stored under nitrogen over anhydrous potassium carbonate. The hydrocarbons employed as internal standards for GLC analysis were obtained from Phillips Petroleum Co. and were labeled >99% pure. Cycloheptene, cyclooctene, norbornene, styrene, α-methylstyrene, and *p*-methoxystyrene were obtained from the Aldrich Chemical Co. The styrene derivatives were stored at 0 °C and distilled from $LiAlH_4$ immediately before use. The remaining alkenes, except norbornene, were distilled from $LiAlH_4$ and stored under nitrogen at ambient temperatures. The other alkenes employed in this study were used as received from the Chemical Samples Division of Albany International after their refractive indices and ^1H NMR spectral characteristics were checked.

GLC Analyses. GLC analyses were carried out with a Varian Model 1200 FID chromatograph equipped with an injection port lined with a 6 in. × 0.25 in. column of 10% THEED on 80/100 mesh Supelcoport to protect the GLC columns from contamination by organoborane species. Olefins with boiling points below 50 °C were analyzed on a 12 ft × 0.125 in. column of 30% adiponitrile on 60/80 mesh Firebrick. All other alkenes were analyzed on a 12 ft × 0.125 in. column of 10% SE-30 on 100/120 mesh Supelcoport.

Competitive Hydroboration of Olefin Pairs with $ThxBHCl{\cdot}SMe_2$. A typical experimental procedure for determining the relative reactivities of cyclooctene vs. cycloheptene follows. A clean, dry, 100-mL round-bottom flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was charged at 0 °C with 5.90 mL of CH_2Cl_2, 0.50 mL of *n*-decane (0.395 g, 2.78 mmol, internal standard), 0.58 mL of cycloheptene (0.499 g, 5.2 mmol), and 0.65 mL of cyclooctene (0.552 g, 5.0 mmol). The resulting solution was stirred at 0 °C for 15 min. A 0.10-mL aliquot was withdrawn to obtain the initial olefin/(*n*-decane) ratios by GLC (12 ft × 0.125 in. 10% SE-30 on 100/120 mesh Supelcoport maintained at 75 °C). The following ratios were obtained: cycloheptene/*n*-decane = 1.26 (theoretical = 0.499/0.395 = 1.26) and cyclooctene/*n*-decane = 1.37 (theoretical = 0.552/0.395 = 1.40). Meanwhile, the flask was immersed in a constant temperature bath, and the contents were quilibrated with stirring at 25.0 ± 0.05 °C for 20 min. Then 2.35 mL of cold 2.1 M $ThxBHCl{\cdot}SMe_2$ (5.0 mmol) in CH_2Cl_2 were quickly added via syringe. The overall concentration of each olefin and $ThxBHCl{\cdot}SMe_2$ was 0.50 M. The resulting solution was then stirred at 25.0 °C for sufficient time to allow complete reaction (3 h), cooled to 0 °C, and quenched with excess NaOH (5.0 mL of 3 N). After 1 h at 0 °C, the aqueous layer was saturated with solid NaCl. A 0.5-mL aliquot of the CH_2Cl_2 layer was withdrawn, dried over anhydrous K_2CO_3, and analyzed immediately by GLC to obtain the final olefin/*n*-decane ratios. Found: cycloheptene/*n*-decane = 1.01 (20% consumed), cyclooctene/*n*-decane = 0.274 (80% consumed). The relative reactivity of this substrate pair, as well as other substrate pairs, was then calculated by using the Ingold–Shaw equation (eq 2),[7] where X_0 and Y_0 are the initial concentrations of x and y and X and Y are the residual concentrations of the two olefins being compared. For this example, $k_{\text{cyclooctene}}/k_{\text{cycloheptene}} = 7.4$.

$$\text{relative rate} = \frac{k_x}{k_y} = \frac{\ln X_0 - \ln X}{\ln Y_0 - \ln Y} \qquad (2)$$

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Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; cyclooctene, 931-88-4; 3-methyl-1-hexene, 3404-61-3; 2-methyl-1-pentene, 763-29-1; cycloheptene, 628-92-2; *cis*-3-hexene, 7642-09-3; *cis*-2-pentene, 627-20-3; *cis*-4-methyl-2-pentene, 691-38-3; 4-vinylanisole, 637-69-4; cyclopentene, 142-29-0; styrene, 100-42-5; 3,3-dimethyl-1-hexene, 3404-77-1; norbornene, 498-66-8; *cis*-4,4-dimethyl-2-pentene, 762-63-0; 2-methyl-2-pentene, 625-27-4; 1-methylcyclopentene, 693-89-0; *trans*-3-hexene, 13269-52-8; *trans*-2-pentene, 646-04-8; *trans*-2-hexene, 4050-45-7; α-methylstyrene, 98-83-9; *trans*-4-methyl-2-pentene, 674-76-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; $ThxBHCl{\cdot}SMe_2$, 75067-06-0.

Active Metals from Potassium–Graphite. Iron–Graphite as a New Debrominating Agent of *vic*-Dibromoalkanes and of α-Bromo Ketones

Diego Savoia, Emilio Tagliavini, Claudio Trombini, and Achille Umani-Ronchi*

Istituto Chimico "G. Ciamician", Università di Bologna, Italy

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Iron–graphite (Fe-Gr), easily prepared by reduction of $FeCl_3$ with potassium–graphite (C_8K) in tetrahydrofuran, is conveniently used for the stereospecific debromination of *vic*-dibromoalkanes to alkenes and for the reductive debromination of α-bromo ketones to ketones in high yields. The latter reaction proceeds via Fe(II) enolates, which undergo deuteration, condensation, or O-silylation by reaction respectively with D_2O, heptanal, or chlorotrimethylsilane. Moreover, the reaction of α,α′-dibromo ketones with Fe-Gr leads to 2-oxyallyl cations which can be trapped by suitable electron-rich olefins (enamines) or dienes (furan).

We have been recently engaged with the preparation of active forms of transition metals by reduction of transition metal salts with potassium–graphite (C_8K).[1] Highly dispersed nickel[2] and palladium[3] on the graphite surface obtained by this method were found to act as effective catalysts in hydrogenation and vinylic substitution reactions.

We now report the preparation of iron–graphite (Fe-Gr) according to stoichiometric eq 1 and its use as a new debrominating agent of *vic*-dibromoalkanes and of α-bromo ketones.

$$3C_8K + FeCl_3 \rightarrow C_{24}Fe + 3KCl \qquad (1)$$

When a solution of anhydrous $FeCl_3$ in tetrahydrofuran (THF) is added dropwise to a stirred suspension of C_8K in THF, a fast and exothermic reaction takes place, affording a black powder, the metal content (15.4%)[4] of

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[2] Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A., *J. Org. Chem.* **1982**, *47*, 564.

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[4] A higher iron loading (22%) can be obtained by starting from $FeCl_2$; however, owing to the poor solubility of this salt in ethereal solvents, it is necessary to reflux the heterogeneous mixture of C_8K and $FeCl_2$ in 1,2-dimethoxyethane at least for 3 h to achieve an almost complete reduction. Furthermore, the obtained material is less active in comparison to that obtained from $FeCl_3$ (see Table II), probably owing to a worse surface area/mass ratio of iron particles.

Table I. Alkenes from *vic*-Dibromoalkanes[a]

substrate	time, min	alkene	% yield[b]
1,2-dibromoundecane (**1a**)	180	1-undecene (**2a**)	95
erythro-1,2-dibromo-1,2-diphenylethane (**1b**)	60	*trans*-stilbene (**2b**)[c]	98
threo-5,6-dibromodecane (**1c**)[d]	150	*cis*-5-decene (**2c**)[e]	90

[a] The reactions are carried out on 3 mmol of substrate and 10 mmol of iron as Fe-Gr at 70 °C in THF/H_2O (35:1). [b] Values determined by GC analysis. [c] No traces of *cis*-stilbene are detected by GC (RRT values of cis and trans isomers in a 0.25 in. × 6 ft column packed with 15% Carbowax 20M on Chromosorb W (80–100 mesh) at 200 °C are 1.00 and 1.85, respectively). [d] Compound **1c** was prepared by starting from a sample of *cis*-5-decene obtained in 98.9% geometrical purity by Ni-Gr1-catalyzed hydrogenation of 5-decyne (see ref 2). [e] The geometrical purity of **2c** was 96.4% (see Experimental Section); 5% of unreacted **1c** was recovered.

Table II. Ketones from Reductive Debromination of α-Bromo Ketones[a]

substrate	time, min	ketone	% yield[b]
α-bromoacetophenone (**3a**)	360	acetophenone (**4a**)[c]	75
	20	α-deuterioacetophenone (**4a**-*d*)[d,e]	96, 65[f]
3-bromocamphor (**3b**)	90	3-deuteriocamphor (**4b**-*d*)[g,d]	94
1-bromo-3,3-dimethylbutan-2-one (**3c**)	20	1-deuterio-3,3-dimethylbutan-2-one (**4c**-*d*)[d]	94

[a] The reactions are carried out on 5-mmol of substrate and 10 mmol of iron as Fe-Gr at 70 °C in THF/D_2O (35:1). [b] Values determined by GC analysis. [c] The reaction is carried out in the absence of water and then quenched with D_2O. Mass spectrum (**4a**), *m/e* (relative intensity) 120, (100), 121 (10), 122 (0.6). Acetophenone shows the following *m/e* values and relative intensities: 120 (100), 121 (9), 122 (0.6). [d] See the Experimental Section. [e] To evaluate deuterium incorporation due to enolization, **4a** was stirred with a twofold excess of Fe-Gr in THF/D_2O (35:1) at 70 °C for 20 min: mass spectrum, *m/e* (relative intensity) 120 (100), 121 (25), 122 (3.6). This indicates the presence of ~15% of deuterated material. [f] Fe-Gr was prepared from C_8K and $FeCl_2$ in refluxing 1,2-dimethoxyethane;[4] 30% of **3a** is present after the reaction mixture is stirred at 70 °C for 20 min. [g] The 3-*exo*-deuterio-/3-*endo*-deuteriocamphor ratio is 85:15.

which agrees with the supposed stoichiometry ($C_{24}Fe$ requires 16.2%) and with a conversion of 95%. X-ray diffraction spectra[5] of Fe-Gr samples, previously washed with water in order to eliminate most of the KCl and unreduced $FeCl_3$, revealed very weak signals of α-Fe besides the strong signals of graphite, suggesting a high dispersion of iron on the graphite surface. Weak reflections due to intercalated species are also observed. Furthermore, washing and drying Fe-Gr with air-exposure gives rise to metal oxidation, detectable with both microscopy and X-ray analysis, which causes complete loss of reactivity. *Therefore, Fe-Gr is prepared under argon and used "in situ" for the successive reactions.*

Stereospecific Debromination of *vic*-Dibromoalkanes. The stereospecificity of bromine addition to carbon–carbon double bonds and the availability of methods for the latter regeneration of the double bond with the original geometry make the bromination reaction the most common protection of olefins toward oxidizing, reducing, and electrophilic agents.[6]

We describe here the debromination reaction of *vic*-dibromoalkanes (**1**) to alkenes (**2**) promoted by Fe-Gr (eq 2). Some runs have been carried out on 1,2-dibromoundecane (**1a**) in the same solvent used for Fe-Gr preparation.

$$\underset{\mathbf{1}}{\mathrm{RCHBrCHBrR'}} + \text{Fe-Gr} \rightarrow \underset{\mathbf{2}}{\mathrm{RCH{=}CHR'}} + \mathrm{FeBr_2} \qquad (2)$$

Whereas only traces of 1-undecene (**2a**) were detected after the reaction mixture was stirred at 25 °C for 12 h, a 50% conversion was obtained after 16 h at 70 °C.[7] A remarkable increase of the reaction rate was obtained when a little amount of deareated water was previously added to Fe-Gr.[8] In fact, 1-undecene (**2a**) was obtained in 95% yield after 3 h at 70 °C. Careful GC analysis excluded the presence of more than 0.5% of isomeric 2-undecenes (Table I). To check the stereospecificity of the reaction, two runs were performed by using *erythro*-1,2-dibromo-1,2-diphenylethane (**1b**) and *threo*-5,6-dibromodecane (**1c**). As expected for an anti debromination mechanism, *trans*-stilbene (**2b**) and *cis*-5-decene (**2c**) were obtained with high isomeric purity. Particularly, the overall loss of geometrical purity of *cis*-5-decene in the two-step sequence of bromination–debromination was only 2.5%.

Reductive Dehalogenation of α-Bromo Ketones. Reductive dehalogenation of organic halides can be effected with a variety of reagents reviewed by Pinder;[9] more recent methods, concerning the dehalogenation of α-bromo ketones, involve the use of $Fe(CO)_5$,[10] polymer-supported $HFe(CO)_4^-$,[11] $NaI/(CH_3)_3N/SO_2$,[12] SO_3/pyridine,[12] $NaI/(CH_3)_3SiCl$,[13] $(CH_3)_3SiI$,[14] NaI in aqueous acidic THF,[15] and PI_3 or P_2I_4.[16]

The results of reductive debromination reactions of α-bromo ketones (**3**) to ketones (**4**) reported in Table II show that Fe-Gr is a competitive reagent in comparison with those reported in the literature.[9–16] Optimum yields were obtained by heating the α-bromo ketone and Fe-Gr in THF and in the presence of deareated water at 70 °C. It is reasonable to assume that the reaction takes place via oxidative addition of iron into the carbon–bromine bond to give a Fe(II) enolate intermediate.[7] In the presence of water the enolate is readily protonated, as confirmed by the quantitative deuterium incorporation when D_2O is used. Carrying out the debromination reaction in the

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(5) Debye–Scherrer camera, diameter 114.6 mm, Fe Kα radiation.

(6) Young, D. W. "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum Press: London, 1973; Chapter 8.

(7) The formation of Fe(III) was confirmed by the red complex obtained after shaking an aliquot of the reaction mixture with an aqueous solution of *o*-phenantroline.

(8) Water dissolves KCl (see eq 1) precipitated on graphite, thus allowing a more effective contact between iron and the reagent.

(9) Pinder, A. R. *Synthesis* **1980**, 425.

(10) Luh, T. Y.; Lai, C. H.; Lei, K. L.; Tam, S. W. *J. Org. Chem.* **1979**, *44*, 641.

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(15) Gemal, A. L.; Luche, J. L. *Tetrahedron Lett.* **1980**, 3195.

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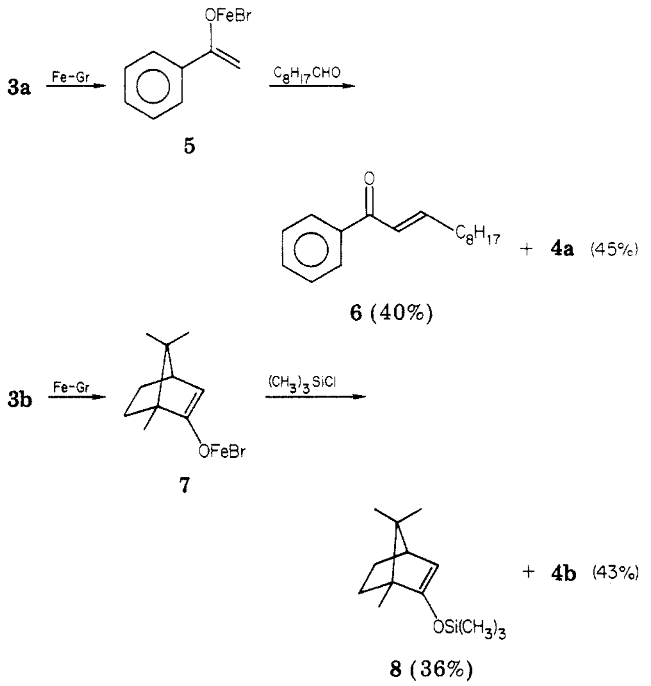
Scheme I



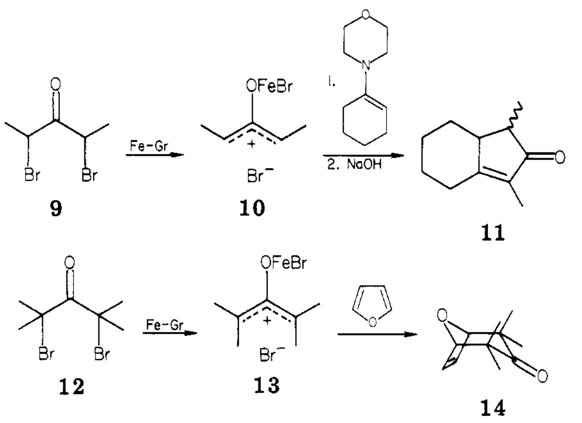
absence of water and then quenching with D_2O, results in a reduced ketone which does not contain deuterium (run 1), and this suggests that, in analogy with the organoiron complexes resulting from the reaction of Fe(CO)$_5$ and α-bromo ketones,[10] the Fe(II) enolate may decompose to an enol-type free radical able to abstract a hydrogen atom from THF. Similar free-radical reactions of Zn(II) enolates have been also reported.[17]

Attempts to trap the Fe(II) enolates **5** and **7** with electrophiles such as heptanal and (CH$_3$)$_3$SiCl confirmed the concurrence of ionic and free-radical reaction pathways. In fact, besides to the expected products **6** and **8**, large amounts of reduced ketones **4a** and **4b** were isolated (Scheme I).

Preparation and Trapping of 2-Oxyallyl Cations from α,α'-Dibromo Ketones. 2-Oxyallyl cations,[18] as well as their synthetic equivalents,[19] emerged during the last few years as suitable electrophilic C-3 synthons for the preparation of five- and seven-membered carbocycles by reaction with olefins and dienes, respectively. The preparation of 2-oxyallyl species generally involves the reaction of an α,α'-dibromo ketone with Fe$_2$(CO)$_9$,[18b,20] Zn/Cu couple,[21] or copper/NaI.[22]

Fe-Gr can be conveniently used for 2-oxyallyl cation formation by starting from α,α'-dibromo ketones, as shown in Scheme II. With this aim, Fe-Gr was prepared in the usual way in THF, the solvent was filtered off under argon, and the residue was covered with anhydrous benzene, which is the solvent of choice in the analogous reactions promoted by Fe$_2$(CO)$_9$. Addition of **9** and of 4-(1-cyclohexen-1-yl)morpholine (twofold excess), followed by stirring for 15 h at 30 °C, afforded the cyclopentenone **11** in 84% yield after treatment with 3% methanolic NaOH solution. Analogously, the reaction of dibromo ketone **12** with Fe-Gr[23] in furan as the solvent gave the cycloadduct **14** in 88% yield after 15 h at 40 °C.

Scheme II



In conclusion, we believe that our route to active transition-metal species will offer to organic chemists new tools to effect chemical transformations under heterogeneous conditions. An example is given by Fe-Gr, a newly available, cheap, and competitive debrominating agent.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were measured with a Perkin-Elmer R12B instrument (60 MHz) using tetramethylsilane as the internal standard, and chemical shifts are reported as δ values. Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer, and the absorptions are given in reciprocal centimeters. Mass spectra were taken on a double-focusing Varian MAT 112S instrument at an ionizing voltage of 70 eV. Analytical gas chromatography (GC) was performed on a Perkin-Elmer Sigma 3 apparatus equipped with a flame-ionization detector and using 0.25 in. × 6 ft columns (A, 5% FFAP on silanized Chromosorb W, 80–100 mesh; B, 2.5% SE-30 on silanized Chromosorb G, 80–100 mesh) with a nitrogen flow of 40 mL/min. Peak areas, yield determi-

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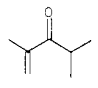
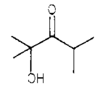
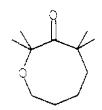
(23) Treatment of dibromo ketone **12** with Fe-Gr (threefold excess) in THF-H$_2$O (35/1) at 70 °C for 1 h afforded a complex product mixture. The three major components, to which structures I–III were assigned on the basis of GC/MS spectra, came from the common intermediate **13** (Scheme II) by hydride elimination, water addition, and THF addition, respectively.



I, *m/e* (relative intensity) 41 (82), 43 (24), 69 (100), 112 (12, M$^+$)



II, *m/e* (relative intensity) 43 (80), 59 (100), 87 (16), 103 (6), 130 (3, M$^+$)



III, *m/e* (relative intensity) 71 (58), 72 (100), 84 (15), 141 (4), 156 (3), 184 (40, M$^+$)

nations, and relative retention times (RRT) were obtained with the aid of a Perkin-Elmer Sigma 10 data station. Graphite powder was obtained from Roth, potassium from Carlo Erba, and anhydrous $FeCl_3$ from Merck. All substrates were commercial compounds or were prepared according to standard procedures. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl, and benzene was distilled and stored over sodium. Boiling points (bp) are uncorrected.

Preparation of Iron–Graphite (Fe–Gr). Graphite (3 g) was poured into a two-necked flask equipped with condenser, argon inlet, and magnetic stirring bar and heated under argon at about 150 °C for 30 min. Freshly cleaned potassium (1.17 g, 30 mmol) was added with stirring to give a homogeneous brown powder of potassium–graphite (C_8K). The flask was cooled to room temperature, the C_8K was covered with THF (15 mL), and $FeCl_3$ (1.62 g, 10 mmol) dissolved in THF (20 mL) was added dropwise with stirring. After 30 min the mixture was heated at 70 °C for 10 min. Fe-Gr so obtained was used in situ under argon for the successive reactions. To verify the stoichiometry of eq 1, we refluxed a sample of Fe-Gr prepared from 30 mmol of C_8K and 10 mmol of $FeCl_3$ with water (150 mL) for 90 min. The aqueous solution contained, after filtration, potassium (1.11 g, 28.5 mmol) and iron (0.028 g, 0.5 mmol) as determined by atomic absorption spectroscopy. Moreover, the solid residue, heated at 100 °C with 1 N HCl (50 mL) for 2 h, afforded a solution containing potassium (0.054 g, 1.4 mmol) and iron (0.53 g, 9.5 mmol).

Debromination of 1,2-Dibromoundecane (1a). Standard Procedure. Deareated water (1 mL) was dropped into a slurry of Fe-Gr (10 mmol of iron) in THF (35 mL). Then, after the mixture was stirred 5 min at 30 °C, **1a** (0.95 g, 3 mmol) and decane (internal standard) were added, and the reaction mixture was vigorously stirred at 70 °C (external oil bath). After 180 min, GC analysis (A, 80–220 °C at 10 °C/min) revealed the formation of 1-undecene (**2a**) in 95% yield, without traces of isomeric 2-undecenes. After graphite filtration and washing with ether (3 × 10 mL), **2a** was isolated by distillation[24] [bp 76 °C (14 mmHg)]. By the same procedure *trans*-stilbene (**2b**)[24] and *cis*-5-decene (**2c**)[2] were obtained. To establish the isomeric purity of the latter olefin, we epoxidized **2c** with 3-chloroperbenzoic acid in dichloromethane at 0 °C. GC analysis (A, 100 °C) allowed evaluation of the relative ratio (96.4:3.6) of erythro (RRT 1.00) and threo (RRT 0.89) epoxides.

Reductive Debromination of α-Bromoacetophenone (3a). Standard Procedure. Deareated D_2O (1 mL) was dropped into a slurry of Fe-Gr (10 mmol of iron) in THF (35 mL), then, after stirring 5 min at 30 °C, **3a** (0.99 g, 5 mmol) and dodecane (internal standard) were added and the reaction mixture was vigorously stirred at 70 °C. GC analysis (B, 150 °C) showed the presence of **4a**-*d* in 96% yield after 20 min. After graphite filtration and washing with ether (3 × 10 mL), silica gel column chromatography (hexane–ether, 97/3) of the crude residue gave α-deuterioacetophenone (**4a**-*d*): 0.57 g; bp 82 °C (15 mmHg); IR 1690; NMR ($CDCl_3$) 7.3–8.2 (m, 5 H), 2.6 (s, 2 H); mass spectrum, *m/e* (relative intensity) 120 (14), 121 (100), 122 (11).

By the same procedure ketones **4b**-*d* and **4c**-*d* were obtained. For **4b**-*d*: mp 178 °C; IR 1740; NMR ($CDCl_3$) 1.2–2.3 (6H), 0.97 (s, 3 H), 0.92 (s, 3 H), 0.84 (s, 3 H); mass spectrum, *m/e* (relative intensity) 152 (12), 153 (100), 154 (12). The epimer ratio of 3-*exo*-deuterio-/3-*endo*-deuteriocamphor was 85/15, as determined by the integrals in the 100-MHz ^1H NMR spectrum of the triplet at δ 1.79 and the multiplet at δ 2.28 assigned by Sauers[25] to 3-endo and 3-exo protons in monodeuterated camphors, respectively. For **4c**-*d*: bp 105 °C; IR 1715; NMR ($CDCl_3$) 2.1 (s, 2 H), 1.15 (s, 9 H); mass spectrum, *m/e* (relative intensity) 100 (14), 101 (100), 102 (10).

Reaction between 3a and Heptanal in the Presence of Fe-Gr. Heptanal (0.78 g, 6 mmol), **3a** (0.99 g, 5 mmol), and dodecane (internal standard) were added to a stirred slurry of Fe-Gr (10 mmol of iron) in THF (40 mL), and the reaction mixture was stirred 2 h at 70 °C. GC analysis (B, 100–300 °C at 10 °C/min) showed the presence of **4a** (45%) and of 1-phenyl-2-nonen-1-one (**6**, 40%) which was purified by silica gel column chromatography (hexane-ether 96/4): oil; IR 1680, 1620, 760, 690; NMR ($CDCl_3$) 7.9 (m, 2 H), 7.5 (m, 3 H), 6.9 (m, 2 H), 2.3 (m, 2 H), 1.35 (m, 8 H), 0.9 (t, 3 H); mass spectrum, *m/e* 216 (M^+).

Reaction between 3b and Chlorotrimethylsilane in the Presence of Fe-Gr. Chlorotrimethylsilane (0.63 mL, 5 mmol) and **3b** (0.58 g, 2.5 mmol) were added to a slurry of Fe-Gr (10 mmol of iron) in THF (35 mL), and the reaction mixture was stirred 5 h at 70 °C. Graphite was filtered and washed with ether (5 × 10 mL), solvents were removed under reduced pressure, and the residue was chromatographed on a neutral alumina column (hexane–ether, 6/4) to give 0.36 g of a mixture of **4b** and trimethyl[(1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)oxy]silane[26] (**8**), identified by spectroscopic means: IR 1625 [ν(C=C)]; NMR ($CDCl_3$, $CHCl_3$ internal standard, Me_4Si as zero) 4.7 (d, J = 3.5 Hz, vinyl proton), 0.22 (s, trimethylsilyl protons). On the basis of integrals of the methyl, trimethylsilyl, and vinyl protons, the **4b**/**8** ratio was 55/45.

7,9-Dimethylbicyclo[4.3.0]non-1(9)-en-8-one (11).[27] In a three-necked flask equipped with a condenser, an argon inlet, and a side arm fitted with a medium frit, was prepared Fe-Gr (15 mmol of iron) in THF (60 mL) according to the usual procedure. The solvent was filtered through the sintered-glass filter under a positive argon pressure, Fe-Gr was covered with benzene (30 mL), and a solution of 2,4-dibromo-3-pentanone (**9**; 1.62 g, 6.7 mmol), 4-(1-cyclohexen-1-yl)morpholine (2.5 g, 15 mmol), and undecane (internal standard) in benzene (5 mL) was added. The reaction mixture was stirred at 30 °C for 15 h, and then treated with 3% methanolic NaOH solution (10 mL) for 30 min. GC analysis (B, 130 °C) showed the presence of *trans*- and *cis*-cyclopentenones **11** in an 85/15 ratio and in 84% overall yield [RRT (*trans*-**11**) 1.00 (lit.[27] RRT 1.00); RRT (*cis*-**11**) 1.15 (lit.[27] RRT 1.3)].

Analytical samples of *trans*- and *cis*-**11** were obtained through silica gel column chromatography (hexane/ether, 97/3) of the crude product obtained by graphite filtration, washing with ether (4 × 10 mL), and solvent evaporation under reduced pressure. For *trans*-**11**: IR 1695, 1640; NMR (CCl_4) 2.9 (m, 1 H), 1.65 (d, J = 1 Hz, 3 H), 1.12 (d, J = 8 Hz, 3 H), 0.95–2.35 (9 H); mass spectrum, *m/e* (relative intensity) 59 (100), 74 (60), 107 (6), 136 (6), 149 (10), 163 (5), 164 (7, M^+). For *cis*-**11**: IR 1697, 1643; NMR (CCl_4) 2.9 (m, 1 H), 1.60 (m, 3 H), 1.08 (d, J = 7 Hz, 3 H), 0.95–2.5 (9 H); mass spectrum, *m/e* (relative intensity) 59 (100), 74 (55), 107 (4), 136 (5), 149 (7), 163 (11), 164 (6, M^+).

2,2,4,4-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (14).[28] In the same reaction flask described above, was prepared Fe-Gr (20 mmol of iron) in THF (60 mL), the solvent was filtered off, and a solution of 2,4-dimethyl-2,4-dibromo-3-pentanone (**12**; 2.72 g, 10 mmol), undecane (internal standard), and furan (20 mL) was added. After the mixture was stirred 15 h at 40 °C, compound **14** was obtained in 88% yield on the basis of GC analysis (B, 140 °C). An analytical sample was obtained by silica gel column chromatography (hexane–ether, 95/5): IR 1705, 1065, 925, 730; NMR (CCl_4) 6.35 (s, 2 H), 4.33 (s, 2 H), 1.3 (s, 6 H), 0.85 (s, 6 H); mass spectrum, *m/e* (relative intensity) 70 (28), 95 (90), 110 (100), 138 (3), 165 (6), 180 (28, M^+).

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Registry No. **1a**, 80262-79-9; **1b**, 13440-24-9; **1c**, 80262-80-2; **2a**, 821-95-4; **2b**, 103-30-0; **2c**, 7433-78-5; **3a**, 70-11-1; **3b**, 76-29-9; **3c**, 5469-26-1; **4a**, 98-86-2; **4a**-*d*, 60507-03-1; *endo*-**4b**-*d*, 13656-90-1; *exo*-**4b**-*d*, 27808-88-4; **4c**-*d*, 80262-81-3; **6**, 80262-82-4; **8**, 56613-17-3; **9**, 815-60-1; *cis*-**11**, 66388-60-1; *trans*-**11**, 66388-59-8; **12**, 17346-16-6; **14**, 22940-31-4; I, 3212-68-8; II, 3212-67-7; III, 80262-83-5; heptanal, 111-71-7; 4-(1-cyclohexen-1-yl)morpholine, 670-80-4; furan, 110-00-9; $FeCl_3$, 7705-08-0; C_8K, 12081-88-8; $C_{24}Fe$, 65522-66-9.

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(24) Identical with an authentic sample.

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