1.80 (s) ppm. The former belonged to 3 and the latter to 4. A second addition was performed on the cooled mixture, using 1.18 g (6.84 mmol) of *m*CPBA in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 15 min. An aliquot of this final solution showed only the single resonance at 1.80 ppm in the NMR spectrum. The CH_2Cl_2 solution was washed with 10 mL of $Na_2S_2O_3$ (10%), 20 mL of 5% NaOH, and twice with 15-mL portions of brine and dried over $MgSO_4$. Rotoevaporation of the CH_2Cl_2 gave 0.93 g (81%) of 4 as a clear oil: ^1H NMR ($CDCl_3$) 10.2 (1 H, s), 2.7 (4 H, m), 1.9 (4 H, m), 1.8 (3 H, s) ppm; ^{13}C NMR (gated decoupled) 189.8 (d), 170.7 (s), 164.8 (s), 123.9 (s), 33.7 (t), 31.2 (t), 25.4 (t), 23.4 (t), 9.0 (q) ppm; IR (neat) 2750, 1755, 1680, 1640, 1170, 1120, 1095, 995 cm^{-1}; mass spectrum, *m/e* 168 (M^+), 85 (base).

Preparation of 2,4-Dinitrophenylhydrazone Derivative of 4. A solution of 4 (170 mg, 1.01 mmol) in methanol was added to an acidic solution of 2,4-dinitrophenylhydrazine in methanol. The product was collected and repeated recrystallizations (ethyl acetate, ethanol, H_2O) gave an orange solid melting at 220–221.5 °C; ^{13}C NMR 171.7, 154.6, 154.3, 145.0, 138.5, 130.1, 129.7, 123.6, 119.5, 116.8, 33.9, 30.6, 26.6, 23.4, 11.5 ppm. Anal. Calcd for $C_{15}H_{16}N_4O_6$: C, 51.73; H, 4.63; N, 16.09. Found: C, 51.33; H, 4.62; N, 15.55.

X-ray Structural Determination of Lactone 2. Crystals of 2 were obtained by slow evaporation of a 9:1 CH_2Cl_2–hexane solution and a specimen suitable for X-ray analysis was mounted in a capillary. X-ray data collection was carried out on a Nicolet R3m automated diffractometer equipped with a Cu target X-ray tube (λ = 1.548 Å) and a graphite crystal monochromator.[13] Unit cell constants were determined to be a = 6.717 (1), b = 14.963 (2), and c = 10.923 (2) Å and β = 95.46 (1)° for a cell of monoclinic symmetry. Systematic absences of $0k0$ ($k = 2n+1$) and $h0l$ ($h + l = 2n + 1$) indicated the space group to be $P2_1/n$ (nonstandard setting of $P2_1/c$) which was confirmed by the successful solution and refinement of the structure. X-ray intensity data were measured for a total of 1117 independent reflections for $2\theta \leq 100°$, of which 1077 were considered observed with $I \geq 3\sigma(I)$. The structure was solved by direct methods which revealed the locations of all nonhydrogen atoms on the initial E map. The structure was refined to a final R value of 4.14% by full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters. All structural determinations and refinement calculations were carried out with the SHELXTL package on the Nicolet R3m crystallographic system.[14] An experimental density measurement of 1.26 g/cm^3 agrees well with a calculated density of 1.27 g/cm^3 based upon four molecules of $C_{12}H_{16}O_3$ in a unit cell with a volume of 1092.9 Å^3. The final difference map revealed no abnormal features. The crystal structure of 2 consists of discrete molecules with the geometry shown in Figure 1.

Acknowledgment. We express our gratitude for financial support of this research by Montana State University and the National Science Foundation Grant CHE 7826160. We gratefully acknowledge the use of an R3m Crystallographic System provided by the Nicolet XRD Corporation. Our appreciation is further extended to J. A. S. Pribanic for technical assistance on the project and manuscript.

Registry No. 1, 1010-77-1; 2, 77136-84-6; 3, 1919-00-2; 4, 77136-85-7; ethyl 2-cyclohexanonecarboxylate, 1655-07-8; ethyl 2-cyclohexanonecarboxylate ketal, 13747-72-3; ethyl 2-cyclohexanonecarboxylate ketal alcohol, 66806-72-2; 2-isopropenylcyclohexanone ethylene ketal, 42798-04-9; 2-isopropenylcyclohexanone ethylene ketal epoxide, 77136-86-8; 4 2,4-dinitrophenylhydrazone derivative, 77136-87-9.

(13) Programs used for centering of reflections, autoindexing, refinement of cell parameters, axial photographs, and data collection were those described in: "Nicolet P3/R3 Data Collection Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corporation: Cupertino, CA, 1980.

(14) Programs used for data reduction, Fourier syntheses, direct method structure solution, least-squares refinement, error analysis, least-squares planes calculation, and calculation of hydrogen position are those described in: "Nicolet SHELXTL Structure Determination Manual"; Sheldreck, G. M., Ed.; Nicolet XRD Corporation: Cupertino, CA, 1980.

Supplementary Material Available: Bond angles, bond distances, positional parameters, and thermal parameters for compound 2 (4 pages). Ordering information is given on any current masthead page.

Stereochemical Consequence of the Coupling of Lithium Dimethylcuprate with a Cyclopentenyl Allylic Lactone. Total Synthesis of *dl*-Iridomyrmecin

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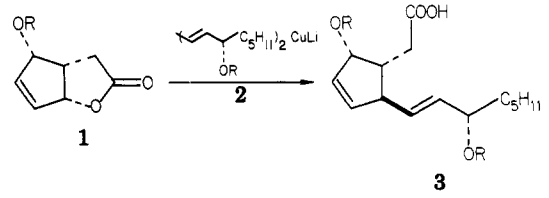
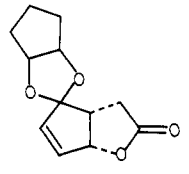
The coupling of allylic esters with lithium dialkylcuprates has received considerable attention since it was first reported by Crabbé and co-workers[2a] in 1969.[2] The studies by Goering and Singleton[2f] in 1976 clearly established that coupling of cyclic allylic acetates with lithium dimethylcuprate proceeds with anti attack and competitive α/γ substitution. More recently Trost[2h] has demonstrated in an elegant series of experiments that vinyl lactones react with alkylcyanocuprates, permitting chirality transfer via a net S_N2' process with inversion of configuration.

In contrast to the work with allylic acetates and vinyl lactones, the coupling of cyclopentenyl allylic lactones, first described by Corey,[2d] appears to be not so straightforward. For example, coupling of unsaturated lactone 1 with lithium dialkenylcuprate reagent 2 proceeds *without rearrangement and with complete inversion of configuration*, giving rise to carboxylic acid 3. The absence of any



R = *t*-Bu(Me)$_2$Si

product derived from S_N2' attack is surprising. In a closely related system,[2d] it was observed that reaction of cuprate 2 with cyclopentenyl allylic lactone 4 gave rise to comparable amounts of S_N2 and S_N2' products. The mode of attack (syn vs. anti) at the γ carbon was not specified.



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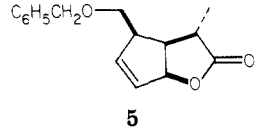
(1) Author to whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

(2) (a) Rona, P.; Tökes, L.; Tremble, J.; Crabbé, P. *Chem. Commun.* **1969**, *43*. (b) Andersen, R. J.; Henrick, C. A.; Siddall, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 735. (c) Andersen, R. J.; Henrick, C. A.; Siddall, J. B.; Zurflüh, R. *Ibid.* **1972**, *94*, 5379. (d) Corey, E. J.; Mann, J. *Ibid.* **1973**, *95*, 6832. (e) Gream, G. E.; Pincombe, C. F. *Aust. J. Chem.* **1974**, *27*, 543. (f) Goering, H. L.; Singleton, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 7854. (g) Gallina, C.; Ciattini, P. G. *Ibid.* **1979**, *101*, 1035. (h) Trost, B. M.; Klun, T. P. *J. Org. Chem.* **1980**, *45*, 4257. (i) Ali, S. M.; Chapleo, C. B.; Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Cave, R. J.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2093.

0022-3263/81/1946-2591$01.25/0

We detail below the results of an investigation which, in the context of a total synthesis of the naturally occurring iridoid iridomyrmecin (6),[3] addressed the questions of (a) α vs. γ substitution and (b) syn vs. anti attack during the coupling of cyclopentenyl allylic lactone 5 with lithium



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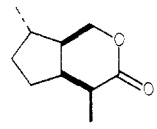
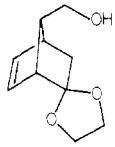


6

dimethylcuprate. Of critical importance to achieving a stereospecific total synthesis of iridoid 6 was the requirement of exclusive anti γ attack on the allylic system.

Substrate 5 was readily prepared in five steps from the known bicyclo[2.2.1]heptane derivative 7.[4] Benzylation and deketalization of 7 provided an 81% overall yield of ketone 8 which upon treatment with basic hydrogen peroxide and exposure of the resultant crude hydroxy carboxylic acid to boron trifluoride etherate in methylene chloride afforded (84%) the crystalline bicyclic lactone 9, mp 57–58 °C. Alkylation of 9 with methyl iodide gave rise exclusively, as anticipated, to bicyclic lactone 5.



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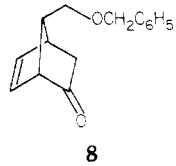

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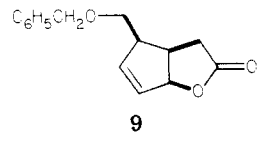

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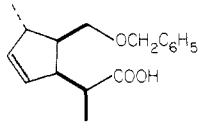
With the synthesis of cyclopentenyl allylic lactone 5 secured, we directed our efforts at coupling 5 with $LiMe_2Cu$. To this end, lactone 5 was treated with 1.5 equiv of lithium dimethylcuprate in ether at ca. −20 °C. Workup resulted in isolation (84%) of a single carboxylic acid which has been assigned structure 10 in accord with the experiments detailed below. Preliminary indication that reaction had occurred exclusively in the S_N2' mode was obtained by subjecting 10 to iodolactonization which yielded (72%) bicyclic lactone 11 [IR (CCl_4) 1790 cm^{-1}].



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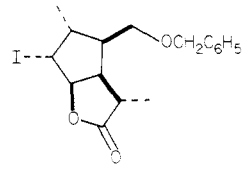
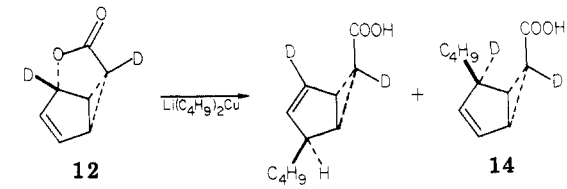


11

The question of anti vs. syn attack at the γ carbon was unambiguously established by treatment of a solution of 10 in ethanol with hydrogen, employing 10% palladium on charcoal as catalyst. Under the reaction conditions simultaneous reduction of the carbon–carbon double bond, cleavage of the benzyl ether, and lactonization of the resultant hydroxy acid occurred. Workup afforded crystalline *dl*-iridomyrmecin (6),[5] mp 58–59 °C (lit.[5c] mp 57–58 °C), whose spectral properties (IR, ^1H NMR, ^{13}C NMR) were identical to those of racemic 6 kindly supplied by Professor Whitesell. The transformation of 5 into 6 via carboxylic acid 10 unequivocally establishes that the S_N2' reaction observed proceeds with complete anti attack. What was somewhat surprising was the exclusive preference for the S_N2' mode of reaction over the S_N2 type.

After the completion of our studies the unsaturated lactone 12 was shown[2i] to give rise upon treatment with lithium di-*n*-butylcuprate to a 6:1 ratio of 13 and 14. Once again the preference for S_N2' reaction accompanied by anti attack was observed.



12 13 14

Experimental Section

Melting points were determined on a Fisher-Johns hot-stage melting-point apparatus. All melting points and boiling points are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 247 grating infrared spectrometer and nuclear magnetic resonance (NMR) spectra were recorded at either 60 (Varian T-60 spectrometer) or 250 MHz as indicated. Chemical shifts are reported in parts per million (δ) relative to Me_4Si (δ_{Me_4Si} = 0.0 ppm) as an internal standard. The ^{13}C spectra were obtained on a JEOLCO FX-60 instrument. High-resolution mass spectra were recorded on a Varian MAT CH-5DF instrument. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reactions were run under an atmosphere of nitrogen. "Dry" solvents were dried immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride; dimethylformamide (DMF), hexamethylphosphoramide (HMPA), dimethyl sulfoxide, and pyridine were distilled from calcium hydride. Diethyl ether was distilled from sodium. Methylene chloride was passed through a column of alumina prior to use. Thin-layer chromatography (TLC) was carried out on Analtech (Uniplate) glass plates precoated with silica gel GF.

(1*R,4*S**,7*S**)-7-[(Benzyloxy)methyl]bicyclo[2.2.1]hept-5-en-2-one (8).** To a suspension of 1.3 g (27.1 mmol) of 50% sodium hydride dispersion in 10 mL of dry benzene containing 1.3 mL of dimethyl sulfoxide was added 2.06 g (11.3 mmol) of spiro[bicyclo[2.2.1]hept-5-ene-2,2′-[1,3]dioxolane]-7-methanol (7).[4] After 4 h at 60 °C, 3.5 mL (29.4 mmol) of benzyl bromide was added and the reaction mixture was stirred at 60 °C for an additional 8 h. The reaction was quenched by the addition of water and the product was isolated by extraction with ether. The combined ether extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure provided 5.88 g of residue which was chromatographed on 200 g of silica gel. Elution with hexane–ether, 10:1, gave 2.57 g (84%) of pure benzyl ether as a colorless liquid: bp 197.5–198.5 °C (bath temperature) (0.2 mmHg); R_f 0.58 (hexane–ether, 1:1); IR (CCl_4) 3060, 3020, 2970, 2930, 2860, 2800, 1512, 1490, 1470, 1450, 1425, 1411, 1370, 1340, 1320, 1300, 1275, 1180, 1155, 1123, 1095, 1065, 1038, 1010, 948, 906, 894, 870, 852, 830 cm^{-1}; NMR (60 MHz, CCl_4) δ 1.42 (dd, 1 H, J = 2.0, 12.5 Hz), 1.80 (dd, 1 H, J = 3.5, 12.5 Hz), 2.22 (m, 1 H), 2.41 (m, 1 H), 2.78 (m, 1 H), 3.4–3.8 (m, 6 H), 4.41 (s, 2 H), 6.18 (m, 2 H), 7.20 (s, 5 H); mol wt calcd for $C_{17}H_{20}O_3$ 272.1412, found 272.1414.

A mixture of 2.10 g (7.7 mmol) of the above benzyl ether in 50 mL of tetrahydrofuran containing 16 mL of 10% aqueous hydrochloric acid solution was stirred at room temperature for 18 h. The product was isolated by extraction with ether. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure and subsequent chromatography on 10 g of silica gel, using hexane–ether (1:1), afforded 1.70 g (97%) of pure ketone 8 as a colorless liquid: bp 168–169 °C (bath temperature) (3.2 mmHg); R_f 0.56 (ether–hexane, 1:1); IR (CCl_4) 3060, 3025, 3000, 2975, 2940, 2860, 2800, 1747, 1498, 1480, 1452, 1420, 1368, 1335, 1310, 1255, 1238, 1209, 1190, 1150, 1120, 1105, 1095, 1065, 1045,

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1030, 1010, 990, 950, 935, 910, 900, 872, 858 cm^{-1}; NMR (60 MHz, CCl_4) δ 1.78 (m, 2 H), 2.5–2.9 (m, 2 H), 3.10 (m, 1 H), 3.2–3.5 (m, 2 H), 4.42 (s, 2 H), 6.14 (m, 1 H), 6.58 (dd, 1 H, J = 3.0, 6.0 Hz), 7.22 (s, 5 H); mol wt calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1147.

(3a*R,4*R**,6a*S**)-3,3a,4,6a-Tetrahydro-4-[(benzyloxy)methyl]-2*H*-cyclopenta[*b*]furan-1-one (9).** To a cooled (0 °C) solution of 360 mg (1.58 mmol) of ketone **8** in 8.0 mL of THF were added 8.0 mL of methanol, 8.0 mL of water, 4.6 mL of a 10% aqueous sodium hydroxide solution, and 1.4 mL of a 50% aqueous solution of hydrogen peroxide. After 1 h at 0 °C, the reaction was warmed to room temperature. The reaction mixture was quenched after 24 h with an aqueous solution of sodium bisulfite and was carefully acidified with concentrated hydrochloric acid. The product was isolated by extraction with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure provided 423 mg of crude product which was used directly in the next reaction.

The above acid (423 mg) was dissolved in 35 mL of dry methylene chloride, cooled to 0 °C, and treated with 5 drops of borontrifluoride etherate. After 1 h at 0 °C and 30 min at room temperature the reaction mixture was diluted with methylene chloride and washed successively with water, sodium bicarbonate solution, and brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo, leaving 350 mg of crude **9**. Purification on 8.0 g of silica gel, using hexane–ether (1:1), gave 322 mg (84%) of pure lactone **9** as a crystalline substance: mp 57–58 °C; R_f 0.46 (hexane–ether, 1:2); IR ($CHCl_3$) 3018, 2960, 2855, 1770, 1603, 1365, 1264, 1172, 1090, 1020 cm^{-1}; NMR (60 MHz, CCl_4) δ 2.2–2.6 (m, 2 H), 2.9–3.6 (m, 4 H), 4.42 (s, 2 H), 5.28 (m, 1 H), 5.84 (br s, 2 H), 7.22 (s, 5 H). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 74.02; H, 6.83.

(3*R,3a*R**,4*S**,6a*R**)-3,3a,4,6a-Tetrahydro-3-methyl-4-[(benzyloxy)methyl]-2*H*-cyclopenta[*b*]furan-2-one (5).** To a solution of lithium diisopropylamide [prepared from 0.95 mL (6.80 mmol) of diisopropylamine and 3.4 mL of a 1.6 M solution of *n*-butyllithium in hexane] in 10 mL of anhydrous tetrahydrofuran cooled to −78 °C was added dropwise a solution of 1.03 g (4.23 mmol) of lactone **9** in 15 mL of dry tetrahydrofuran. After 30 min at −78 °C, the temperature was gradually warmed to 0 °C over a 2-h period. Prior to addition of methyl iodide (1.5 mL, 23.2 mmol) the temperature was lowered to −78 °C. After 30 min at −78 °C, the temperature was raised to 25 °C. The reaction was quenched after 45 min with a saturated ammonium chloride solution. The product was isolated by extraction with ether. The combined ether extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo left 980 mg of a yellow viscous oil which was purified on 20 g of silica gel. Elution with hexane–ether (1:1) afforded 772 mg (71%) of pure product (**5**) as a colorless oil: R_f 0.63 (ether–hexane, 2:1); IR (CCl_4) 3060, 3025, 2930, 2850, 1778, 1540, 1450, 1375, 1360, 1340, 1328, 1285, 1240, 1208, 1175, 1135, 1090, 1060, 1030, 1018, 1000, 980, 938, 890 cm^{-1}; NMR (60 MHz, CCl_4) δ 1.20 (d, 3 H, J = 7 Hz), 2.2–3.8 (m, 5 H), 4.41 (s, 2 H), 5.25 (dd, 1 H, J = 1, 8 Hz), 5.82 (s, 2 H), 7.22 (s, 5 H); mol wt calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1254.

Reaction of Lithium Dimethylcuprate with Cyclopentenyl Allylic Lactone 5. To a cooled (−15 °C) solution of lithium dimethylcuprate [prepared from 0.45 mL (0.63 mmol) of methyllithium (1.4 M in ether) and 64 mg (0.34 mmol) of cuprous iodide] in 2.0 mL of anhydrous ether was added 54 mg (0.21 mmol) of lactone **5** in 3.0 mL of dry ether. The reaction mixture was stirred at ca. −20 °C for 75 min. The reaction mixture was quenched by the addition of a 10% aqueous hydrochloric acid solution and was extracted with ether. The combined ether layers were extracted with a 10% aqueous sodium hydroxide solution. The combined aqueous layers were acidified with concentrated hydrochloric acid and extracted with ether. The organic phase was washed with brine and dried ($MgSO_4$). Evaporation of the solvent in vacuo left 48 mg (84%) of pure carboxylic acids **10**: IR ($CHCl_3$) 3300–2400, 1701 cm^{-1}; NMR (60 MHz) $CDCl_3$ δ 1.02 (d, 3 H, J = 6.5 Hz), 1.18 (d, 3 H, J = 6.5 Hz), 2.11 (m, 1 H), 2.4–3.2 (m, 3 H), 3.6 (m, 2 H), 4.52 (s, 2 H), 5.64 (br s, 2 H), 7.30 (s, 5 H).

***dl*-Iridomyrmecin (6).** To a solution of 109 mg (0.40 mmol) of carboxylic acid **10** in 6.0 mL of ethanol under an atmosphere of hydrogen was added 25 mg of 10% palladium on charcoal. After 24 h at room temperature the reaction mixture was diluted with ether and washed with water. The ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure gave 56 mg of crude product which was purified on 10 g of silica gel. Elution with ether–hexane, 1:3, provided 51 mg (76%) of pure crystalline racemic iridomyrmecin (**6**): mp 57–58 °C; R_f 0.68 (ether–hexane, 2:1); IR ($CHCl_3$ 2951, 2925, 2898, 2860, 1735, 1475, 1457, 1448, 1390, 1382, 1360, 1283, 1255, 1230, 1209, 1176, 1160, 1132, 1110, 1070, 1024, 995, 985, 968, 940 cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 0.96–1.28 (m, 2 H), 1.05 (d, 3 H, J = 6.5 Hz), 1.08 (d, 3 H, J = 6.5 Hz), 1.70–1.97 (m, 4 H), 2.45–2.67 (m, 2 H), 4.08 (d, 1 H, J = 11.8 Hz), 4.18 (dd, 1 H, J = 11.8, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 12.7, 18.4, 29.8, 34.3, 37.4, 38.0, 41.4, 45.6, 68.0, 176.2. An analytical sample was prepared by recrystallization from pentane, mp 58–59 °C (lit.[5c] mp 57–58 °C).

Acknowledgment. This research was supported by a Public Health Research Grant from the National Institutes of Health and, in part, by a grant from G. D. Searle and Co. We are grateful to Professor J. K. Whitesell for providing us with the IR, ^{1}H NMR, and ^{13}C NMR spectra of racemic iridomyrmecin. We thank William Schillinger and William Weber for recording the 250-MHz ^{1}H NMR and ^{13}C NMR spectra, respectively.

Registry No. (±)-**5**, 77256-85-0; (±)-**6**, 1436-51-7; **7**, 77286-93-2; **7** benzyl ether, 77256-86-1; **8**, 77256-87-2; (±)-**9**, 77286-94-3; (±)-**10**, 77256-88-3; (±)-2α-hydroxy-5α-phenylmethoxymethyl-3-cyclopentene-1α-acetic acid, 77286-95-4; lithium dimethylcuprate, 15681-48-8; (±)-11, 77256-89-4.

Preparation of Azo Compounds and Amines by Triiron Dodecacarbonyl or Molybdenum Hexacarbonyl on Alumina

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Received December 23, 1980

Metal carbonyls are useful reagents for organic synthesis.[1] Reactions involving these organometallics have generally been effected in homogeneous media. Recently, there has been considerable interest in applying heterogeneous conditions to these reactions, the goals being the use of mild reaction conditions and the realization, in certain instances, of different reaction pathways in comparison with the conventional methods.

One of us has described the applications of two such heterogeneous processes in metal carbonyl chemistry: phase-transfer catalysis[2] and the deposition of metal carbonyls on refractory oxides. Regarding the latter, triiron dodecacarbonyl on basic alumina is useful for reducing nitroarenes to anilines[3] and for transforming, albeit at low conversions, carbon monoxide and hydrogen to low molecular weight olefins.[4] Molybdenum hexacarbonyl, adsorbed on silica or alumina, can effect dehalogenation,[5] olefin disproportionation and isomerization,[6] and desulfurization[7] reactions. We now report the application of molybdenum hexacarbonyl and triiron dodecacarbonyl to the deoxygenation of azoxy compounds and *N*-oxides, a

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