232-17-7; 22, 61192-16-3; 23, 7697-14-5; 24, 61192-23-2; 25, 89232-12-2; 28, 89232-11-1; CH<sub>3</sub>OD, 1455-13-6; (PhO)<sub>3</sub>P, 101-02-0; CH<sub>3</sub>I, 74-88-4; cyclohexanol, 108-93-0; cyclohexanol-1-*d*, 21273-02-9; 2-adamantanone, 700-58-3; 2-adamantanol-2-*d*, 55834-71-4.

## Oxygenation of Olefins under Reductive Conditions. Cobalt-Catalyzed Selective Conversion of Aromatic Olefins to Benzylic Alcohols by Molecular Oxygen and Tetrahydroborate

Tadashi Okamoto\* and Shinzaburo Oka

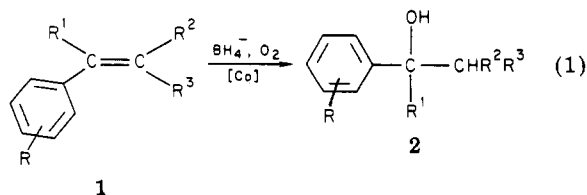
*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611, Japan*

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A high-yield catalytic conversion of aryl olefins 1 to benzylic alcohols 2 was developed by the use of molecular oxygen and BH<sub>4</sub><sup>-</sup> in the presence of a catalytic amount of Co(TPP). Acid-labile alcohols were prepared in good yields. The reaction was regioselective to give benzylic alcohols exclusively and nonstereoselective. Comparison of the results of the catalytic oxygenation of styrene, the stoichiometric oxygenation of alkylcobalt complex 6, and the decomposition of 1-phenylethyl hydroperoxide (7) in distribution of products and deuterium incorporation at room and low temperatures indicated the participation of 7 as the primary product, which is formed by the reaction of 6 with molecular oxygen. Co(TPP) catalyzed three elementary reactions in the overall catalytic process: formation of 7, decomposition of 7 to 2 and aryl ketone 5, and reduction of 5.

Transition-metal-catalyzed reactions of molecular oxygen with organic compounds are important processes for the mimesis of various metal-containing oxidases and oxygenases.<sup>1</sup> Since an electron donor such as NADH or ascorbic acid is usually required for the reaction catalyzed by monooxygenases,<sup>2</sup> a catalyst composed of a reductant and a transition-metal complex attracted attention as the model system of NADH-dependent oxygenases. Tabushi<sup>3</sup> and Gaudemer<sup>4</sup> reported the reactions of hydrocarbons with molecular oxygen to give an alcohol, a ketone, or an epoxide by the catalysis of (tetraphenylporphyrinato)-manganese(III) under the influence of a reducing agent

such as tetrahydroborate or molecular hydrogen over colloidal platinum. However, the mechanisms of these model reactions are not elucidated at present and it is a question whether a true activation of molecular oxygen is involved during the reaction. We communicated previously the reaction of aryl olefins with molecular oxygen and BH<sub>4</sub><sup>-</sup> (eq 1) to give low yields of benzylic alcohols in the



(1) Hamilton, G. A. "Molecular Mechanism of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405.

(2) Nozaki, M. *Top. Curr. Chem.* 1979, 78, 145-186.

(3) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* 1979, 101, 6456-6458. Tabushi, I.; Yazaki, A. *Ibid.* 1981, 103, 7371-7373.

(4) Fauvet, M. P.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* 1981, 874-875.

presence of a catalytic amount of bis(dimethylglyoximate)chloro(pyridine)cobalt.<sup>5</sup> In this paper the

(5) Okamoto, T.; Oka, S. *Tetrahedron Lett.* 1981, 2191-2194.