

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 $\text{C}_{15}\text{H}_{16}\text{O}_2$ 228.1150, found 228.1147.

(3aR*,4R*,6aS*)-3,3a,4,6a-Tetrahydro-4-[(benzyloxy)methyl]-2H-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 $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 74.02; H, 6.83.

(3R*,3aR*,4S*,6aR*)-3,3a,4,6a-Tetrahydro-3-methyl-4-[(benzyloxy)methyl]-2H-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 $\text{C}_{16}\text{H}_{18}\text{O}_3$ 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 methylolithium (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 acid 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, ^1H NMR, and ^{13}C NMR spectra of racemic iridomyrmecin. We thank William Schillinger and William Weber for recording the 250-MHz ^1H NMR and ^{13}C NMR spectra, respectively.

Registry No. (\pm)-5, 77256-85-0; (\pm)-6, 1436-51-7; 7, 77286-93-2; 7 benzyl ether, 77256-86-1; 8, 77256-87-2; (\pm)-9, 77286-94-3; (\pm)-10, 77256-88-3; (\pm)-2 α -hydroxy-5 α -phenylmethoxymethyl-3-cyclopentene-1 α -acetic acid, 77286-95-4; lithium dimethylcuprate, 15681-48-8; (\pm)-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 catalysis² and the deposition of metal carbonyls on refractory oxides. Regarding the latter, triiron dodecacarbonyl on basic alumina is useful for reducing nitroarenes to anilines³ 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 desulfurization⁷ 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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Table I. Yields of Products Obtained from Azoxy Compounds and *N*-Oxides

reactant	product	% yield ^a	
		Mo(CO) ₆ /Al ₂ O ₃	Fe ₃ (CO) ₁₂ /Al ₂ O ₃
azoxybenzene	azobenzene	28	61
4,4'-azoxyanisole	4,4'-azoanisole	34	68
4,4'-azoxyphenetole	4,4'-azophenetole	15	59
quinoline <i>N</i> -oxide	quinoline	41	79
4-picoline <i>N</i> -oxide	4-picoline	32	86
nicotinamide <i>N</i> -oxide	nicotinamide	71	

^a Yields are of isolated, pure materials. Products were identified by comparison of physical properties with those for authentic materials.

synthetically useful conversion.

After molybdenum hexacarbonyl had been adsorbed on alumina by heating for 1 h at 105 °C, it was treated with an azoxy compound or heterocyclic *N*-oxide overnight in refluxing 1,2-dimethoxyethane. Simple workup gave the deoxygenated products in 15–71% yields (Table I).

Significantly higher product yields were realized with triiron dodecacarbonyl on alumina (Table I). Furthermore, these reactions were effected at room temperature.

The nature of the species produced by the adsorption of Mo(CO)₆ on alumina depends, among other factors, on the temperatures at which the adsorbent was dried and the metal carbonyl was deposited on the oxide.⁸ Good evidence has been obtained for the intermediacy of the hydridoundecacarbonyltriferrate anion with Fe₃(CO)₁₂ and alumina.⁹

The product yields obtained by using triiron dodecacarbonyl on alumina are both lower, or in some cases higher, than that for iron pentacarbonyl in butyl ether. However, the latter process requires much more drastic conditions [140 °C, 17–24 h].¹⁰ The above-described method is also competitive with, or superior to, the use of other reagents for effecting the same transformations.^{11,12} For example, the recently reported¹¹ deoxygenation of pyridine *N*-oxides by trimethyl(ethyl)amine sulfur dioxide complexes occurs in refluxing dioxane (~100 °C) [for 4-picoline *N*-oxide—the only case for direct comparison—the yield of deoxygenated material is lower (70–75%) than that realized with Fe₃(CO)₁₂/Al₂O₃].

Experimental Section

General Procedure for Reaction of Azoxybenzenes and *N*-Oxides with Mo(CO)₆/Al₂O₃. After being dried overnight at 350 °C, alumina (30 g, Fisher A-540, 80–200 mesh) was suspended in dry, degassed hexane (150 mL) containing Mo(CO)₆ (2.64 g, 10.0 mmol) (nitrogen atmosphere). The hexane was removed by rotary evaporation, and the Mo(CO)₆/Al₂O₃ was heated for 1 h at 105 °C. The *N*-oxide or azoxy compound (3.0 mmol) was added to the cooled solid, along with 1,2-dimethoxyethane (60 mL), and the reaction mixture was stirred at reflux overnight. The mixture was cooled and filtered, the solid was treated with ether or methylene chloride, and the ether was added to the filtrate. Concentration of the filtrate gave the crude product, which was purified by chromatographic techniques (Florisil, silica gel).

General Procedure for Reaction of Azoxybenzenes and *N*-Oxides with Fe₃(CO)₁₂/Al₂O₃. Alumina (20 g, Biorad AG 7, 100–200 mesh) was dried at 150 °C (4–5 mmHg). Triiron dodecacarbonyl (2.0 mmol) in anhydrous hexane (60 mL) was added to the cooled alumina and the mixture was stirred for 2 h at room temperature (nitrogen atmosphere). The azoxy com-

pound or *N*-oxide (2–4 mmol) was added, either as such or in benzene (10 mL), and the reaction mixture was stirred overnight at room temperature. Workup was effected as described for Mo(CO)₆/Al₂O₃.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council. One of us (M.G.) thanks the Government of India for a National Scholarship.

Registry No. Azoxybenzene, 495-48-7; azobenzene, 103-33-3; 4,4'-azoxyanisole, 1562-94-3; 4,4'-azoanisole, 501-58-6; 4,4'-azoxyphenetole, 4792-83-0; 4,4'-azophenetole, 588-52-3; quinoline *N*-oxide, 1613-37-2; quinoline, 91-22-5; 4-picoline *N*-oxide, 1003-67-4; 4-picoline, 108-89-4; nicotinamide *N*-oxide, 1986-81-8; nicotinamide, 98-92-0; Mo(CO)₆, 13939-06-5; Fe₃(CO)₁₂, 17685-52-8.

Formation of Macrocyclic Lactones in Microemulsions^{1a}

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Received September 12, 1980

Detergentless microemulsions have been identified and structurally characterized through the use of conductivity, ultracentrifugation, light scattering, and nuclear magnetic resonance.²⁻⁵ Detergentless systems thus far reported consist of a dispersion of water droplets (~100-Å diameter) in a hydrocarbon continuum. They differ from conventional microemulsions in that they form in the absence of long-chain surfactants and by virtue of the fact that they contain up to 30% of the aqueous, dispersed phase.

Microemulsions would appear to be excellent media for facilitating chemical reactions. The presence of both polar and nonpolar phases allows the dissolution of a wide variety of chemical reagents while the very large interfacial area enhances the probability of a reagent encounter, measurably accelerating the rate of reaction compared to a normal two-phase system. A further control on the rate of reaction can be introduced through the utilization of surfactants with different charges on the head groups⁶ though an advantage of employing detergentless microemulsions for chemical reactions is that purification is

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