109 (35), 95 (40), 81 (50), 71 (35), 69 (50). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.27; H, 10.48.

4: an amorphous solid, mp 110–119 °C; $[\alpha]^{20}_D$ −25.9° (c 0.35, MeOH); IR (KBr) 3420 (br, OH), 2950, 2880, 1455, 1390, 1380, 1040, 1030, 990 cm^{-1}; ^1H NMR δ 4.57 (1 H, m, $W_{1/2}$ = 9 Hz, H-12), 4.10 (1 H, q, J = 6 Hz, H-14), 3.36 (1 H, dd, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-3), 1.48 (3 H, d, J = 6 Hz, 3H-15), CMe singlets at 1.53, 1.19, 1.11, 0.96, and 0.79. Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.26; H, 10.31.

Application of Horeau's Method to Compounds 1, 3, and 4. This was performed in the usual manner.[6] Compound 1 (24.67 mg, 0.0765 mmol) and (±)-α-phenylbutyric anhydride (APBA, 142.47 mg, 0.459 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.300$ for the 3R and 12R centers. Compound 3 (26.00 mg, 0.0765 mmol) and APBA (142.47 mg, 0.459 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.414$ for the 3R, 12R, and 14 centers; thus, $0.414 - 0.300 = +0.114$ for the C(14)-hydroxyl group, configuration 14R. Compound 4 (26.00 mg, 0.0765 mmol) and APBA (142.47 mg, 0.459 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.171$ for the 3R, 12R, and 14 centers; thus, $0.171 - 0.300 = -0.129$ for the C(14)-hydroxyl group, configuration 14S. This experiment was performed with identical time reaction (17 h) and temperature (19 °C) for the three compounds.

(14*R*)-*ent*-8,13β-Epoxylabdane-3β,12β,14-triol (8) and (14*S*)-*ent*-8,13β-Epoxylabdane-3β,12β,14-triol (9) from Compound 5. The keto derivative 5[4] (400 mg) was treated with $LiAlH_4$ in Et_2O solution at room temperature for 4 h, yielding 12-epivarodiol (6, 350 mg): mp 99–101 °C (EtOAc–n-hexane); $[\alpha]^{23}_D$ −48.7° (c 0.37, MeOH); IR (KBr) 3490, 3420, 3260 (hydroxyl groups), 3080, 1660, 920 (vinyl group), 2950, 2880, 1460, 1390, 1070, 1040 cm^{-1}; ^1H NMR δ 6.41 (1 H, dd, J_1 = 18 Hz, J_2 = 10 Hz, H-14), 5.47 (1 H, dd, J_1 = 18 Hz, J_2 = 1.8 Hz, H-15), 5.20 (1 H, dd, J_1 = 10 Hz, J_2 = 1.8 Hz, H'-15), 3.57 (1 H, dd, $J_{aa'}$ = 10 Hz, $J_{ae'}$ = 6 Hz, H-12), 3.21 (1 H, dd, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-3), CMe singlets at 1.39, 1.24, 1.00, and 0.76 (6 H); mass spectrum (EI, 75 eV, direct inlet), m/z (relative intensity) M^+ absent, 307 ($M^+ - 15$, 8), 279 (10), 208 (50), 190 (100), 175 (85), 147 (32), 121 (38), 101 (28), 81 (40), 71 (45), 69 (38). Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.36; H, 10.55. Compound 6 was transformed into its diacetyl derivative 7 in the usual manner, and this diacetate (7, 350 mg) was treated with MCPBA as previously described for compound 2 to give a mixture of the C(14) epimeric 14,15-epoxy derivatives (355 mg). This mixture was treated in a Et_2O solution with $LiAlH_4$ in the usual manner yielding a mixture of the C(14) epimers 8 and 9, which was chromatographed [silica gel column, $CHCl_3$–MeOH (49:1)], yielding pure 8 (100 mg) and 9 (123 mg).

8: mp 209–210 °C (Me_2CO–n-hexane); $[\alpha]^{20}_D$ −24.3° (c 0.31, MeOH); IR (KBr) 3475, 3405, 3350 (hydroxyl groups), 3020, 2930, 2880, 1465, 1390, 1050, 1035, 1000, 960, 945, 915 cm^{-1}; ^1H NMR δ 4.33 (1 H, dd, $J_{aa'}$ = 10 Hz, $J_{ae'}$ = 6 Hz, H-12), 3.84 (1 H, q, J = 6 Hz, H-14), 3.38 (1 H, dd, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-3), 1.31 (3 H, d, J = 6 Hz, 3H-15), CMe singlets at 1.47, 1.19, 1.12, 0.96, and 0.77; mass spectrum (EI, 75 eV, direct inlet), m/z (relative intensity) M^+ absent, 325 ($M^+ - 15$, 8), 295 (75), 277 (95), 259 (70), 241 (30), 207 (90), 191 (40), 190 (65), 189 (80), 175 (70), 135 (100), 109 (50), 107 (65), 95 (70), 81 (70), 71 (50), 69 (60). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.69; H, 10.54.

9: mp 252–253 °C (Me_2CO–n-hexane); $[\alpha]^{20}_D$ −26.6° (c 0.30, MeOH); IR (KBr) 3410, 3360, 3300 (hydroxyl groups), 3010, 2940, 2880, 1455, 1390, 1380, 1360, 1090, 1045, 1000, 990, 915 cm^{-1}; ^1H NMR δ 4.62 (1 H, q, J = 6 Hz, H-14), 3.87 (1 H, dd, $J_{aa'}$ = 10 Hz, $J_{ae'}$ = 4.5 Hz, H-12), 3.36 (1 H, dd, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-3), 1.33 (3 H, d, J = 6 Hz, 3H-15), CMe singlets at 1.30, 1.20, 1.10, 0.89, and 0.70; mass spectrum (EI, 75 eV, direct inlet), m/z (relative intensity) M^+ absent, 325 ($M^+ - 15$, 5), 295 (95), 277 (100), 259 (70), 241 (40), 207 (90), 191 (40), 190 (80), 189 (60), 175 (60), 135 (90), 109 (40), 107 (40), 95 (40), 81 (60), 71 (40), 69 (70). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.31; H, 10.37.

Application of Horeau's Method[6] to Compounds 6, 8, and 9. Compound 6 (28.55 mg, 0.089 mmol) and APBA (see above, 165.75 mg, 0.5346 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.028$ for the 3R and 12S centers. Compound 8 (30.26 mg, 0.089 mmol) and APBA (165.75 mg, 0.5346 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.230$ for the 3R, 12S, and 14 centers; thus, $0.230 - 0.028 = +0.202$ for the C(14)-hydroxyl group, configuration 14R. Compound 9 (30.27 mg, 0.089 mmol) and APBA (165.75 mg, 0.5346 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = -0.156$ for the 3R, 12S, and 14 centers; thus, $-0.156 - 0.028 = -0.184$ for the C(14)-hydroxyl group, configuration 14S. This experiment was performed with identical time reaction (17 h) and temperature (20 °C) for the three compounds.

Acknowledgment. We thank Professor A. García-Granados, Department of Organic Chemistry, University of Granada, Spain, for providing the samples of compounds 1 and 5, and Miss M. D. Casado and Mrs. M. Plaza, our Institute, for recording the ^{13}C NMR spectra. This work was supported in part by the Comisión Asesora de Investigación Científica y Técnica, Madrid (Grant No. 11/1981).

Registry No. 2, 88143-08-2; 3, 92346-75-3; 3 (borate), 92346-74-2; 4, 92419-32-4; 4 (borate), 92419-27-7; 5, 88143-09-3; 6, 92419-30-2; 7, 92419-31-3; 8, 92419-33-5; 8 (borate), 92419-28-8; 9, 92419-34-6; 9 (borate), 92419-29-9.

Selective Preparation. 40. A New Preparative Route to 8,16-Dimethyl[2.2]metacyclophan-1-ene[1]

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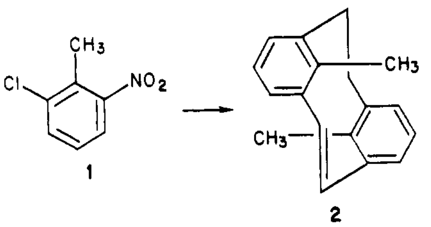
Although Boekelheide and his co-workers reported a synthesis of 8,16-dimethyl[2.2]metacyclophan-1-ene (2) in low total yield from 2-chloro-6-cyanotoluene (1) by a sequence including 13 steps, the starting compound 1 is not readily available.[2,3]



We now report a convenient preparation of 2 in 12 steps from *p-tert*-butyltoluene (3) involving the use of *tert*-butyl group as a positional protective group (Scheme I).

The preparation of 2-bromo-4-*tert*-butyltoluene (4) from 3 was described in the previous reports.[4] The titanium(IV) chloride catalyzed chloromethylation of 4 with chloromethyl methyl ether afforded the chloride 5 in 73% yield, which was converted to 6 by Grignard reaction. When 6 was treated with aluminum chloride in benzene, the desired 7 was obtained in 75% yield together with 8. Compound 7 was treated with n-butyllithium in ether followed by treatment with dry ice to give 9 in 69% yield.[2] The desired dichloride 12 was easily obtained from 9 via 10 and 11 in the usual manner.[2] Reaction of 12 with sodium

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[1] Part 41: Tashiro, M.; Yoshiya, H., submitted for publication.

[2] Lindsay, W. S.; Stokes, P.; Fumber, L. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1961**, *83*, 943.

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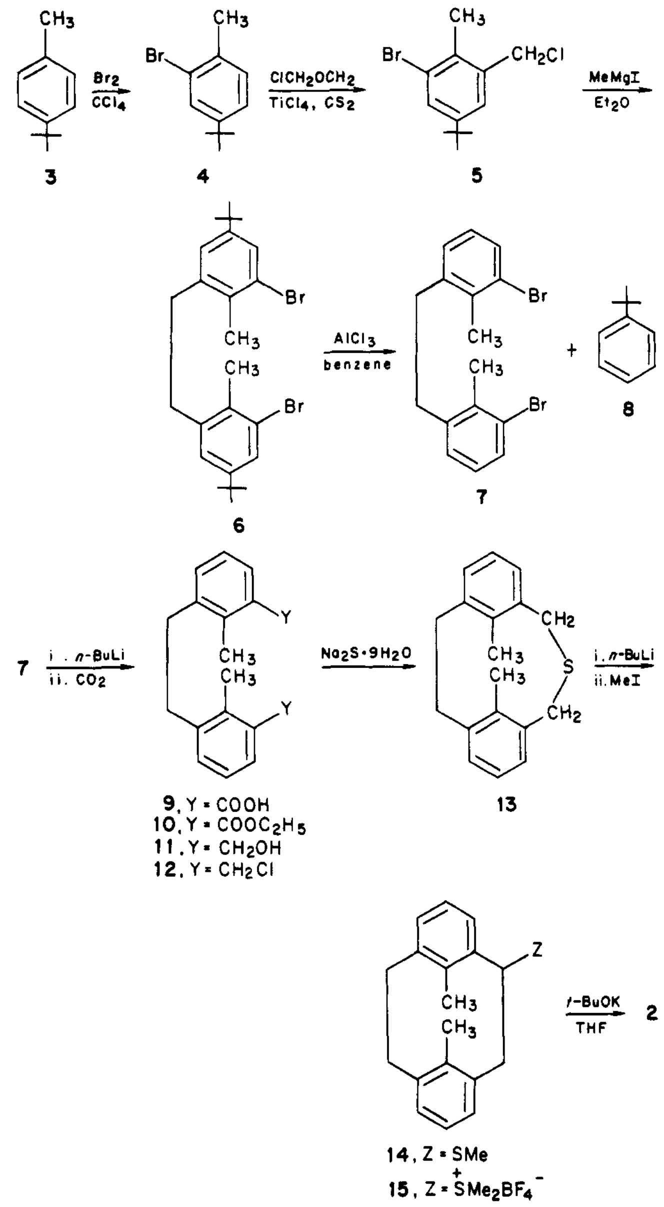
Scheme I



sulfide under highly diluted conditions afforded the sulfide **13** in 52% yield. The desired compound **2** was easily prepared from **13** according to the reported methods.[5]

Although this preparative route to **2** is not much shorter than that of Boekelheide's method, the starting material **1** is an easily available compound. This method should be widely applicable to the preparation of [2.2]metacyclophan-1-enes having substituents other than methyl at positions 8 and 16.

Experimental Section

Preparation of 2-Methyl-3-bromo-5-*tert*-butylbenzyl Chloride (5). To a solution of 2-bromo-4-*tert*-butyltoluene (**4**)[4] (113.5 g, 0.5 mol), chloromethyl methyl ether (80 g, 1 mol), and carbon disulfide (300 mL) is added at −5 to 5 °C titanium(IV) chloride (28 mL). After the reaction mixture has been stirred at 15 °C for 90 min, it is quenched with ice/water (200 mL) and extracted with ether. The etheral solution is dried over sodium sulfate and evaporated in vacuo to afford the crude product, which is distilled under the reduced pressure to give **5** as colorless liquid: yield 100 g (72.6%); bp 116–118 °C (3 mmHg); IR (NaCl) ν_{max} = 3040, 2970, 1600, 1550, 1480, 1360, 1260, 1170, 1000, 870, 820, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 2.41 (s, 3 H), 4.54 (s, 2 H), 7.19 (d, 1 H, J = 2.5 Hz), 7.49 (d, 1 H, J = 2.5 Hz); mass spectrum (m/e), 274, 276, 278 (M^+). Anal. Calcd for $C_{12}H_{16}BrCl$: C, 52.29; H, 5.85. Found: C, 51.98; H, 5.84.

Preparation of 5,5′-Di-*tert*-butyl-3,3′-dibromo-2,2′-dimethyldiphenylethane (6). To a solution of MeMgI (prepared from 60 g of methyl iodide and 10 g of magnesium) in 150 mL of ether is gradually added a solution of **5** in 1 h under the conditions of reflux. After the reaction mixture is refluxed for additional 12 h, it is quenched with 10% hydrochloric acid and extracted with ether. The ether extract is dried over sodium sulfate and evaporated in vacuo to leave the residue, in which a small amount of ethanol is added to afford 30 g (80.6%) of crude **6** as colorless crystals, which on recrystallization from hexane gives pure **6** as colorless needles: mp 102–103 °C; IR (KBr) ν_{max} 3040, 2960, 1600, 1545, 1480, 1460, 1390, 1270, 1250, 9 95, 865, 830, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 18 H), 2.28 (s, 6 H), 2.88 (s, 4 H), 6.86 (d, 2 H, J = 2.5 Hz), 7.36 (d, 2 H, J = 2.5 Hz); mass spectrum (m/e), 478, 480, 482 (M^+). Anal. Calcd for $C_{24}H_{32}Br_2$: C, 74.45; H, 8.65. Found: C, 74.89; H, 8.84.

Preparation of 3,3′-Dibromo-2,2′-dimethyldiphenylethane (7). To a solution of **6** (9.6 g, 20 mmol) in benzene (300 mL) is gradually added aluminum chloride (3 g, 22.7 mmol) at 50 °C. After the reaction mixture has been stirred for 30 min, it is quenched with ice/water. The organic layer is extracted with ether. The ether solution is washed with water, dried over sodium sulfate, and evaporated in vacuo to leave the crude product which is recrystallized from hexane: yield 4.7 g (63.9%); mp 131–132 °C (lit.[2] mp 132–133 °C), colorless prisms.

Preparation of 3,3′-dicarboxy-2,2′-dimethyldiphenylethane (9): colorless prisms (AcOH); mp 276–277 °C (lit.[2] mp 264–265 °C).

Preparation of 3,3′-dicarbethoxy-2,2′-dimethyldiphenylethane (10): colorless prisms (EtOH); mp 76–77 °C (lit.[2] mp 77.5–78.0 °C).

Preparation of 3,3′-bis(hydroxymethyl)-2,2′-dimethyldiphenylethane (11): colorless prisms (EtOH); mp 164–165 °C (lit. mp 158–160 °C).

Preparation of 3,3′-bis(chloromethyl)-2,2′-dimethyldiphenylethane (12). To a suspension of 3,3′-bis(hydroxymethyl)-2,2′-dimethyldiphenylethane (**11**) (5.4 g, 20 mmol) and 1 drop of pyridine in benzene (120 mL) is added thionyl chloride (20 mL) at room temperature while stirring with a magnetic stirrer. After the solution was stirred at room temperature for 30 min, it is boiled under reflux for 30 min. The solvent is evaporated in vacuo to leave the residue which is extracted with dichloromethane and washed with water successively. The dichloromethane extract was dried over sodium sulfate and evaporated in vacuo to leave the residue which is recrystallized from hexane:benzene (1:1) to give **12** as colorless prisms: yield 4.4 g (71.7%); mp 145–147 °C; IR (KBr) ν_{max} 3030, 2950, 1460, 1380, 1275, 1250, 880, 790, 720, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.86 (d, 4 h), 4.58 (s, 4 H), 7.04–7.20 (m, 6 H); mass spectrum (m/e), 306, 308, 310 (M^+). Anal. Calcd for $C_{18}H_{20}Cl_2$: C, 70.36; H, 6.56. Found: C, 70.38; H, 6.54.

Preparation of 9,17-Dimethyl-2-thia[3.2]metacyclophane (13). To a solution of **12** (4.3 g, 14 mmol) in absolute ethanol (4:1) is added dropwise a solution of $Na_2S·9H_2O$ (15 g, 62.6 mmol) in water (60 mL) from a Hershberg funnel while stirring with nitrogen. When the addition is complete (1 h), the mixture is refluxed for 36 h while stirring. The reaction mixture is concentrated and the residue extracted with 500 mL of dichloromethane. The dichloromethane extract is concentrated and the residue chromatographed over an active Al_2O_3 using a 1:2 benzene:hexane mixture for elution. The crystals isolated from the elute are recrystallized from hexane:benzene (3:1) to give **13** as colorless prisms: yield 2.3 g (61.2%); mp 174–176 °C; IR (KBr) ν_{max} 3050, 2930, 1565, 1450, 1410, 1195, 1065, 800, 775, 730, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6 H), 2.46–3.08 (m, 4 H), 3.68 3.88 (4 H, AB pattern, J = 16 Hz), 6.87–7.15 (m, 6 H); mass spectrum (m/e), 268 (M^+). Anal. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51. Found: C, 80.46; H, 7.43.

Preparation of 1-(Methylthio)-8,16-dimethyl[2.2]metacyclophane (14). To a stirred solution of **13** (1.88 g, 7 mmol) in dry tetrahydrofuran (30 mL) under nitrogen is added a 15% hexane solution of n-butyllithium (0.6 mL, 14 mmol) with ice

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cooling. After the solution has been stirred for 10 min at room temperature, methyl iodide (1.21 mL, 20 mmol) is added. The reaction mixture is worked up by addition of H_2O and CH_2Cl_2. After the dichloromethane extract has been washed with water, dried over Na_2SO_4, and concentrated, the products are purified by filtration through silica gel with hexane:benzene (1:1) to give **14** as a colorless oil: yield 1.86 g (93.9%); IR (KBr) ν_{max} 3050, 2940, 1580, 1450, 1430, 1370, 1170, 1055, 1020, 800, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 0.58 (s, 3 H), 2.10 (s, 3 H), 2.70 (dd, 1 H, J = 11 Hz, 4 Hz), 6.72 7.20 (m, 5 H), 7.68 (dd, J = 7 Hz, 1.5 Hz); mass spectrum (m/e), 282 (M^+). Anal. Calcd for $C_{19}H_{22}S$: C, 80.79; H, 7.85. Found: C, 81.57; H, 7.88.

Preparation of Sulfonium Salt 15. To a suspension of dimethoxycarbonium fluoroborate (2.1 g) in dichloromethane (5 mL) is added a solution of **14** (1.76 g, 6.23 mmol) in dichloromethane (10 mL) held at −30 °C under an atmosphere of nitrogen. The mixture is allowed to warm to room temperature and is stirred for additional 4 h. Then, ethyl acetate (40 mL) was added, the mixture was stirred, and the solvent was decanted. Fresh ethyl acetate (20 mL) is added to the oily residue and it is stirred overnight. The resulting crystalline precipitate is collected and dried, giving **15** as colorless prisms: yield 1.3 g (54.4%); mp 225–230 °C dec; IR (KBr) ν_{max} 3425, 3040, 2940, 1580, 1430, 1050, 800, 760, 710 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.60 (s, 3 H), 0.65 (s, 3 H), 2.65–3.06 (m, 5 H), 2.92 (s, 6 H), 3.45 (dd, 1 H, J = 12 Hz, 4 Hz), 4.73 (dd, 1 H, J = 11 Hz, 4 Hz), 6.81–7.40 (m, 6 H). Anal. Calcd for $C_{20}H_{25}BF_4S$: C, 62.51; H, 6.56. Found: C, 62.52; H, 6.52.

Preparation of 8,16-Dimethyl[2.2]metacyclophan-1-ene (2). To a solution of patassium *tert*-butoxide (610 mg, 45 mmol) in tetrahydrofuran (30 mL) there is added with stirring sulfonium salt **15** (1.2 g, 3.12 mmol). After the reaction mixture has been stirred at room temperature under a nitrogen atmosphere for 4 h, benzene is added and the mixture is made acidic by addition of dilute aqueous hydrochloric acid. The organic layer is separated, washed with water, dried, and concentrated. The residue is recrystallized from methanol to give **2** as colorless needles: yield 700 mg (95.8%); mp 147–148 °C (lit.[3] mp 151–152 °C).

Registry No. 2, 28746-29-4; **4**, 61024-94-0; **5**, 92396-96-8; **6**, 92396-97-9; **7**, 92396-98-0; **9**, 92396-99-1; **10**, 92397-00-7; **11**, 92397-01-8; **12**, 92397-02-9; **13**, 92397-03-0; **14**, 92396-93-5; **15**, 92396-95-7; Na_2S, 1313-82-2.

C-H Insertion, Hydrogen Exchange, and Dimerization of Ethylene upon Condensation with Iron Atoms at 77 K and Subsequent Warming

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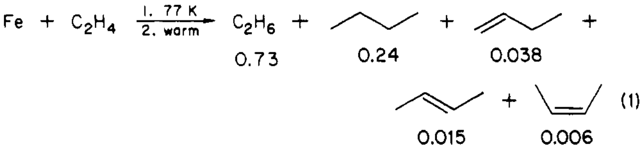
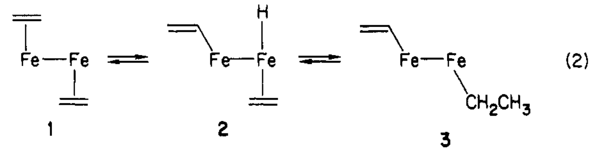
The interaction of an olefin with a metal center is of considerable interest in the areas of heterogeneous[1] and homogeneous catalysis[2] and surface chemistry.[3] In order to model this interaction between an alkene and an unsaturated metal center, we have investigated the reaction between iron atoms and ethylene at 77 K.

When iron atoms, generated by evaporating iron in a resistively heated molybdenum–alumina crucible, are cocondensed with ethylene and the resultant mixture is allowed to warm to room temperature, the products shown in eq 1, along with their relative yields, are obtained. Table I gives representative product yields under a variety of conditions.

Thus, the cocondensation of Fe and C_2H_4 brings about reduction, dimerization, and reductive dimerization of the ethylene. The fact that reduction is observed implicates an iron hydride which may be the result of an initial insertion of iron into a C–H bond as in eq 2. In order to asess the extent of such a process, a mixture of C_2H_4 and C_2D_4 (5 mmol of each) was cocondensed with iron. The infrared spectrum of the ethylene recovered from this reaction after warmup was essentially identical with that of a statistical mixture of the deuterated and protiated ethylenes. In order to rationalize this rapid exchange of vinylic hydrogens, we propose that an initial iron ethylene complex, **1**, undergoes insertion into a C–H bond to generate vinyl hydride **2** which can then insert another ethylene into the Fe–H bond to generate **3** as shown in eq 2.[4]





If this reaction is rapid and reversible, substitution of C_2D_4 for one of the ethylene molecules in eq 2 will lead to a statistical mixture of the deuterated and protiated ethylenes. This rapid exchange of vinylic hydrogens is reminescent of the work of Touroude and Gault who reported vinylic hydrogen exchange between propene-d_6 and a number of 1-alkenes on an iron surface at 236 K.[5] In the present study, we have also found that exchange will occur between ethylene and ethylene-d_4 on an iron surface. Thus, Fe atoms were condensed at 77 K and allowed to warm to room temperature, and the resultant surface was treated with a 1:1 mixture of C_2H_4 and C_2D_4 for 10 min. Analysis of the recovered ethylene again revealed statistical H–D scrambeling. These results are consistent with numerous spectroscopic studies of ethylene on a surface of iron[6] and other metals[7] in which loss of hydrogen to generate a surface-bound acetylene invariably occurs. A logical first step in such a process is the C–H insertion to generate a σ-vinyl intermediate as depicted in eq 2. Studies of the interaction of deuterium gas with alkenes on Ni and Fe surfaces have provided evidence for σ-vinyl intermediates similar to **2**.[8]

In another experiment, C_2D_4 was condensed with Fe followed by the addition of propene to the matrix after condensation. When this mixture was allowed to warm to room temperature and stand for 1 h, mass spectrometry indicated substantial deuterium incorporation into the propene. However, when this experiment was repeated

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(4) The mechanistic equations in which reactions are depicted as occurring on two metal centers are meant to be schematic representations of the mechanisms only. No firm evidence as to the nuclearity of the reactions has been obtained.

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