

mp 284–287 °C; IR (KBr) 3320 (OH), 3200 (NH), 1160 (P=O) cm^{-1} ; the base peak in the mass spectrum was the molecular ion, m/e 245. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{P}$: C, 63.68; H, 4.93. Found: C, 63.67; H, 5.03.

3-Tolyl[3-(trifluoromethyl)phenyl]phosphoramidous Dichloride and 3-Methyl-7-(trifluoromethyl)-5,10-dihydrophenophosphazine 10-Oxide. A mixture of 3-methyl-3'-(trifluoromethyl)diphenylamine (**2c**; 12.1 g, 0.048 mol) and PCl_3 (9.6 g, 0.070 mol) in 25 mL of dry benzene was refluxed for 18 h, and then the solvent and excess PCl_3 were stripped off in vacuo. The residual oil was purified by distillation (130–137 °C, 0.5 mm) to give 13.9 g (82%) of 3-tolyl[3-(trifluoromethyl)phenyl]phosphoramidous dichloride as a highly water-sensitive liquid. The ^1H NMR and IR spectra did not show any N–H absorption. Treatment of a sample of the dichloride with H_2O gave a quantitative yield of **2c**.

The dichloride (5.5 g, 0.016 mol) was heated at about 238 °C for 4 h, the reaction mixture was allowed to cool to room temperature, and the resulting solid was powdered and treated with hot H_2O . Two recrystallizations from MeOH gave 1.1 g (24%) of 3-methyl-7-(trifluoromethyl)-5,10-dihydrophenophosphazine 10-oxide: mp > 350 °C; IR (Nujol) 3200, 3100 (NH), 2275 (PH), 1130 (P=O) cm^{-1} ; the molecular ion (m/e 297) was 82% of the base peak (m/e 296) of the mass spectrum. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NOP}$: C, 56.58; H, 3.72; N, 4.71. Found: C, 56.24; H, 3.72; N, 4.71.

1,3-Dimethyl-5,10-dihydrophenophosphazine 10-Oxide (3). 3,5-Dimethyldiphenylamine (**2e**; 19.7 g, 0.100 mol) and PCl_3 (15.1 g, 0.110 mol) were allowed to interact under conditions similar to those described above for amines **2a** and **2b**. When the resin

reaction kettle² was allowed to cool to room temperature, it was noted that most of the reaction mixture consisted of a yellow solid that had sublimed to the top and sides of the kettle. The solid was powdered, stirred with hot H_2O , washed with Et_2O , and then recrystallized from MeOH to give 7.3 g (30%) of 1,3-dimethyl-5,10-dihydrophenophosphazine 10-oxide (**3**): mp 276 °C dec; IR (Nujol) 3260, 3165 (NH), 2340 (PH), 1150 (P=O) cm^{-1} ; ^1H NMR (TFA) δ 1.97 (s, 3, Me), 2.2 (s, 3, Me), 6.3–7.7 (m, 6, aromatic H); the base peak in the mass spectrum was the molecular ion, m/e 243. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{NOP}$: C, 69.13; H, 5.80; N, 5.76. Found: C, 69.22; H, 5.79; N, 5.80.

Acknowledgment. We are grateful to several individuals at Burroughs Wellcome Co. for providing assistance with the generation and interpretation of certain spectra: Dr. David Brent, Robert Johnson, and Bernd Soltman for their mass spectral work and Aris Ragouzeos and Dr. B. Stuart Hurlbert for their ^1H NMR work.

Registry No. **2a**, 101-23-5; **2b**, 1205-64-7; **2c**, 80814-74-0; **2e**, 51786-49-3; **3**, 80814-78-4; PCl_3 , 7719-12-2; 3-(trifluoromethyl)-5,10-dihydrophenophosphazine 10-oxide, 80814-75-1; 3-(trifluoromethyl)-10-hydroxy-5,10-dihydrophenophosphazine 10-oxide, 83291-34-3; 3,3'-dimethyl-10,10'-(5*H*,5'*H*)-spirobiphenophosphazinium chloride, 83270-05-7; 3-methyl-10-hydroxy-5,10-dihydrophenophosphazine 10-oxide, 83270-06-8; 3-methyl-5,10-dihydrophenophosphazine 10-oxide, 83270-07-9; 3-tolyl[3-(trifluoromethyl)phenyl]phosphoramidous dichloride, 83270-08-0; 3-methyl-7-(trifluoromethyl)-5,10-dihydrophenophosphazine 10-oxide, 80814-76-2.

Metal Catalysis in Organic Reactions. 16.¹ Conjugate Reduction of α,β -Unsaturated Ketones by Trialkylalane-Nickel Systems

Anna Maria Caporusso,* Giampaolo Giacomelli, and Luciano Lardicci

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente attive, Istituto di Chimica Organica, Facoltà di Scienze MFN, Università di Pisa, 56100 Pisa, Italy

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The reaction between triisobutylaluminum and α,β -unsaturated ketones, in pentane at room temperature, leads to products which correspond to 1,2-reduction and 1,2-addition processes. The extent of such reactions is dependent on both the structure of the enone and the reagent-to-substrate ratio. Under the same experimental conditions, bis(*N*-methylsalicylaldimine)nickel catalyzes the conjugate reduction of α,β -enones by triisobutylaluminum; acyclic and cyclic enones have been converted into the corresponding saturated ketones in good to excellent yields. The catalytic process is discussed in terms of a catalytic cycle involving a hydridonickel species.

In the context of investigations on the reactivity of β -branched trialkylalanes toward functional substrates,² we have studied the asymmetric reductions of dialkyl ketones by optically active aluminum trialkyls.³ Recently, these reagents have been employed for the regioselective and enantioselective conversion of α,β -unsaturated carbonyl compounds into the corresponding allylic carbinols.⁴ Our interest also in the area of transition-metal-catalyzed re-

actions of main-group organometallic reagents⁵ has led us to develop a novel method for effecting conjugate reduction of α,β -enones using triisobutylaluminum and catalytic amounts of bis(*N*-methylsalicylaldimine)nickel [$\text{Ni}(\text{mesal})_2$] in hydrocarbon solvents.

We report here a detailed study of this catalytic reduction which appears somewhat attractive for the general applicability to enones of different nature and structure.

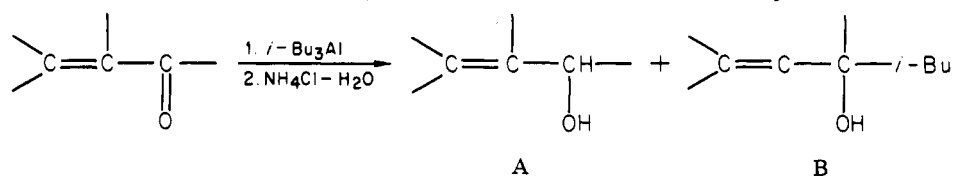
(1) Part 15: Giacomelli, G.; Lardicci, L.; Bertero, L. *Tetrahedron Lett.* 1981, 22, 883–886.

(2) Winterfeldt, E. *Synthesis* 1975, 617–630.

(3) Giacomelli, G.; Menicagli, R.; Caporusso, A. M.; Lardicci, L. *J. Org. Chem.* 1978, 43, 1790–1793 and references therein.

(4) Giacomelli, G.; Caporusso, A. M.; Lardicci, L. *Tetrahedron Lett.* 1981, 22, 3663–3666.

(5) (a) Giacomelli, G.; Caporusso, A. M.; Lardicci, L. *J. Org. Chem.* 1979, 44, 231–237. (b) Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *Ibid.* 1979, 44, 1496–1501. (c) Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *J. Chem. Soc., Perkin Trans. 1* 1979, 3139–3145. (d) Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *Ibid.* 1981, 1900–1908. (e) Giacomelli, G.; Caporusso, A. M.; Lardicci, L.; Marcacci, F. *Chim. Ind. (Milan)* 1981, 63, 482–485. (f) Giacomelli, G.; Bertero, L.; Lardicci, L.; Menicagli, R. *J. Org. Chem.* 1981, 3707–3711 and references therein.

Table I. Reactions of Representative α,β -Unsaturated Ketones with Triisobutylaluminum in Pentane^a

entry	ketone	molar ratio of $i\text{-Bu}_3\text{Al}/$ ketone	reaction time	% yield ^b	
				A	B
1	1	1.0	10 min	86 (78)	14
2 ^c		2.0	10 min	77	17
3	2	1.0	10 min	64 (58)	36 (31)
4	3	1.0	30 min	77 (71)	23 (18)
5 ^d	4	0.5	1 h	86	14
6		1.0	1 h	64 (60)	36 (29)
7		2.0	1 h	24	76 (71)
8 ^e		1.0	1 h	96	
9	5	1.0	30 min	87 (83)	13
10	6	1.0	1 h	63 (59)	37
11		2.0	1 h	23	77 (73)
12	7	1.0	1 h	98 (93)	2
13	8	1.0	15 h	100 (98)	
14 ^f		2.0	1 h	59	
15	9	1.0	30 min	98 (90)	
16 ^g	10	1.0	1 h	86 (cis)	

^a Experiments were performed in pentane (5 mL) at room temperature on a 10-mmol scale with respect to the ketone. All reactions were complete unless otherwise noted. ^b Absolute yields were determined by GLC analysis with internal standards. Isolated yields are in parentheses. ^c About 6% of 2-butanol was also formed. ^d Conversion based on the carbonyl compound was 53%. ^e The reaction was carried out with $i\text{-Bu}_3\text{Al-OEt}_2$. ^f Conversion 82%; 17% of 3,3,5-trimethylcyclohexanone was also present. ^g The other products were isomers of pulegol, mainly *p*-menth-3-en-3-ol.

Results and Discussion

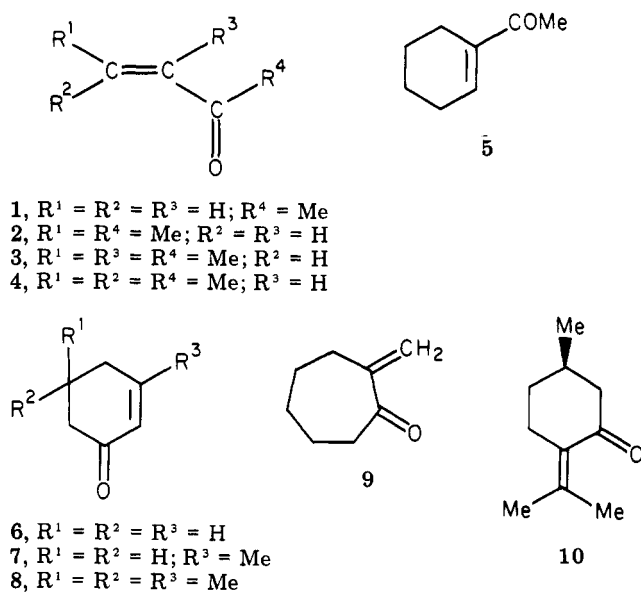
As we have previously reported,⁴ $i\text{-Bu}_3\text{Al}$ reduces representative α,β -unsaturated carbonyl compounds 1–10 (Chart I) to the corresponding allylic carbinols with nearly quantitative yields and complete regioselectivity in diethyl ether at room temperature.

The nature of the solvent plays a very important role in the rate and course of the reaction.⁴ As an extension of this observation we investigated more fully the reaction of enones 1–10 with $i\text{-Bu}_3\text{Al}$ in the absence of catalyst in hydrocarbon solvents.

Reaction of Triisobutylaluminum with α,β -Unsaturated Ketones in Pentane Solution. The experiments were carried out at room temperature in anhydrous pentane, the hydrolytic workup was accomplished by addition of a saturated NH_4Cl solution, and the reaction products were analyzed directly by GLC.

The results reported in Table I show that in all the cases investigated neither significant conjugate reduction nor conjugate addition to the α,β -unsaturated system occur, and, surprisingly in the light of the known inability of $i\text{-Bu}_3\text{Al}$ to alkylate saturated ketones, 1,2-addition of the isobutyl group is generally competitive with 1,2-reduction, depending on both the structure of the enone and the reagent-to-substrate ratio. The yields in 1,2-addition product, as indicated by some examples (entries 2, 7, and 11), are enhanced when an excess of aluminum reagent is used. Conversely, the presence of excess carbonyl substrate favors the 1,2-reduction process. Thus, mesityl oxide (4) reacts with a twofold molar excess of $i\text{-Bu}_3\text{Al}$ to give 2,4,6-trimethyl-2-hepten-4-ol as the main product (entry 7), whereas at lower $i\text{-Bu}_3\text{Al}/\text{ketone}$ molar ratios the allylic alcohol reduction product predominates (entries 5 and 6).⁶ These findings seem to suggest that the competitive ad-

Chart I

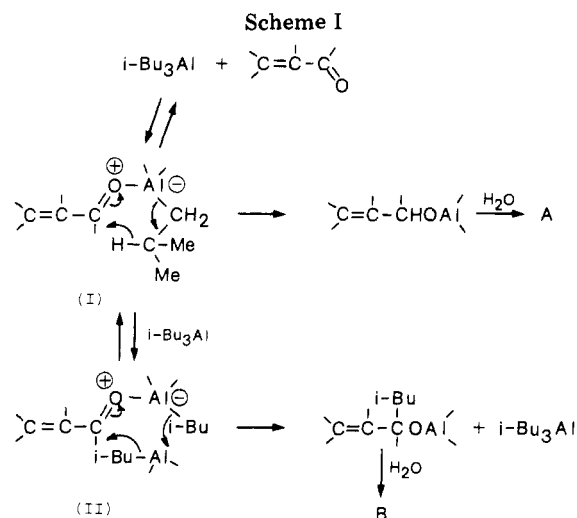


dition and reduction processes require different mechanistic pathways.

Even the nature of the unsaturated ketone influences markedly the course of the reaction. As the substitution at or near the α and β vinylic carbon atoms increases, both acyclic and cyclic enones generally give lowered yields of 1,2-addition products, demonstrating that the 1,2-addition of the isobutyl group is extremely sensitive to steric factors. For example, conjugate cyclohexenone systems which are substituted at a β vinylic carbon atom undergo exclusive 1,2-reduction; for isophorone (8), 1-isobutyl-3,5,5-trimethyl-2-cyclohexenol cannot be detected, even when an excess of $i\text{-Bu}_3\text{Al}$ is used (entry 14).

Particularly noteworthy among the remaining examples cited in Table I is the reaction of α -methylene-cycloheptanone (9): this unhindered ketone, which is con-

(6) It is noteworthy that reaction of a twofold molar excess of mesityl oxide with $i\text{-Bu}_3\text{Al}$ (entry 5) occurs with a 53% conversion based on the carbonyl compound, showing that only one isobutyl group of the organometallic compound reacts.



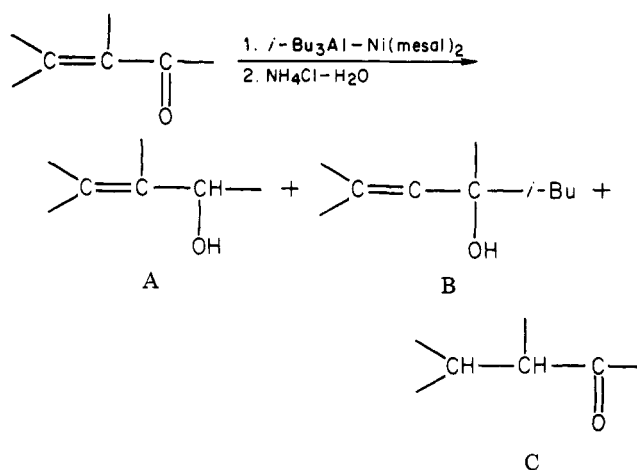
strained to a cisoid geometry, gives the reduction allylic alcohol in quantitative yield and in 100% regioselectivity. Not surprisingly, reaction of pulegone (10) follows a similar course (entry 16). These results suggest that only transoid enones should undergo 1,2-addition with *i*-Bu₃Al.

Finally, analogous to similar reactions in diethyl ether,⁴ steric hindrance in α,β -enones effects the reaction rate (Table I). Whereas ketones 1 and 2 react with *i*-Bu₃Al very rapidly, conversions being practically complete within 10 min (entries 1 and 3), the reaction rate drops noticeably with the more highly substituted enones: thus, reaction with isophorone (8) requires more than 15 h for completion (entry 13).⁷

In view of a previous conclusion,^{3,8} these observations suggest that the formation of 1,2-reduction (A) and 1,2-addition (B) products proceeds from the coordination adduct I via two different mechanistic pathways (Scheme I). The subsequent intramolecular rearrangement of this adduct should lead to the formation of the reduction product, while the addition product should involve the reaction of I with another organoaluminum molecule through a six-membered cyclic transition state (II, Scheme I).⁹ This mechanism agrees with the data obtained from reactions carried out in diethyl ether⁴ and with the observation that *i*-Bu₃Al-OEt₂ reacts with mesityl oxide (4) in pentane to afford only the 1,2-reduction product (Table I, entry 8). In these cases, the 1,2-addition product cannot be formed, as diethyl ether, which coordinates the aluminum atom, should prevent the formation of the cyclic transition state II.

Nickel-Catalyzed Conjugate Reductions. In the presence of small amounts of Ni(mesal)₂, the reactions between α,β -unsaturated ketones and triisobutylaluminum, carried out in pentane, occur much more rapidly and with increased selectivity for conjugate reduction of the substrate, producing the corresponding saturated ketone (Table II). The success of the catalytic reduction depends on the proper selection of experimental conditions; however, the procedure is simple and straightforward and was optimized for compounds 4 and 8. Ni(mesal)₂ (usually 3 mol %) is allowed to react with *i*-Bu₃Al at 0 °C;^{5a} dry

Table II. Nickel-Catalyzed Conjugate Reduction of α,β -Unsaturated Ketones^a



entry	ketone	% yield ^b		
		A	B	C
17	3	42	12	46
18	4	20	4	73
19 ^{c,d}		79		6
20	5	57	11	32
21 ^e		52	10	38
22 ^f	6	4	2	71
23	7	22	10	65
24	8	14		85
25 ^g		36		56
26 ^h		9		90
27 ⁱ		3		93
28	9	33		51

^a Unless otherwise stated, the reactions were performed in pentane (5 mL) at room temperature for 15 min on a 10-mmol scale by using 3 mol % of nickel catalyst and a molar ratio of aluminum reagent-ketone of 1:1. ^b Absolute yields were determined by GLC analysis with internal standards. ^c Reaction time 1 h. ^d Diethyl ether (8 mL) was used as the solvent. ^e This reaction was carried out with 6 mol % of nickel catalyst. ^f Cyclohexanol (10%) and 1-isobutylcyclohexanol (13%) were also detected. ^g The reaction was carried out with *i*-Bu₃Al-OEt₂; reaction time 12 h. ^h The reaction was carried out with tris(2-methylbutyl)aluminum. ⁱ The reaction was carried out with *i*-Bu₃Al-DMMA complex.

pentane and the enones are successively added at the same temperature over a period of a few minutes, before the reaction mixture is allowed to warm to room temperature. The reaction is exothermic and usually complete within a short time (15 min).⁷ Hydrolytic workup is accomplished by the addition of a saturated NH₄Cl solution, and the reaction products are analyzed directly by GLC. Thus, compounds 4 and 8 afforded the corresponding saturated ketones in 73% and 85% yields, respectively (entries 18 and 24).

Under the same experimental conditions, the conjugate reduction of many other representative unsaturated ketones proceeds satisfactorily. The results in Table II show that the saturated ketones C are obtained in 40–90% yields, depending on the structure of the substrate. Lower conjugate reduction yields are obtained with α -substituted α,β -unsaturated ketones; in these cases, the formation of uncatalyzed 1,2-reduction and 1,2-addition products is competitive with the nickel-promoted processes (entries 17, 20, and 28).¹⁰ The corresponding reaction with α -

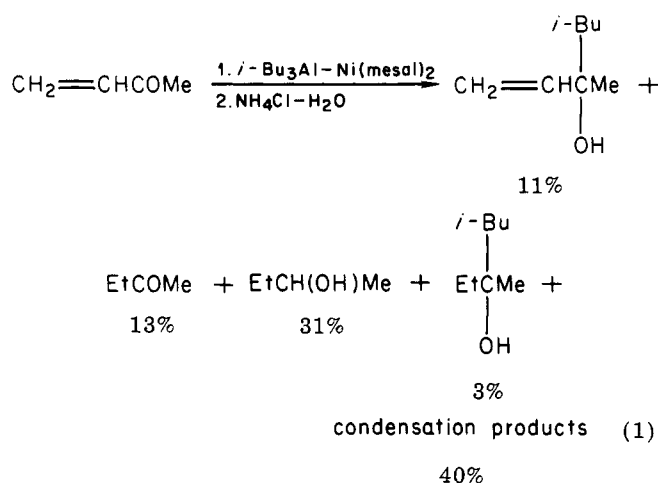
(7) Conversions have been obtained by sequential quenching of aliquots from the reaction mixtures.

(8) Giacomelli, G.; Lardicci, L. *J. Chem. Soc., Perkin Trans. 2*, 1973, 1129–1132.

(9) The formation of the adduct II might be favored by the possible interactions between the π electrons of the C=C double bond of the ketone and the second molecule of *i*-Bu₃Al; this hypothesis should so rationalize the lack of alkylative processes of saturated ketones by β -branched organoaluminum compounds too.

(10) Addition of increasing amounts of Ni(mesal)₂ to the reaction mixture of 5 with *i*-Bu₃Al has little effect on the yield of the saturated ketone (entry 21).

unsubstituted enones produced highest yields with the more β -substituted substrate (Table II). In the cases of the most reactive substrates, the conjugate reduction is accompanied by the formation of side products arising from overreduction and from Michael-type condensations of the saturated ketone enolate.¹¹ Thus, numerous attempts to effect the conjugate reduction of methyl vinyl ketone led to a complex mixture which included 2-butanol and high molecular weight condensation products as major products (eq 1). A similar trend is observed when (*E*)-



3-penten-2-one (2) is used as the substrate. Moreover, even the nickel-catalyzed reduction of 2-cyclohexenone (6) gives small amounts of saturated alcohols (entry 22). The presence of Ni(mesal)₂ has no detectable effect on the reaction between pulegone (10) and *i*-Bu₃Al. In this case, presumably because of steric reasons, the selective reduction of the carbonyl group is again the preferred course of the reaction.

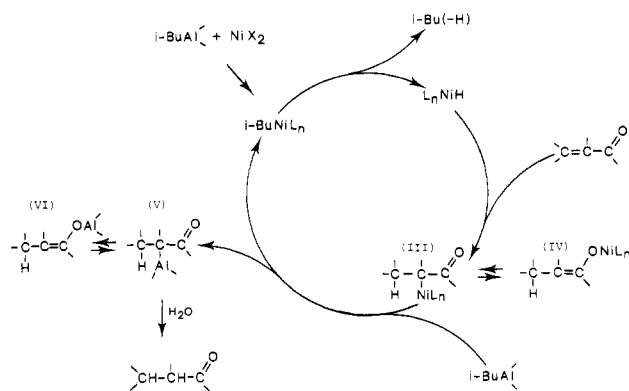
Some additional features of Table II deserve comments. First, coordinating solvents retard the reaction and lead to substantial amounts of 1,2-reduction product. Mesityl oxide (4, entry 19) reacts in diethyl ether with *i*-Bu₃Al in the presence of 3 mol % of Ni(mesal)₂ to give, after 1 h at room temperature, only a 6% yield of 4-methyl-2-pentanone (C) along with a 79% yield of 4-methyl-3-penten-2-ol (A). Second, the nickel-catalyzed reaction appears to be affected by the nature of the aluminum reagent too. A comparison of the data in entries 24–27 shows that the use of *i*-Bu₃Al–OEt₂ in pentane causes an appreciable decrease of the reaction rate along with a decreased regioselectivity, with respect to the equivalent reaction carried out with uncomplexed trialkylalane, whereas both tris(2-methylbutyl)aluminum and *i*-Bu₃Al–*N,N*-dimethylmenthylamine [*i*-Bu₃Al–DMMA], behave as good conjugate reducing agents. These aluminum reagents, in the presence of Ni(mesal)₂, react with isophorone (8) to afford nearly quantitative yields of the corresponding saturated ketone within 15 min at room temperature.

Moreover, it is noteworthy that when tris[(*S*)-2-methylbutyl]aluminum or *i*-Bu₃Al–DMMA is used, no chiral discriminating phenomena are observed: in all cases the racemic saturated ketone is recovered.

On the basis of the overall results, the conjugate reduction of α,β -unsaturated ketones by the Ni(mesal)₂–*i*-Bu₃Al system can be interpreted in terms of a hydridonickel addition mechanism, followed by fast exchange

(11) (a) Ashby, E. C.; Heinsohn, G. *J. Org. Chem.* 1974, 39, 3297–3299. (b) Bagnell, L.; Jeffery, E. A.; Meisters, A.; Mole, T. *Aust. J. Chem.* 1975, 28, 801–815.

Scheme II



reactions with the excess aluminum reagent. Hydridonickel species are effectively formed by reaction of *i*-Bu₃Al with the nickel complex,^{5a,f} the actual catalyst being a very complex system in which nickel and aluminum atoms are close together.^{5f}

In order to gain further insight about the nature of the reduction process, we hydrolyzed the reaction mixture from *i*-Bu₃Al and mesityl oxide (4), in the presence of Ni(mesal)₂, with D₂O. Mass spectrometric analysis of the saturated ketone showed it to be 100% singly D labeled at C-3.¹² This result clearly indicates that the hydrogen added in the β -position of the α,β -unsaturated ketone arises from the nickel hydride species, while the hydrogen added at the α -position results from hydrolytic workup. This observation and the fact that steric bulk at the α -position of the α,β -unsaturated moiety retards the reaction suggest that conjugate reduction of enones proceeds via the catalytic cycle shown in Scheme II. The initial step might involve a regioselective insertion of the activated double bond of the enone into the nickel–hydrogen bond to give the transient intermediate III. However, a rapid tautomeric equilibrium would permit its transformation into the corresponding nickel enolate, IV.¹⁴ Subsequent alkyl exchange or transmetalation with excess *i*-Bu₃Al must follow to afford the aluminum derivatives V and VI, also allowing the nickel catalyst to recycle.

Support for this proposal is provided by the finding that the sterically hindered nickel hydrides such as those obtained from (–)-(diop)NiCl₂^{5f} exhibit an entirely different regioselectivity in the reduction of conjugated cyclohexenone systems. The reactions of 2-cyclohexenone (6) and isophorone (8) with *i*-Bu₃Al in the presence of 3 mol % of (–)-(diop)NiCl₂ in pentane at room temperature afford only traces of the corresponding saturated ketones, while the 1,2-reduction carbinols are obtained in nearly quantitative yields.¹⁵

Optically active allylic carbinols are recovered from the reaction mixtures; for example, (–)-(S)-isophorol with an optical purity of 2.3%¹⁶ is obtained from isophorone.

(12) The position of the deuterium in the 4-methyl-3-deuterio-2-pentanone was obvious from a comparison of its mass spectrum [*m/e* (relative intensity) 101 (*M*⁺, 9), 86 (10), 59 (33), 58 (22), 43 (100), 41 (17), 39 (8), 29 (10), 27 (9)] with that of methyl isobutyl ketone.¹³ The relative abundances of ions in the parent ion region of the mass spectrum also indicated the presence of one deuterium in ~100% of the molecules.

(13) Cornu, A.; Massot, R. "Compilation of Mass Spectral Data", 2nd ed.; Heyden & Son: London, 1975; p25A.

(14) Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* 1974, 74, 365–371.

(15) In these cases, the uncatalyzed 1,2-reduction should be competitive with the catalytic one, as indicated by the reaction times which are analogous to those observed for reactions carried out in the absence of any catalyst (see Table I, entries 10 and 13).

(16) Takeya, K.; Itokawa, H. *Chem. Pharm. Bull.* 1977, 25, 1947–1951.

These stereochemical results indicate that a nickel hydride species participates effectively to catalyze both 1,2- and 1,4-reductions.

Experimental Section

¹H NMR spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as an internal standard. Mass spectra were taken at 70 eV on a Varian CH7 GC/MS spectrometer. GLC analyses were performed on Perkin-Elmer F 30 and 3920 B instruments (flame-ionization detectors; 200 × 0.30 cm columns packed with 5% silicone SE 301 on 80/100-mesh Chromosorb A at 40–200 °C, 8% Carbowax 20M + 2% KOH on 80/100-mesh Chromosorb W at 40–200 °C, and 20% PEG 30 on 80/100-mesh Celite at 160 °C; nitrogen flow rate of 15–30 mL min⁻¹). Optical rotations were measured with a Perkin-Elmer 142 polarimeter.

Materials. Solvents were commercial reagent grade materials, purified by standard methods and redistilled under nitrogen from LiAlH₄ before use. Most of the α,β-unsaturated ketones were commercial products (Fluka or Aldrich) which were purified by distillation. (*E*)-3-Methyl-3-penten-2-one (**3**)¹⁷ and α-methylenecycloheptanone (**9**)¹⁸ were prepared according to published procedures. Bis(*N*-methylsalicylaldimine)nickel [Ni(mesal)₂] and (-)-(DIOP)NiCl₂ were prepared and purified as reported elsewhere.^{19,20} Triisobutylaluminum (Fluka) and tris[(*S*)-2-methylbutyl]aluminum ([α]_D²⁵ +27.01°)²¹ were carefully redistilled under nitrogen and stored in sealed capillary glass vials in weighed amounts. *N,N*-Dimethylmenthylamine (DMMA, α_D²⁵ -46.59° (*l* = 1)) was obtained from the corresponding amine.^{5f} Triisobutylaluminum diethyl etherate and triisobutylaluminum-DMMA complex were prepared by adding the stoichiometric amount of the ligand to the trialkylalane at 0 °C.

General Procedure. All reactions were carried out at least in duplicate under a dry nitrogen atmosphere. In a typical uncatalyzed reaction, a weighed amount of triisobutylaluminum (10 mmol) was transferred from the sealed capillary glass vial to a two-necked, 25-mL flask equipped with a stirring bar, a reflux condenser, and a Versilic silicone cap. The vessel, cooled to 0 °C, was charged with pentane (5 mL), and the required amount of the α,β-unsaturated ketone was added by a syringe. In the nickel-catalyzed reactions, the nickel complex (0.3 mmol) was first allowed to react with the aluminum reagent (10 mmol) at 0 °C,^{5a} after a 2-min agitation, a solution of the carbonyl substrate in 5 mL of solvent was injected. The resulting mixtures were allowed to stir at room temperature for the desired time (Table I and II).⁷ In all cases a hydrolytic work-up was carried out by using a saturated aqueous solution of NH₄Cl. The organic phase was extracted with ether, and the ether extracts were dried over Na₂SO₄. Quantitative analyses of the reaction products were

performed by GLC. The 1,2- and 1,4-reduction products were identified by comparison of GLC retention times and spectral data (¹H NMR and mass spectra) with corresponding data from commercial or independently synthesized material.

1,2-Addition products were isolated and identified on the basis of their spectroscopic properties (¹H NMR and mass spectra); when necessary, larger scale reactions were used for these separations.

Representative experiments are described below.

Reaction between Triisobutylaluminum and Mesityl Oxide (4) in Pentane (Entry 6). According to the general procedure, a pentane solution of *i*-Bu₃Al (2.02 g, 10.2 mmol, 5 mL) was allowed to react at room temperature for 1 h with mesityl oxide (**4**; 1.00 g, 10.2 mmol). The crude products obtained upon hydrolysis were analyzed by GLC and fractionally distilled to yield 0.61 g (60%) of 4-methyl-3-penten-2-ol²² [bp 58 °C (25 torr); *n*_D²⁰ 1.4330; mass spectrum, *m/e* (relative intensity) 100 (*M*⁺, 12), 85 (100), 67 (35), 57 (11), 55 (14), 53 (7), 45 (12), 43 (41), 41 (42), 39 (25), 29 (17), 27 (16)]; ¹H NMR (CDCl₃) δ 1.05 (d, 3 H, CH₃CHOH), 1.37 (m, 6 H, allylic CH₃), 3.45 (s, 1 H, OH), 4.08 (m, 1 H, CHOH), 4.78 (br d, 1 H, =CH) and 0.46 g (29%) of 2,4,6-trimethyl-2-hepten-4-ol [bp 80–81 °C (15 torr); mass spectrum, *m/e* (relative intensity) 156 (*M*⁺), 141 (6), 138 (2), 123 (7), 99 (100), 81 (20), 67 (5), 55 (9), 53 (6), 43 (32), 41 (15), 39 (6), 29 (6), 27 (5)]; ¹H NMR (CDCl₃) δ 0.87 (d, 6 H, CH₃), 1.22 (s, 3 H, CH₃COH), 1.33–1.80 (m, 9 H, CH, CH₂COH, and allylic CH₃), 1.85 (s, 1 H, OH), 4.93 (br s, 1 H, =CH)].

Nickel-Catalyzed Reduction of Mesityl Oxide (4) by Triisobutylaluminum (Entry 8). As described above,^{5a} *i*-Bu₃Al (2.50 g, 12.6 mmol) was reacted with Ni(mesal)₂ (0.124 g, 0.379 mmol) at 0 °C; 6 mL of dry pentane and 1.24 g (12.6 mmol) of the ketone were successively added at the same temperature to the brownish homogeneous mixture which was then allowed to warm to room temperature. After 15 min, the mixture was cautiously hydrolyzed and extracted with ether. GLC analysis (8% Carbowax 20M + 2% KOH) of the ethereal solution showed the presence of methyl isobutyl ketone as the major product (73%) which was identified by comparison of retention time with a commercial sample. After removal of the solvent, fractional distillation gave 0.82 g (65% yield) of the saturated ketone: bp 116–117 °C; *n*_D²⁰ 1.3962.

Reduction of Isophorone with the Triisobutylaluminum-(-)-(diop)NiCl₂ System. According to the general procedure, isophorone (**8**; 1.20 g, 9.11 mmol) was reacted with *i*-Bu₃Al (1.81 g, 9.11 mmol) in the presence of (-)-(diop)NiCl₂ (0.170 g, 0.270 mmol) in pentane at room temperature for 15 h.⁷ The reaction mixture was hydrolyzed and extracted with ether as above. After GLC analysis, distillation gave 1.15 g (96% yield) of (-)-(S)-isophorol: bp 81 °C (8 torr); [α]_D²⁵ -0.324° (hexane).¹⁶

Registry No. 1, 78-94-4; 2, 3102-33-8; 3, 1567-73-3; 4, 141-79-7; 5, 932-66-1; 6, 930-68-7; 7, 1193-18-6; 8, 78-59-1; 9, 3045-99-6; 10, 5587-79-1; *i*-Bu₃Al, 100-99-2; Ni(MeSal)₂, 14322-02-2; (-)-(diop)NiCl₂, 41677-72-9; (-)-(S)-isophorol, 64543-48-2; 4-Methyl-3-penten-2-ol, 4325-82-0; 2,4,6-trimethyl-2-hepten-4-ol, 80311-49-5; 4-Methyl-3-deuterio-2-pentanone, 35300-04-0.

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